USING MAJOR IONS AND STABLE ISOTOPES TO CHARACTERIZE THE GROUNDWATER AQUIFER IN DELHI STATE, INDIA

Shilpi Saxena[1], J.P. Shrivastava[1], M.S. Rao[2], C.P. Kumar[2], G. Krishan[2], B. Kumar[3]

Abstract: In recent years, with the progress of new observation techniques and related theories, the tracing technique of environmental isotopes has been widely applied to investigate the groundwater dynamic process. It's expected that the isotopic technique of environmental isotopes will contribute to identifying the dynamic information of groundwater. Isotopic technique can identify the source of contamination and yield information on process such as redox or chemical evolution, mixing and migration. Environmental isotopes are naturally occurring conservative tracers that can provide important information about the origin of pollutants, the contribution of different sources to a multi-source plume, characterization of their complex transport (rate and mechanism) and for evaluating the success of contaminated site remediation. In order to investigate the effect of pollution load and the quality of groundwater in lined and un-lined track of the Najafgarh drain basin area at Delhi region a systematic study has been taken up to map the chemical characteristics and isotope signatures of groundwater. Najafgarh drain is the biggest drain in Delhi and contributes about 60% of the total wastewater that gets discharged from Delhi into river Yamuna. The drain traverses a length of 51 km before joining river Yamuna, and is unlined for about 31 km along its initial stretch. Since shallow aquifer is highest vulnerable to surface pollution, 51 groundwater samples were collected using hand-pumps at a depth in range of 10.66 to 36.57m and jet pump ranging from 60 to 80m in close proximity to the drain reach during October 2010, February 2011 and in June 2011 from 17 different sampling stations and analyzed for different parameters covering major ions, heavy metals and stable isotopes by following the "Standard Methods of Examination of Water and Wastewater" 21st edition, (APHA) Washington DC, 2005. The 18O/16O ratio was measured on DI-IRMS with Masslynx software Ver. 4.0 following a modified [Epstein and Mayeda, 1953] technique, [Thode et at.1961]; [Coleman et al., 1982]; [Shakur, 1982] by equilibrating a tank CO_2 gas at 25oC. Measurement of Deuterium (D/H) ratio in sample were done on CF-IRMS, similar to oxygen isotope analysis with a difference that the equilibration is carried out with hydrogen gas in the presence of platinum (Pt catalyst, marketed as Hokko Beads) in place of CO_2 gas. The Isotopic signatures of water sample are reported in the conventional δ (%o) notation as a deviation with respect to the isotopic ratio of reference Vienna Standard Mean Ocean Water (V-SMOW) for water. Typical precisions are The analytical reproducibility of the laboratory standard is ±0.1%o for δ 18O and ±1.0%o for δ2H. Hydro chemical and isotopic signature of groundwater provided a unique understanding of pollution dynamics in the groundwater. There are indications of pollutants transport from the western, north-western and western parts; there is evidence of increasing groundwater pollution and leachate transport to groundwater through surface drainage. The shallow groundwater along Najafgarh drain is contaminated at a stretches and the area is not suitable for the purpose of drinking there is need of immediate plan and action for the effective management to protect the groundwater resources.

Keywords: Groundwater characterization, Water quality modelling, Stable Isotopes and Major Ions.

[1] *Geochemical Laboratory, Department of Geology, University of Delhi, Delhi-110007, India.*
E-mail: docs.shilpi@gmail.com
[2] *National Institute of Hydrology, Roorkee, Uttarakhand-247 667. India.*
[3] *Isotope Hydrology Section, International Atomic Energy Agency, Vienna Austria.*

INTRODUCTION

Description of the Study Area

The present study area is the Najafgarh Drain Basin, where it starts from South West of Delhi near Delhi-Gurgoan border at Chhawla village extends through QutubVihar, Goyala Khurd, Najafgarh, Nangli Dairy, Kakrola, Vikaspuri, Raghuveer Nagar, Meera Bagh, Moti Nagar, Shakti Nagar, Inderlok, Roop Nagar, Kinsgway Camp, Hakikat Nagar, Timarpur, Nehru Vihar and

Mukherjee Nagar. The Najafgarh drain basin area in Delhi region is about 832 sq. km and most of the industrial units of Delhi including few major medium scales are situated in this drain basin area. The other important drain that passes through Delhi is the River Sohibi. It enters in Delhi near Dhansa where Dhansa Bund (regulator) is constructed. The floodwater of river Sohibi is drained through Najafgarh drain into the river Yamuna. On its way to the River Yamuna, the Najafgarh drain receives discharge from other drains like Palam Drain (Ganda Nala), Mungeshpur Drain, Mundka Drain, Nangloi.

Fig. 1: Map of Delhi (sources CGWB 2006)

Drain, Western Yamuna Canal (Delhi Tail Distributary) and finally from from Supplimentry drain just before its culmination into the river Yamuna near Wazirabad Barrage. Including the Najafgarh Drain there are 21 drains that conveys sewage and rainwater from different parts of the City to the river Yamuna. Out of these drains, Najafgarh Drain, Okhla Drain and Shahdara drain are the major drains. Its sewered catchment area is around 374sq.km. Because of severe constraints in the sewerage system in its drainage basin carries a very large quantity of raw sewage. In addition, it receives treated effluent from various STPs and freshwater from tail-end of the Western Yamuna Canal. Najafgarh drain basin in East Delhi has been being ranked eleventh in the country's highly polluted 88 industrial clusters. The Najafgarh drain basin which is also the biggest polluter to Yamuna tops the list of thirty-three "critically" polluted industrial hubs, scoring 70-80% in the Comprehensive Environmental Pollution Index (CEPI). And the drain has scored 79.54 points, which is attributed to huge effluents and sewage in its drainage basin.

Physiography of the Study Area

The Delhi region is a part of the Indo-Gangetic Alluvial Plains, situated at an elevation ranging between 198 and 220 m above mean sea level (msl), transacted by a quartzite rocky ridge (maximum elevation of 318.52 m above msl) extending roughly from north-east to south-east. The ridge forms the principal watershed of the area and acts as a groundwater divide between the western and eastern parts of NCT, Delhi. Physiographical, the NCT, Delhi can be divided into four parts: (1) the Delhi Ridge, (2) the alluvial plain to the east of the Delhi Ridge; (3) the alluvial plain to the west of the Delhi Ridge; and (4) the closed basin of Chatttarpur. The territory is made up of quartzite ridge tending from north-north east (NNE) to south- southwest (SSW). The alluvial plain on the east of the ridge and sand dunes at the west are observed at the south western part. The territory is drained by the river Yamuna which enters from the north eastern direction and flows through the south eastern area. The quartzite ridge is the prolongation of the Aaravalli group of the rock and enters from the southern borders and ends in the north of Delhi on the west bank of Yamuna. The ridge forms the principal watershed in the area, the eastern drainage passing into the Yamuna and the western in to the Najafgarh basin. The area selected for the present study is the Najafgarh drain basin area.
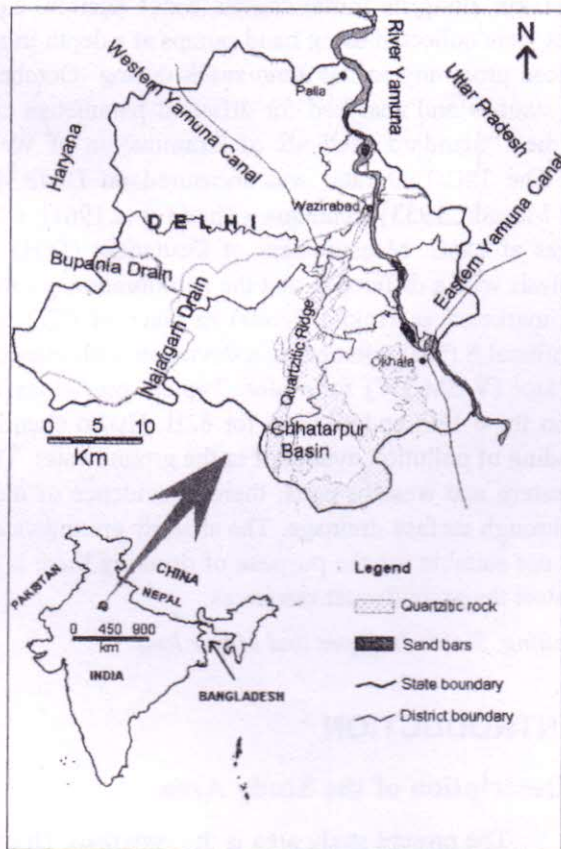
Hydrogeology of the Study Area

Geological formation of the north eastern area of Najafgarh drain basin are generally composed of unconsolidated silts, sand and nodular calcareous material in the vicinity of the river Yamuna. These have more permeable horizons than the older alluviums. The younger alluviums of this zone Alipur block have moderate to fairly good potential of groundwater. The ground water availability in the territory is controlled by the hydro geological situation characterized by occurrence of alluvial formation and quartzite hard rocks.
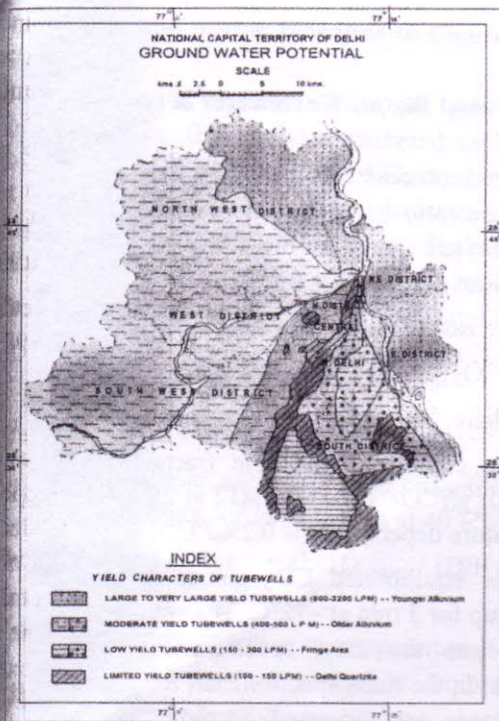
Fig. 2: The groundwater potential of the different formations in NCT Delhi (source: CGWB 2006)

The NCT Delhi can be divided into following distinct hydro geological units:. Newer Alluvium - Yamuna flood plain deposits, Older Alluvium - Eastern and western sides of the ridge, Older Alluvium - Isolated and nearly closed Chattarpur alluvial basin and Quartzite Formation - NNE-SSW trending Quartzite Ridge. The alluvial deposits are of Quaternary age. The newer alluvium belongs to recent age and is referred to the sediments deposited in the flood plains of Yamuna River. These sediments range in texture from clay/silt mixed with tiny mica flakes to medium/coarse sand and gravel. Newer alluvium, in general, is characterised by absence of kankar. The older alluvium consists of sediments deposited as a result of past cycles of sedimentation of Pleistocene age and occurs extensively in the alluvial plains of the territory. This is comprised of inter bedded, lenticular and inter-fingering deposits of clay, silt and sand ranging in size from very fine to very coarse with occasional gravels. The kankar or secondary carbonates of lime occur with clay/silt deposits and sometimes as hard/compact pans. Older alluvium is predominantly clayey in nature in major parts of territory except the nearly closed alluvial basin of Chattarpur where the alluvial formation is derived from the weathered quartzite rocks. The hard rock formations; mainly the Alwar quartzite of Delhi System exposed in the area belong to

Pre-Cambrian age. The quartzites are pinkish to grey in colour, hard, compact, highly jointed/ fractured and weathered. These occur with interbeds of mica-schist and are intruded locally by pegmatites and quartz veins. The strike of these rocks varies northeast southwest to north-northeast south southwest with steep dips towards southeast and east except for some local variations due to folding. Quartzites are ferruginous and gritty types on weathering and subsequent disintegration give rise to coarse sand (Badarpur sands). Chemical weathering of deeper horizons is also common.

MATERIAL AND METHODS

Field Investigations

The Najafgarh drain basin area in Delhi region is about 832 sq. km and most of the industrial units of Delhi including few major medium scales are situated in this drain basin area. Keeping these points in view, 17 sampling stations (Fig.3) were selected throughout the stretch of basin. The sampling coordinates were noted on a global positioning system (GPS III, Garmin). This was further supported by topographic sheets made available from Survey of India. For the analysis of hydro chemical and isotopic (oxygen-18 and deuterium) analysis we have collected 51 groundwater samples using hand-pumps at a shallow depth in range of 10.66 to 36.57m and using jet pump at a deeper depth ranging from 60 to 80m in close proximity to the drain reach, during the October 2010, February 2011and June 2011 from 17 different sampling stations and analyzed for various parameters covering major ions, heavy metals and stable isotopes by following the "Standard Methods of Examination of Water and Wastewater" 21st edition, (APHA) Washington DC, 2005 and for Isotopes analysis we have followed "Standard methods of International Atomic Energy Agency, Vienna" (IAEA).

Samples were taken only from those pumps which are actively in use. Sufficient water is flushed out before sampling to ensure that aquifer water and not the stagnant water is sampled. All the samples so collected were packed in a well sealed HDPE bottles and stored at low temperature to avoid any evaporation to occur before they get analyzed for isotopic ratios. Electrical conductivity, pH, temperature of samples were measured at sampling locations at the time of sampling. Four litre sample for chemical analysis and 250ml for isotopes analysis from each sampling station were collected and preserved with the sulphuric acid for the analysis of major ions.
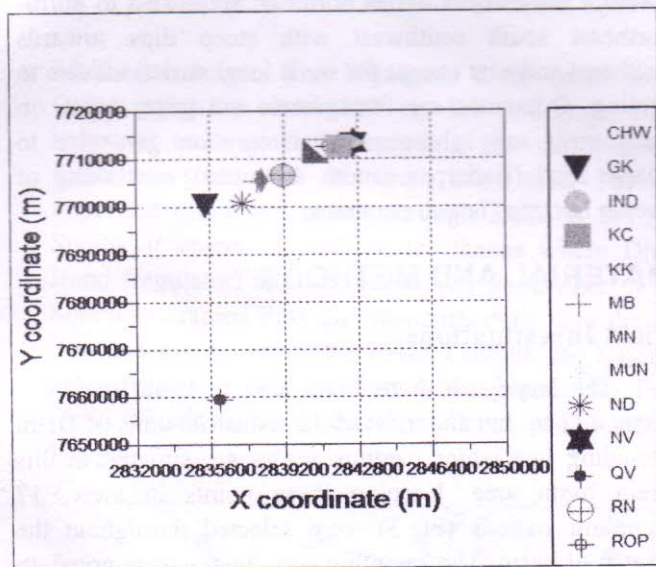
Fig. 3: X-Y plot for sample location based on GPS reading

Chemical Techniques

All groundwater samples were collected and filtered using 0.45 μm Millipore membranes. The samples were brought to the laboratory and stored at temperatures below 4 °C. Major ions were determined by using a Spectronic20, Flame photometer (CL-378) and titration methods. Analysis of the chemical parameters will be done by following the "Standard Methods of Examination of Water and Wastewater" 21st edition, American Public Health Association (APHA) Washington DC, 2005. Apart from the collection and analysis of water samples, additional information related to geology, climate, soil type, and land use of the area were collected from the Central Ground Water Board (CGWB), Indian Meteorology Department (IMD) and Central Pollution Control Board (CPCB), New Delhi.

Nuclear Techniques

Measurement of $\delta^{18}O$

Oxygen analysis was carried out using CO_2 equilibration method (Epstain and Mayeda, 1953). 400 μl of sample water and secondary standard sample water were taken in 3.5ml vials in a batch of 60 vials. The secondary standards used in the batch were pre-calibrated using the primary standards SLAP, VSMOW and GISP and also using the pre-analyzed samples procured from BARC, Mumbai and IAEA, Vienna. The batch samples were evacuated and equilibrated with Tank CO_2 gas (which is taken as calibrated Reference gas) for 7 hours at 40^0C (±0.1^{0}C). Isotope exchange between sample water oxygen and oxygen of gas CO_2 occurs during the equilibrium process. The gas after the equilibrium attains an isotope ratio of oxygen depending upon the sample water oxygen isotopic ratio and the temperature of equilibrium.

The isotopic exchange can be described as;

$$C^{16}O_2 {}_{(g)} + H_2{}^{18}O_{(l)} \underline{k} = C^{18}O^{16}O {}_{(g)} + H_2{}^{16}O_{(l)},$$
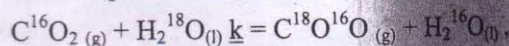
Where, K is the isotopic exchange rate constant.

The equilibrium isotopic fractionation factor α = ($^{18}O/^{16}O$) g/($^{18}O/^{16}O$) g = 1.0412 at 25^0C (Hut, 1987), the temperature dependency is 0.2‰/^{0}C.

The equilibrated CO_2 gas is dehydrated using a water trap for 3 min at -72^0C. The equilibrated gas is then passed into the mass spectrometer for isotope ratio analysis. In the mass spectrometer, the gas is ionized, and its isotopes are dispersed according to their mass to charge ratio using combination of electric and magnetic field. The ionic currents of the separated isotopic beams (44, 45 and 46 in the case of CO_2) are measured using Faraday cups. After each measurement of isotopic ratio in a sample (46/44) s and in tank-CO_2 Gas (46/44) R, δ in the sample is estimated as;

$$\delta = [(44/46)_s - (44/46)_R / (44/46)_R] \times 10^3 \text{‰} = [(44/46) s/ (44/46)_R - 1] \times 10^3 \text{‰}$$

(Where, 44 = $^{12}C^{16}O^{16}O$ and 46= $^{12}C^{16}O^{18}O$; Abbreviations: R stands for reference (Tank Gas) and s for sample (including that for secondary standard))

In the measurement, Tank Gas (Reference) and also the sample gas is broken into 10 equal parts and the ratios (44/46) are measured on each of these sub-portion As the instrument alternately switches between sample and Tank Gas, in the ten switch-overs ten δ's get estimated. These ten δ's are averaged after removing outliers using ±1σ criterion and the mean δ is quoted as the δ for the sample. The estimated δ is then converted into $\delta^{18}O$ by introducing isotopic correction factor for the small presence of ^{17}O (Gonfiantini 1981). The precision of the estimated $\delta^{18}O$ is within ±0.1‰. For statistical consistency two aliquots are taken for each sample. The $\delta^{18}O$ of sample is taken from the average $\delta^{18}O$ of these two aliquots. The secondary standards provides an overall check on the stability of the system during the batch analysis, long term stability of the system and in calibrating the Tank Gas at the time of its replacement.

Measurement of δD

Measurement of D/H ratio in sample is done similar to oxygen isotope analysis with a difference that the

uilibration is carried out with hydrogen gas in the presence of platinum (Pt catalyst, marketed as Hokko Beads) in place of CO_2 gas. The catalyst Hokko beads are made of 1 wt % Pt coated on 1mm diameter styrene divinyl benzene porous resin that provides hydrophobic support to the platinum. These are re-usable by simply activating them by washing in distilled water and drying at 80-90 °C.

The exchange reaction takes place as;

$$HD_{(g)} + H_2O_{(l)} k \Leftrightarrow H_{2(g)} + HDO_{(l)},$$
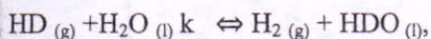
where, k is the isotopic exchange rate constant. The equilibration is carried out for 180 minutes at 40°C.

The fractionation factor α = (D/H) $_{water}$ / (D/H) $_{gas}$ = 3.81 at 25°C.

The reaction is very sensitive to temperature (6.3 ‰ per °C and precise temperature control is required (± 0.05°C corresponds to 0.3‰ error).

RESULT AND DISCUSSION

The Chemical and isotopic study of groundwater of Najafgarh drain basin area was carried out during the year 2010-2011 and groundwater samples were collected during October 2010, February 2011 and June 2011 for the various parameters covering major ions, heavy metals and stable isotopes study. The results of all chemical and isotopic study for 51 groundwater samples of 17 sampling station are given through the graphical and statistical presentation.

Isotope Hydrochemistry

The results of present study reveal (fig.4) that the variations in δD were found ranging from (min.)-68.325‰ to -33.219‰(max.) and the variation in δ ^{18}O from to -10.266‰ to -4.337‰ during June 2011 and the variation in δD were found ranging from -61.45‰ to -14.978‰ and the variation in δ ^{18}O from to -9.405‰ to -1.248‰ during October 2010. These results show that the depletion in isotopic signature of groundwater from North to South-west area.
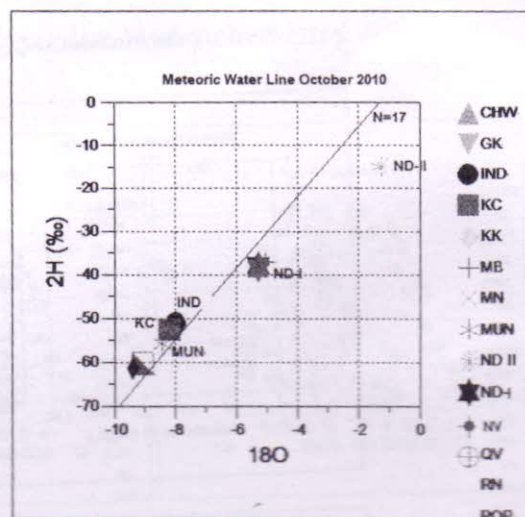

(a)
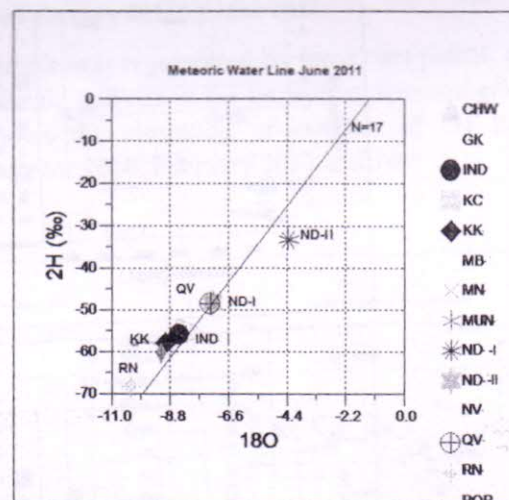
(b)

Fig. 4: Meteoric Water Line (MWL) Plot (a) October 2010 (b) June 2011

In this diagram water samples plotted close to the world Meteoric Water Line (MWL) suggest a meteoric origin. The plot shows ^{18}O on the X-axis and ^{2}H on the Y-axis. The Global meteoric water line is defined by the following equation: $^2H = 8.2x\ ^{18}O + 10.8$

The difference in the stable isotope composition between samples from the northern and those from the southern part of the basin and is probably due to regional and/or seasonal variations in the stable isotope composition of groundwater.
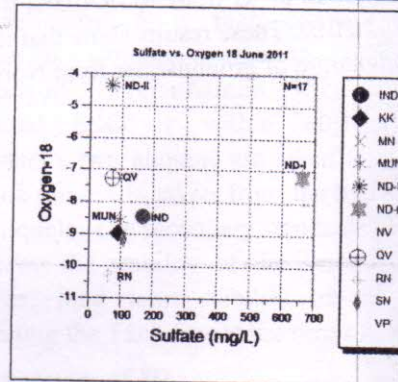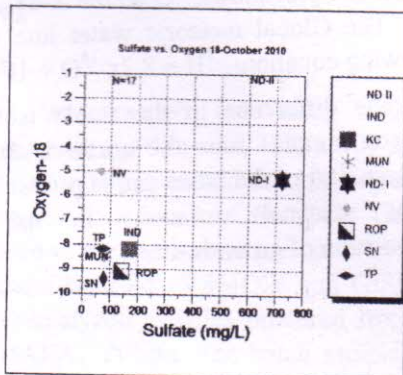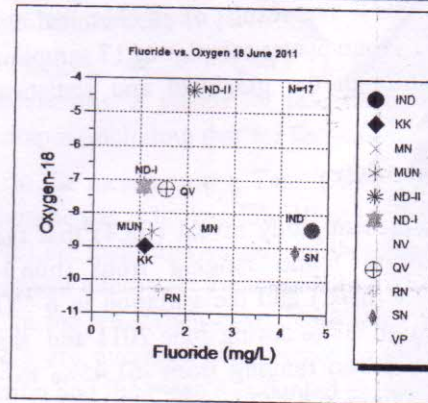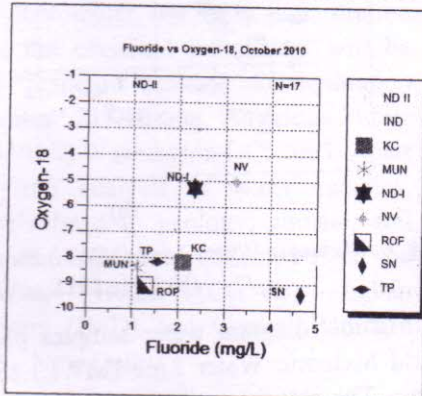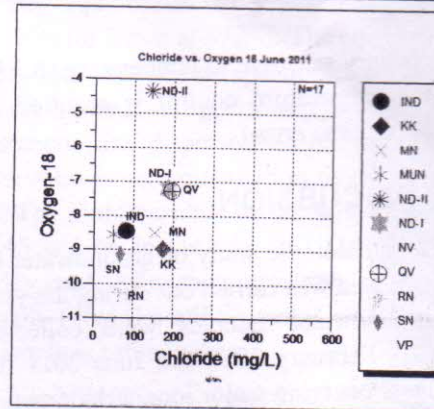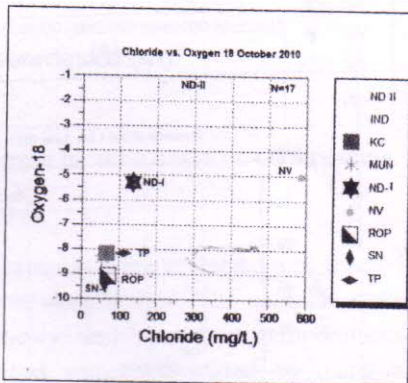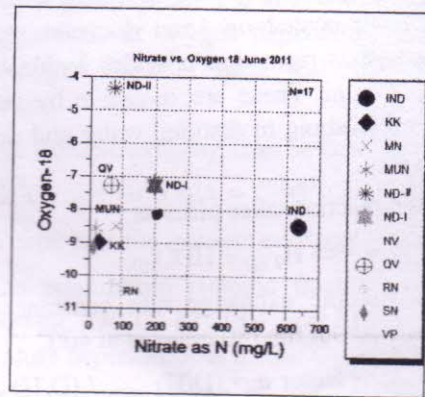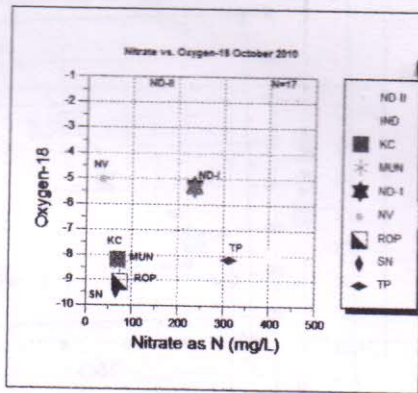
(a)   (b)

Fig. 5: Relationship of Oxygen-18 vs. Nitrate, Chloride, Fluoride and Sulfate (a) October 2010 (b) June 2011

Figure 5 reveals the integrated study of stable isotopes i.e Oxygen-18 relationship with the major anions (Nitrate, Chloride, fluoride and Sulfate). Chemical information integrated with isotopic information can give us the exact status of chemical distribution at a stretch of study area.

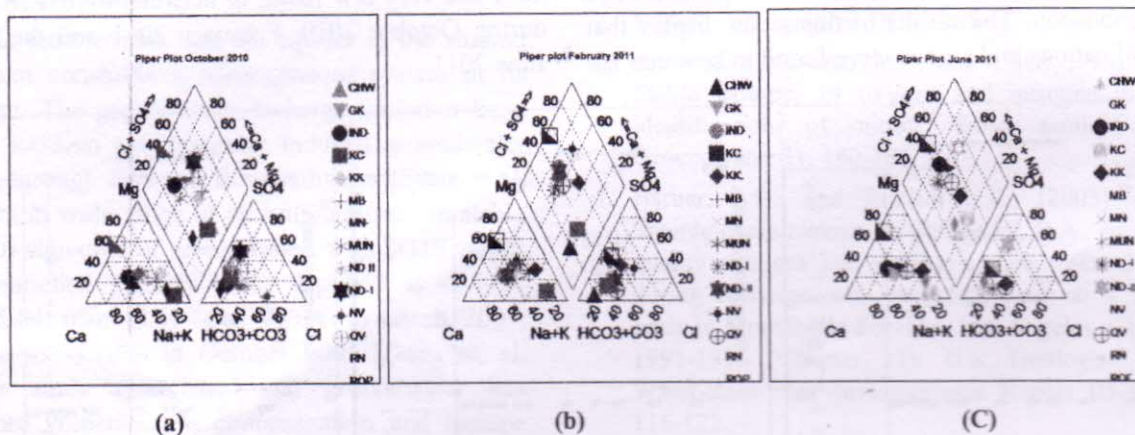## Major Ion Hydrochemistry

Fig. 6: Piper plot (a) October 2010 (b) February 2011(c) June 2011

In piper plot (Fig.6) major ion were plotted as cation and anion percentage of milliequivalents in two base triangles. The projection reveals certain useful properties of total ion relationships. The total cations in meq/l, and total anions in meq/l were set equal to 100%. Every sample was represented by three data points; one in each triangle and one in the projection diamond grid. This plot shows the clustering of samples of the months viz., October 2010, February 2011 and June 2011.
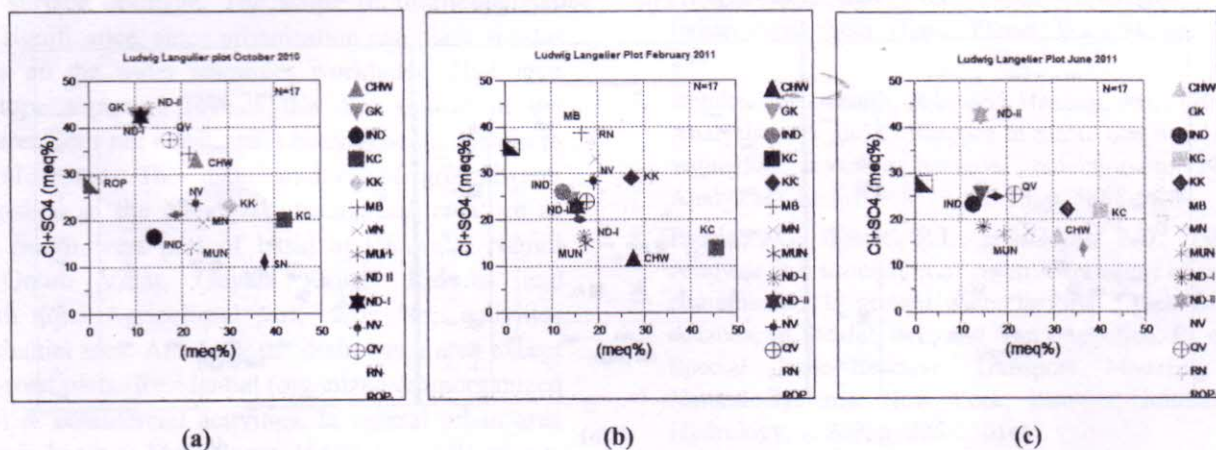

Fig. 7: Ludwig Langelier plot (a) October 2010 (b) February 2011(c) June 2011

With the help of this Ludwig-Langelier plot (Fig.7) we have observed quickly patterns and the correlations between the major cations and anions for multiple samples. By convention, the sum of selected cations is plotted on the X-Axis and the sum of selected anions is plotted on Y-Axis. Each axis ranges from 0 to 50 meq%. Sample points are calculated as follows:

$$\sum anions = Cl + SO_4 + HCO_3,$$

$$\sum cations = Ca + Mg + Na + K$$

$$\% Na = 50 \, Na/\textstyle\sum cat$$

$$\% Cl = 50 \, Cl/\textstyle\sum an$$

Suitable groupings of cations and anions are selected and plotted as percentages:

$$\%Ca + \%Mg = 50 - (\%Na + \%K),$$

$$\%Cl = 50 - (\%HCO3 + \%SO4).$$

These plots display the pattern and correlation between the major cations and anions for multiple

samples of groundwater of two periods viz., pre monsoon and post monsoon. The results of this study display that the most of cations and anions were found in between 10- 40% and very few found in between 0-10% and 40-50% during October 2010, February 2011 and the month of June 2011.
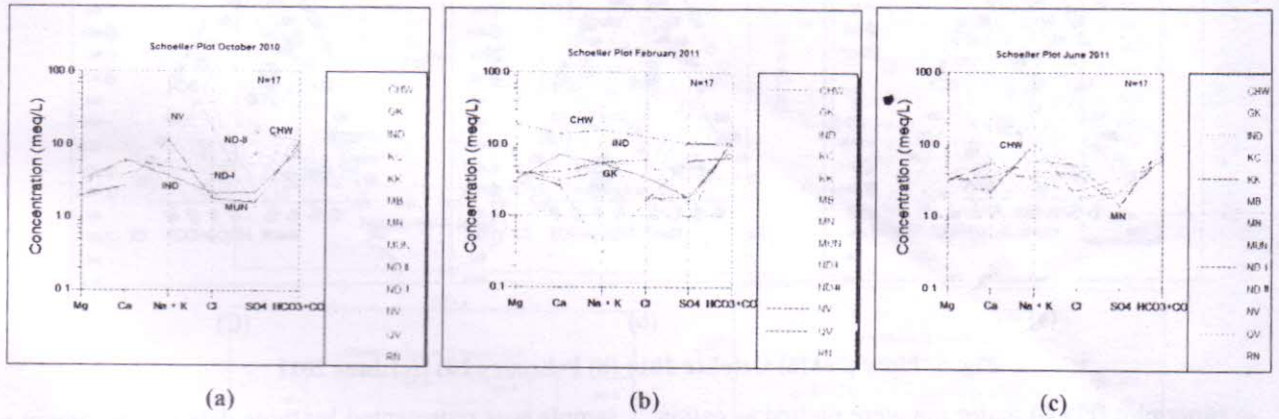

(a)   (b)   (c)

Fig. 8: Schoeller plot (a) October 2010 (b)February 2011(c) June 2011

The Schoeller plot (Fig.8) indicates intermixing of groundwater that have different chemical compositions and water type, viz., Ca-Mg-HCO3; Na-Ca-HCO3-Cl; Mg-Na-HCO3; Na-HCO3; Na-Cl-HCO3; Na-mg-Cl; Na- Cl and Ca-Mg-Cl. These semi-algorithmic diagrams were developed to represent major ion analyses in meq/l and to demonstrate different hydro chemical water types on the same diagram.
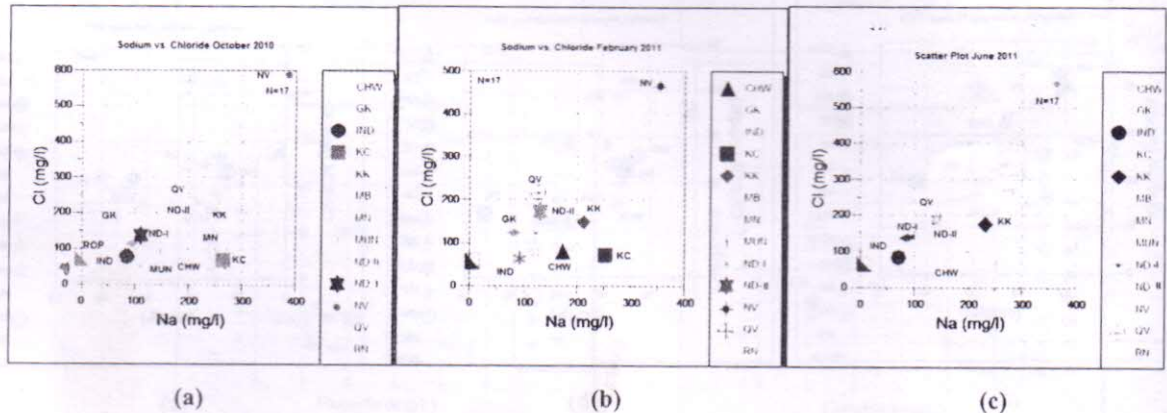

(a)   (b)   (c)

Fig. 9: Sodium vs. Chloride (a) October 2010 (b)February 2011(c) June 2011

This Fig.9 were shows scatter diagram of Sodium vs. Chloride in mg/l shows the relation between sodium and chloride for the total 51 samples from year 2010-11.

CONCLUSION

Chemical quality of ground water in NCT Delhi varies with depth and space. Brackish ground water mainly exists at shallow depths in Northwest, West and Southwest districts with minor patches in North and Central districts. In alluvial formations, the quality of ground water deteriorates with depth, which is variable in different areas. The ground water is fresh at all depths in the areas around the ridge falling in Central, New Delhi, South and Southwest districts and also Chattarpur basin.

In the areas west of the ridge, in general, the thickness of fresh water aquifers decreases towards northwest, the thickness of fresh water zones is limited in most parts of west and southwest. In the flood plains of Yamuna, in general, fresh water aquifers exist down to 30-70 m. In addition, the open land dumping of solid waste, discharge of liquid waste of both industrial and domestic origin and improperly lined drains lead to high groundwater contamination through leaching and seepage and this phenomenon is further accelerated due to gradient slop of this basin. The fluoride contamination in groundwater has been noticed in samples of groundwater collected from south west district and West districts. The high fluoride levels are mostly found in areas where groundwater is

ish to saline in nature. The nitrate concentration in undwater has been reported mostly from areas where domestic effluent is discharged in to open unlined drains. The high nitrate concentrations are mainly from point source of contamination.

Isotopic data reveals that the aquifer in the studied area does not constitute a homogeneous system in its lateral extent. The groundwater recharge variation from location to location and pumping induced groundwater intermixing through different flow pathways (Datta et al, 1996) results in wide range of spatial variations in stable isotope (^{18}O) signature of groundwater, with $\delta O18$ values as highly enriched +0.59% to as. depleted as -7.59‰ during 2003-04; from -0.60‰ to -7.70‰ in march, 2005, and -1.80‰ to -8.10‰ in October 2005 (Datta et, al, 2008). The study establishes that groundwater has become more vulnerable to contamination and isotope studies should be conducted as part of comprehensive hydro chemical investigation of ground water vulnerability. There are indications of pollutants transport from the western, northwestern and southwestern areas to the urbanized and overexploited parts. In the northwestern and western parts, there is evidence of increasing ground water pollution and leachate transport to ground water through surface drainage. The scope of this study has broader significance, since urbanization can place similar pressures on the water resources worldwide. Hydrogen and Isotope signature reveals that the aquifer in the studied area does not constitute a homogeneous system in its lateral extent. The main sources of groundwater contamination in the Najafgarh drain basin area are as follows: South west part of basin at Chawala, Nangli Dairy, Qutub Vihar, Goyala Khurd, Kakrola and Najafgarh area- Agricultural part, cattle farm activities and residential area. All along the drain basin area except at south-west parts- Residential (organized & unorganized colonies) & commercial activities. In central urban area of the drain basin at Moti Nagar, Inderlok and Wazirpur-Major industrial units like Insecticide, Caustic soda, Vanaspati, Electroplating etc.

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