ORIGINAL ARTICLE

Hydrochemical characteristics and seasonal variations in groundwater quality of an alluvial aquifer in parts of Central Ganga Plain, Western Uttar Pradesh, India

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Abstract The present study was undertaken to assess major ion chemistry of groundwater in parts of the Central Ganga Plain and observe seasonal variations in its chemical quality. Systematic sampling was carried out during November 2005 and June 2006. The major ion chemistry of groundwater shows large variations, so much so that at times the meteoric signature seems to be completely obliterated. In many samples the concentrations of SO_4, NO_3 and F are above the permissible limit for human consumption. The graphical treatment of major ion chemistry helps in identifying four types of groundwater. All possible ionic species such as NaCl, KCl, $NaHCO_3$, $NaSO_4$, KNO_3, $NaNO_3$, $CaHCO_3$, $MgHCO_3$, $MgSO_4$ are likely to occur in groundwater system. The observed chemical variations may be attributed to sediment water interaction, ion exchange, dissolution mechanisms and anthropogenic influences such as application of fertilizers and effluents from sugar factories and paper mills. A general increase in TDS is observed in samples during June 2006. The increase in salinity is attributed to evaporation from water table, irrigation return flows, anthropogenic activities and below average rainfall in 2005 and 2006.

Keywords Chemical characteristics · Mixing phenomenon · Seasonal variations · Drinking water quality · Western Uttar Pradesh · India

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Introduction

Groundwater utilization has increased at an alarming rate over a period of three decades in the study area (Ahmed and Umar 2008). The net result is that the groundwater regime of the area has been affected detrimentally, both qualitatively and quantitatively.

The study of a relatively large group of samples from a given area offers possible trends of chemical alteration which the meteoric water undergoes before acquiring distinct chemical characteristics and attaining a steady state. These identified trends may be related to natural and anthropogenic causative factors (Umar and Absar 2003). With this simple objective systematic sampling was carried out to understand various possible sources of dissolved ions and assess seasonal variation in groundwater quality.

Study area

Location and physiography

The study area, in the Muzaffarnagar district of Uttar Pradesh in India lies between latitudes 29°15′ and 29°41′45″N and longitudes 77°05′ and 77°27′E (Survey of India toposheets 53 G/2, 53 G/3, 53 G/6 and 53 G/7) and covers an area of about 1,060 km^2, lying to the west of Muzaffarnagar township. Rivers Yamuna and Krishni respectively form the western and eastern boundary of the study area (Fig. 1).

Compared to Yamuna, Krishni River flows in a relatively well-defined channel. Yamuna River is characterized by a large tract of low lying area of newer alluvium locally known as *khadir*. In the vicinity of Krishni, development of soil is relatively poor but low land areas are conducive for rice cultivation. Saline soil development has affected the
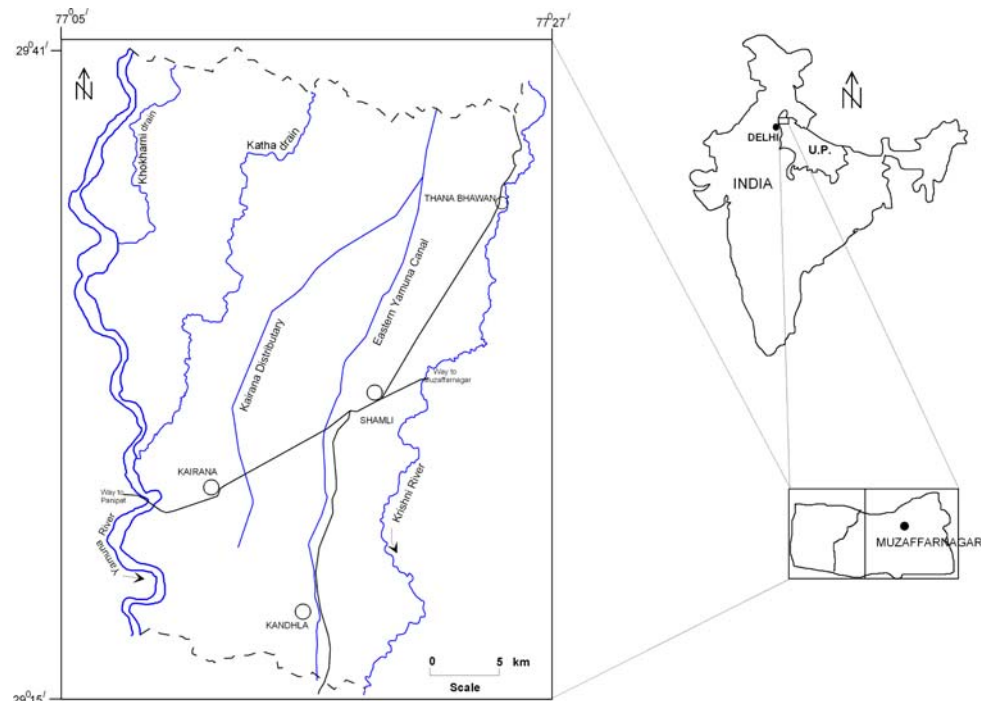
western part between Yamuna and Katha outlet. The area
exhibits a gentle slope to the south and southwest where the
elevations range between 230 and 245 m amsl. The central
upland region has elevations from 240 to 255 m amsl.

Rainfall and climate

The area on an average receives 727 mm of annual rainfall,
the bulk of which is during the peak of the monsoon in the
months of August and September. The rainfall in the study
area for 2005 and 2006 had been below the average, i.e.
606 and 435 mm, respectively.

The area enjoys a subtropical climate, with very hot
summers and moderately cold winters, the maximum and
the minimum temperatures being 45°C in June and 4°C in
January.

Land use/land cover

The area under cultivation has marginally decreased from
90.5 to 88.8% during 1972–2005. The same period has
witnessed doubling of population from 1.8 to 3.54 million.
The area occupied by settlements has increased from 2 to
10%. Groundwater use had increased proportionally.

Hydrogeological framework

Geologically, the area is characterized by a thick pile of
>1,000 m of Quaternary sediments or newer alluvium
which rest over basement rock quartzites of Delhi Super
Group. Delhi quartzites are underlain by Bundelkhand

Granitoid Complex (Kumar 2005). The subsurface data
available from shallow boreholes (Supplementary Fig. 1)
indicate that the top clay layer is persistent through out the
area, varying in thickness from 3 to 20 m. This is underlain
by a more porous granular zone, intervened by several sub-
regional clay beds. Local aquifers tend to behave as a
single aquifer. The granular zone, composed of medium to
coarse sand and gravel, forms >80% of the total thickness
of formations encountered, particularly in southeastern and
southern parts of the basin. This area, which is a faulted
block of the S–W trending Muzaffarnagar fault, may have
become received more sand than the area north of the fault.
The Muzaffarnagar fault is an East–West trending trans-
verse fault passing through the river courses of Yamuna,
Krishni, Hindon and Kali (Bhosle et al. 2006).

During the pre-monsoon period (June 2006), the depth
to water table ranges from 6.20 to 21.96 m bgl. The deeper
water table conditions are in the central part of the study
area. General groundwater movement is from NNE to
SSW. The Eastern Yamuna Canal acts as a groundwater
divide (Fig. 2). The groundwater flow direction at the left
bank of the canal is towards the Krishni River, with an
average hydraulic gradient of 1.25 m/km. From its right
bank, groundwater flows from NE to SW direction. The
elevation of water table ranges from 246 m at Dulawa in
NE to 219 m at Pautikalan. Prominent groundwater troughs
are seen in proximity to River Yamuna.

Pumping tests were conducted in the study area by Uttar
Pradesh State Groundwater Department (UPSGWD) and
Central Groundwater Board (CGWB). Transmissivity and
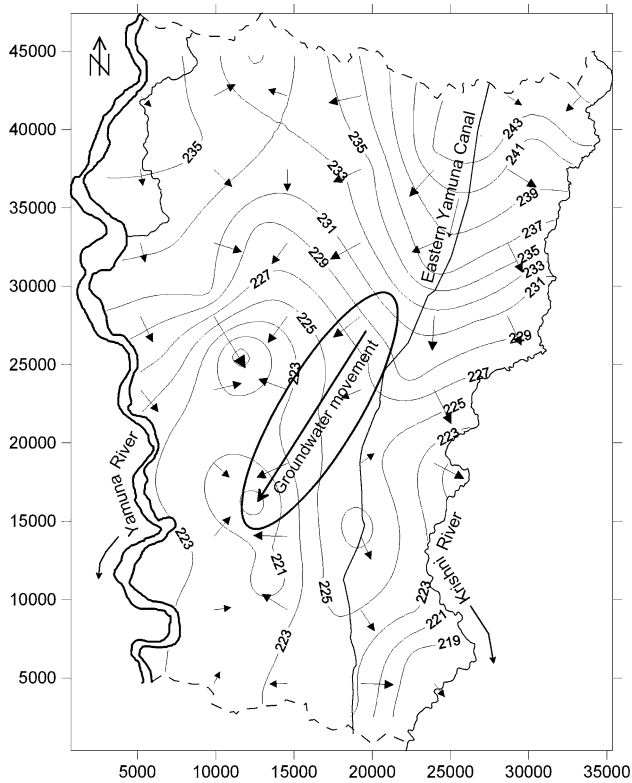hydraulic conductivity were evaluated for the first group of
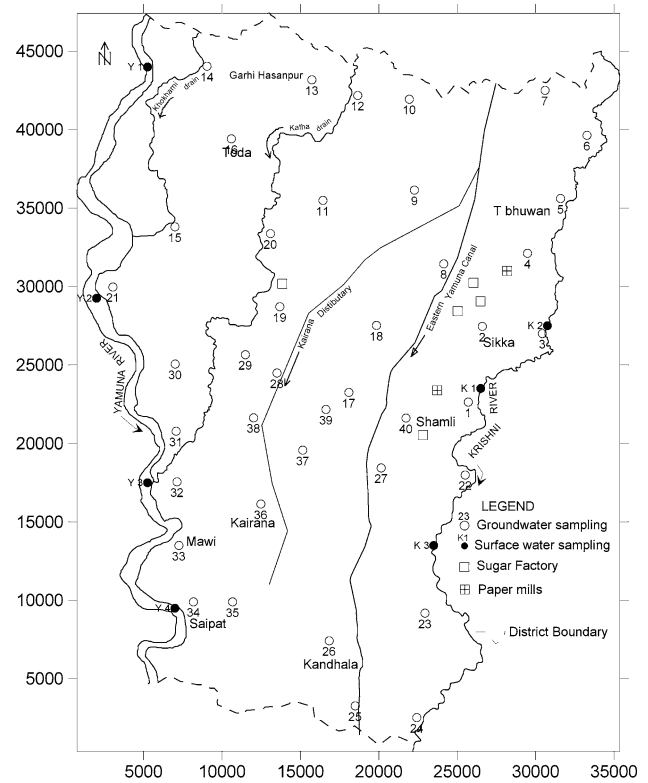
Fig. 2 Water table contour map of June 2006 (amsl)

Fig. 3 Sampling locations map

aquifers. The T and K values vary between 1,265 and 4,003 m²/day, 10–27 m/day, respectively (Bhatnagar et al. 1982). Based on variation in hydraulic conductivity, the area has been divided in to seven zones. The groundwater flow velocity ranges from 0.008 to 0.037 m/day. The average flow velocity for the entire area is 0.022 m/day.

The groundwater resource evaluation was carried for 1 year (6–7 June). Recharge to the first aquifers takes place through rainfall, irrigation return flow, canal seepage and subsurface inflows. The percentage of recharge through rainfall, irrigation return, canal seepage and subsurface inflows are 28, 47, 16 and 9%, respectively.

Hydrochemical characteristics of groundwater

Water samples for chemical analysis were collected in November 2005 and June 2006 from 40 locations (Fig. 3), representing post- and pre-monsoon periods, respectively. The depth of sampled handpumps is 5–30 m. Seven water samples were also collected from Yamuna and Krishni Rivers during November 2005.

The physico-chemical characteristic of water samples was determined according to the standard methods of APHA (1992). Ca^{++}, Mg^{++}, HCO_3^- and Cl^- were determined by titrimetric method. Flame emission photometry

was used for determination of Na^+ and K^+. Sulphate was analysed by gravimetric method, and for NO_3^- and F^- colorimetric method was employed. Chemical analyses are reported in Supplementary Tables 1a, 1b and 2.

The area is characterized by relatively high total dissolved solids (TDS), ranging between 491 and 1,574 mg/l and averaging around 922 mg/l during November 2005. Marginally higher TDS during June 2006 ranged between 497 and 1,922 mg/l, averaging 1,019 mg/l in pre-monsoon samples. A total of 39 out of 40 samples are above the desirable limit of 500 mg/l (BIS 1991) for drinking water in both sampling seasons. The distribution of TDS values in the study area (Supplementary Fig. 2) shows two distinct highs, one in the eastern part and between Krishni River and Eastern Yamuna Canal, and the other in the southwestern sector on the left bank of Yamuna. The Krishni River anomaly is located within the zone with high density of industries. The southwestern sampling location with higher TDS values does not seem to have any explicit anthropogenic influences. Concentration ranges of major ions during post- and pre-monsoon periods are summarized in Supplementary Table 3.

A number of x–y plots were prepared for various chemical trends of groundwaters. Alkalis are distinctly far more abundant than Ca^{++} and Mg^{++} in both the sets of samples (Supplementary Fig. 3a). The HCO_3^- versus

$Cl^- + SO_4^-$ plot (Supplementary Fig. 3b) tends to classify the groundwater in the study area in two groups, i.e. (i) $HCO_3^- > Cl^- + SO_4^{-2}$ and (ii) $Cl^- + SO_4^{-2} < HCO_3^-$. Both plots indicate that chemical differences between pre- and post-monsoon sets of samples are negligible.

The natural tendency between cations and anions to form ionic complexes has been tested $Na^+ + K^+$ and Cl^- (Supplementary Fig. 3c) and $Ca^{++} + Mg^{++}$ and HCO_3^- (Supplementary Fig. 3d). The majority of the samples plot below 1:1 line on alkali versus Cl^- plot, implying surplus Na^+ ion over and above those used in Na–Cl bonding. Relative abundance of Na^+ ions is also implied in molar Cl^-/Na^+ ratios averaging around 0.25. The $Ca^{++} + Mg^{++}$ and HCO_3^- plot depicts a moderately good correlation for about 40% of all pre- and post-monsoon samples. Nevertheless, there is considerable scatter in the plot due to relative preponderance of HCO_3^-, and the relative abundance of alkali over Ca^{++} and Mg^{++} (Supplementary Fig. 3a) and surplus Na^+ ions (Supplementary Fig. 3c), implies that in a considerable number of samples, Na–HCO_3 may be the most dominant ionic complex.

Groundwater from the study area is enriched in SO_4^{-2} (Supplementary Tables 1a and 1b). Processes such as oxidation of sulphides and dissolution of gypsum (Valdiya 1980 and Chakrapani 2005) are not inferred to play a significant role in acquisition of sulphate ion by the groundwater of the area. Dissolution of gypsum (either naturally occurring as gypsite in some parts of Indo-gangetic plains or that used as a fertilizer) has almost no role to play in determining the concentration in groundwaters of the study area, as indicated by the Ca–SO_4 plot (Supplementary Fig. 3e), which depicts an overwhelming abundance of SO_4^{-2} compared to that of Ca^{++}.

The nitrate concentration exceeds the highest desirable for drinking water in 14 samples (June 2006). The possible sources for nitrate contamination are extensive use of fertilizers and manures, soil types, presence of subsurface clay beds, poor sanitation, and septic tanks. Under conditions of high oxygen and water solubility, part of the ammonium sulphate $(NH_4)_2SO_4$ and urea $CO(NH_2)_2$ applied as fertilizer would be rapidly converted in to NO_3^-, which is not as easily sorbed to the negatively charged sites on soil and clay, and moves readily to the water table (Follet 1995).

Chemical classification of groundwaters

Based on relative abundances of anions, the groundwater may be classified into four major types. Based on concentration levels of cations they may be further divided into groups. In the order of decreasing abundance, the four major types of groundwater in the area are:

I. HCO_3–SO_4 type
  (1) Na–HCO_3–SO_4
  (2) Mg–Ca–HCO_3–SO_4
II. Cl–SO_4 type
  (1) Na–Cl–SO_4
  (2) Mg–Ca–SO_4–Cl
III. HCO_3 type
  (1) Na–HCO_3
  (2) Mg–Ca–HCO_3
IV. SO_4 type
  (1) Na–SO_4
  (2) Mg–Ca-SO_4

About 50% of the samples analysed belong to type I and 35% to type II. Type III samples constitute 10% of the total; and type IV, the least abundant constitutes only 5% of the sample analysed.

Seven surface water samples from Yamuna and Krishni Rivers were analysed to assess their relationship with the groundwater regime. The samples from Krishni show very high concentrations of HCO_3^-, SO_4^-, Na^+ and K^+. The TDS values are higher as well (Supplementary Table 2).

The four Yamuna samples, with the exception of sample Y_4, show good correlation between Cl^-/Na^+ and $HCO_3^-/Ca^{2+} + Mg^{2+}$ and have moderate TDS values of 400 and 500 mg/l. Strikingly high TDS value of >1,000 mg/l is recorded for sample Y_4.

Discussion

The chemical classification is further corroborated by L–L diagram (Langelier and Ludwig 1942) of post-monsoon and pre-monsoon samples (Fig. 4a, b). Groups I, II and III in this plot conform to sub-types of HCO_3–SO_4 and Cl–SO_4 waters. The samples, relatively enriched in HCO_3 and characterized by Ca + Mg > Na + K, might naturally be considered less altered and closer to the composition of meteoric water, but the meteoric signatures have been mostly been obliterated. The excess of HCO_3^- is introduced through decay of organic matter. Abundance of HCO_3^- encourages Na–HCO_3 in the groundwater. The groundwater with high Na^+ concentration is probably from the mixing of two or more types of groundwaters. Sodium ions behave conservatively and are not used up in biological processes. Na^+ entered the groundwater system and remained for a long time.

Dissolution of gypsum/gypsite as a source of SO_4 is not likely in the light of the geology of the area, as well as the Ca–SO_4 plot (Supplementary Fig. 3e). It is more probably released from pyritious–carbonaceous slate and phyllites in the basin. The sulphur which is used abundantly in sugar factories, on oxidation may form SO_4 which could find its way to shallow aquifers (Umar and Ahmed 2007). The high
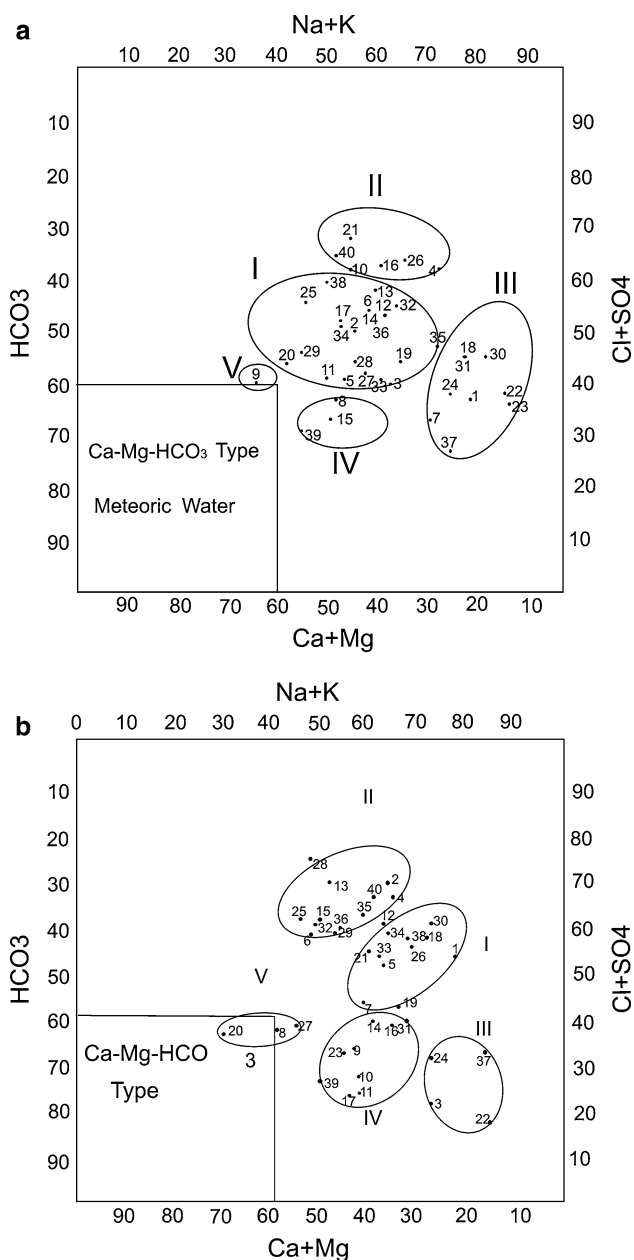
Fig. 4 a Classification of groundwater on L–L diagram (November 2005). **b** Classification of groundwater on L–L diagram (June 2006)

SO_4 concentration and its weak correlation with Ca (Supplementary Fig. 3e) indicate sources other than gypsum or fertilizers, perhaps from industrial wastes. Surface water samples collected from the Krishni show very high SO_4 concentration (Supplementary Table 2).

The monsoonal effect on groundwater geochemistry as revealed by comparing Fig. 4a with that of pre-monsoon samples (Fig. 4b). It is not homogeneous. The change depicted in the chemistry of groundwater during pre- and post-monsoon period are not explicable in terms of processes, such as, evaporation, dilution, water rock

interaction and variations in residence time. This is also borne out by the fact that no clear alteration trend is depicted in L–L plot of pre- and post-monsoon samples (Fig. 4a, b). What broadly emerges is that a set of samples with a composition close to meteoric water has basically gained Na and SO_4 to form the various types of groundwater observed in the area. Mixing of two or more types of groundwater or surface water may also have played a significant role. This phenomenon is depicted to some extent when the water table map is compared with the map showing distribution of TDS values (Supplementary Fig. 2). TDS values of >1,100 mg/l are observed between Krishni and Eastern Yamuna Canal in the eastern part and on the left bank of Yamuna in the western part of the study area. Samples from Krishni river show very high TDS values associated with high SO_4 concentration, inferring that the eastern high TDS zone is the result of contributions from surface of local industrial waste, from sugar factories, paper mills and steel factories. The western high TDS zone is evidently due to east to west migration of groundwater (Fig. 2). Except for sample Y4, other samples collected from Yamuna river have moderate TDS values of <500 mg/l. No industries are located in this sector. The effluent nature of Yamuna river at sampling site Y4 (Saipat) is evident on the water table contour map. River–aquifer interaction has influenced the chemical parameters of the groundwater.

Conclusion

The present study was initiated to evaluate and determine variation in groundwater chemistry and changes in post- and pre-monsoon groundwater quality. A chemical classification of groundwater was attempted on the L–L diagram. Four major group characterized by distinct chemical compositions were identified. Change was noted in the chemistry of groundwater during post- and pre-monsoon period with out any significant contribution from evaporation, water rock interaction and variation in residence time. The monsoonal effect on groundwater chemistry is not homogeneous and is related to mixing of groundwater and river aquifers. There is clear cut evidence for migration of high TDS groundwater from east to west, which also supports dominance of mixing phenomenon over other processes. Both sulphate and nitrate values seem to have anthropogenic origins. The reaction involved in the humic zone and dissolution of kankar, accumulation of salts through evaporation and river–aquifer interaction also affects the hydrochemical regime.

The groundwater is generally suitable for human consumption. In a few samples, concentrations of SO_4, NO_3 and F are above the permissible limit for human intake.

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