Isotopic and Hydrochemical Signatures in Characterizing Pollutants Movement in Overexploited Groundwater Aquifers of Delhi State

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Abstract
Over the last two decades, intense urbanization in Delhi area created several cut slopes of the rugged topography. Iso-contours and multi-component mixing models of pollutants and isotopic composition of groundwater provided a unique understanding of the pollutants dynamics in groundwater. Over 60% of the wells have become vulnerable to increased chloride and nitrate contamination based. The major sources of chloride and nitrate are anthropogenic wastes, landfills, sewage irrigation and sewage treatment plants, turf grass fertilizer and surface water runoff. ^{18}O isotope and major elements that accompany in the groundwater may distinguish sources of nitrate with less ambiguity, under different land use conditions. Cl, Na, Mg, Ca, SO_4 and NO_3 show promising results as nitrate tracers on ternary diagram and through element vs. element plots. Additional Ca^{2+} may be released to groundwater by corrosion of subsurface concrete materials. Guidance has been provided on the overall approach for protection of groundwater resource.

Keywords: Pollutant, groundwater, hydrochemical, Delhi.

Introduction
Over the years, increase in population, urbanization and industrialization in Delhi area created several cut slopes of the rugged topography. Indiscriminate disposal of anthropogenic wastes and leaching of pollutants from these resulted in an ever-increasing threat to the quality of ground water resource base. Large-scale groundwater withdrawal for domestic, irrigation, and industrial purposes lead to widespread decline of ground water table. For protection of groundwater from pollution, it is a matter of concern for the planners and decision makers to clearly characterize the groundwater renewal, quality of water and causes of its deterioration, sources of pollution, trace the movement of pollutants and containment of spreading from known sources. The characteristics of pollutants level and transport in groundwater are associated with variations in one or two parameters at one scale and several parameters at another scale. While, a broad qualitative understanding of most of the aforementioned effects is known, most of the various parameters and physico-chemical process as a whole in the hidden complex groundwater system are not completely understood. Iso-contour diagrams and multi-component mixing models of pollutants and ^{18}O isotopic composition of groundwater along the flow path provided a unique understanding of the groundwater flow system and its vulnerability.

Physiography, Geohydrology and Climate
The semi-arid Delhi region (Figure-1) (area: 1483 Sq.Km. between 28^{o}24'17"-28^{o}53'00" N and 76^{o}50'24"-77^{o}20'37" E), situated on the banks of the river Yamuna which flows from north to south, is a part of the Indo-Gangetic Alluvial Plains.

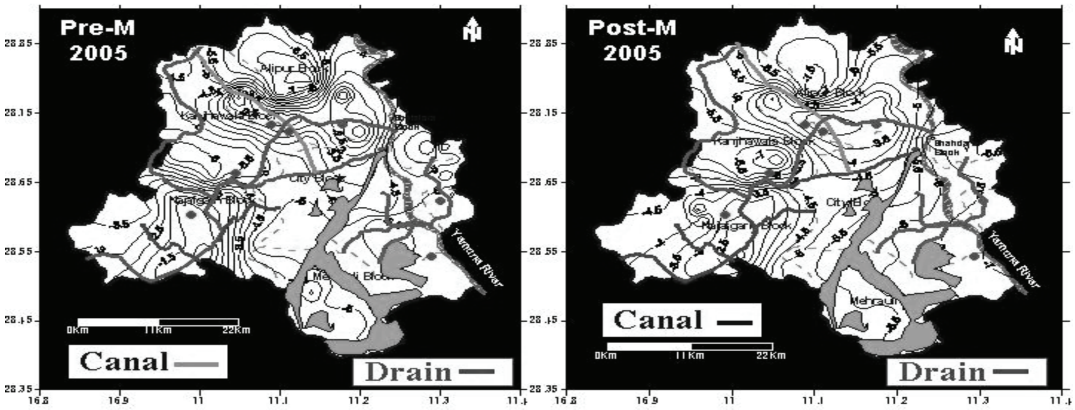

Figure – 1 Model of d^{18}O (‰) distribution in groundwater of Delhi region. Groundwater in Pre-monsoon 2005 and 2004 is isotopically similar, indicating depression focused recharge from isotopically enriched rainfall. Post-monsoon 2005 is relatively depleted, suggesting dilution effect due to lateral flow from surrounding areas.

The aquifer disposition in the area is overlain predominantly by sand in the top 20-30 m, and clay and kankar below that. The Alluvium thickness in the area varies from 100 m to more than 300 m and groundwater occurs under semi-confined conditions. The hydrogeological situation is characterized by the occurrence of alluvial and hard rock formations.

The climate of the region is semi-arid. The average annual rainfall (1931-99) is 711 mm, most of which falls between June to September and is generally erratic, infrequent and heavy sometimes. The average normal rainfall during July, August and September is 192.3 mm, 192.4 mm and 139.6 mm respectively. The mean minimum and maximum temperatures are 18.7^{O}C and 30.5^{O}C respectively.

Analytical Methods

Through extensive field survey and topographic survey, representative sites under changing land use were selected, geographically equitably distributed covering the area, representing various geohydrological conditions. Groundwater samples were collected at sixty-seven different locations during June-July, 2003; at hundred different locations during June, 2004, at 84 locations during March, 2005 and at 84 locations during October, 2005.

Temperature, pH, specific conductance were measured in the field. The samples were analyzed as early as possible for the major anions (HCO_3, Cl, NO_3 and SO_4), cations (Na, K, Mg and Ca), and electrical conductivity by standard methods. The analytical precision for the measurement of major ions is generally kept within ± 5% and expressed in mg/l or meq/l. The $^{18}O/^{16}O$ ratio was measured following a modified Epstein-Mayeda technique and using Micromass Isotope Ratio Mass-Spectrometer, by equilibrating a tank CO_2 gas at 25°C. The isotopic composition of water samples is expressed in terms of per mille deviation (δ ‰) with respect to the isotopic ratio of the reference Standard Mean Ocean Water (SMOW). The analytical reproducibility of the laboratory standard is ± 0.1‰.

Groundwater isotopic and chemical composition

The isotopic data reveals that the aquifer in the studied area does not constitute a homogeneous system in its lateral extent. The groundwater recharge variation (<1% to 66.0%) from location to location, and pumping induced groundwater intermixing through different flow pathways (Datta et al, 1996), result in wide range of spatial variations in the stable isotope (^{18}O) signatures of groundwater, with $\delta^{18}O$ 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. In general, the groundwater isotopic composition is relatively enriched as compared to the long-term weighted average value (-6.09‰) of Delhi rainfall (Datta et al, 1991). The groundwater are mostly alkaline with pH ranging from 6.9 to 7.7, and are moderately to highly saline, with EC ranging from 567-10340 umhos/cm in northern parts; 440-11944 umhos/cm in northwestern parts; 810-15370 umhos/cm in western parts; 680-2420 umhos/cm in southern parts; 550-3231 umhos/cm in eastern parts and 764-6950 umhos/cm in City parts. The Chloride levels range from 10-7160 mg/l in northern parts; 10-4100 mg/l in northwestern parts; 50-860 mg/l in City area; 60-6080 mg/l in western parts; 10-280 mg/l in southern parts and 10-830 mg/l in eastern parts.

Large part of the area to the west of the ridge is severely affected by nitrate pollution of groundwater (Datta et al, 1997), exceeding the WHO prescribed maximum permissible limit (45 mg/l) in drinking water at many places. During 2003, the Nitrate levels in groundwater ranged from <1-135 mg/l in northern parts; <1-159 mg/l in northwestern parts; 2-32 mg/l in City area; 2-716 mg/l in western parts; 19-303 mg/l in southern parts and 1-69 mg/l in eastern parts. During 2004, the Nitrate levels in groundwater ranged from <1-197 mg/l in northern parts; <1-193 mg/l in northwestern parts; <1-433 mg/l in City area; 1.5-445 mg/l in western parts; 2.2-173 mg/l in southern parts and <1-158 mg/l in eastern parts. During March 2005, the Nitrate levels in groundwater ranged from <1-250 mg/l in northern parts; <1-220 mg/l in northwestern parts; 4.9-958 mg/l in City area; 7-504 mg/l in western parts; 24-465 mg/l in southern parts and <1-144 mg/l in eastern parts. During October 2005, the Nitrate levels in groundwater ranged from <1-7.4 mg/l in northern parts; <1-14.5 mg/l in northwestern parts; 1.6-387 mg/l in City area; 2.5-82 mg/l in western parts; 2.5-26 mg/l in southern parts and <1-35 mg/l in eastern parts. EC, Chloride and Nitrate levels show an increasing tendency during the last decade in the northern parts, in the southwestern parts and in the western parts. Chemical composition of the groundwaters, in general, remained more or less the same from year to year.

Isotopic distribution and chloride dynamics in groundwater and recharge zones

Superimposition of $\delta^{18}O$ (‰) distributions on the Surfer-8 based topography model suggests that the pattern of $\delta^{18}O$ (‰) distributions has remained unchanged from year to year (Figure-1). But, groundwater in 2004 and pre-monsoon 2005 is highly saline, contaminated and isotopically enriched, as compared to rainwater mean δ–value of -6.09‰, suggesting selection effect in favour of isotopically enriched rainfall in contributing depression focused recharge, with longer time stay on low elevated land. Post-monsoon 2005 is relatively depleted, suggesting dilution effect due to lateral flow from surrounding areas, as observed earlier (Datta et al, 1994).

In the aquifer, adjacent to the western bank of the Yamuna river at some stretches, similarly enriched ^{18}O composition of both river water and groundwater compared to that of rainwater during pre-monsoon, 2005 suggests that the river water recharges the groundwater after being subjected to evaporative effects. However, relatively depleted ^{18}O composition of both river water and groundwater during post-monsoon suggests fresh rainfall recharge to the groundwater in these locations, and possibly contributions from the transport of the top layers of the groundwater from the nearby surrounding areas, as induced by pumping. A simple mixing model (Datta and Tyagi, 1995), based on the spatial and depth variations in $^{18}O/^{16}O$ ratio of groundwater and canal/river water, considering equal inflow of groundwater through the screens of the tubewells, indicated that canal/river water contributes to the groundwater recharge upto 5-10m depth of the aquifer adjacent to the canal/river.

Moderate to highly saline groundwater occurrence suggests that the rainfall recharge is very limited and that groundwater flushing is incomplete. Iso-contouring of chloride and nitrate dynamics (Figure-2 & 3) indicates that from 2003 to 2005, there had been lateral extension of high pollutants plumes towards the central urban parts along specific flowpaths, possibly induced by withdrawal not in balance with recharge. The chloride distribution further suggests that due to excessive concretization of the region, recharge area from direct infiltration of rainfall has reduced considerably and changes from 2003 to 2005, and the potential recharge zone remained confined only in the piedmont areas of southern parts. During 2003, there are small patches of potential recharge zone along the western Yamuna canal almost on the boundary separating the northern and northwestern parts and adjacent to the Yamuna river in the northern parts. Another recharging zone is along the southern and eastern boundary of southern parts.

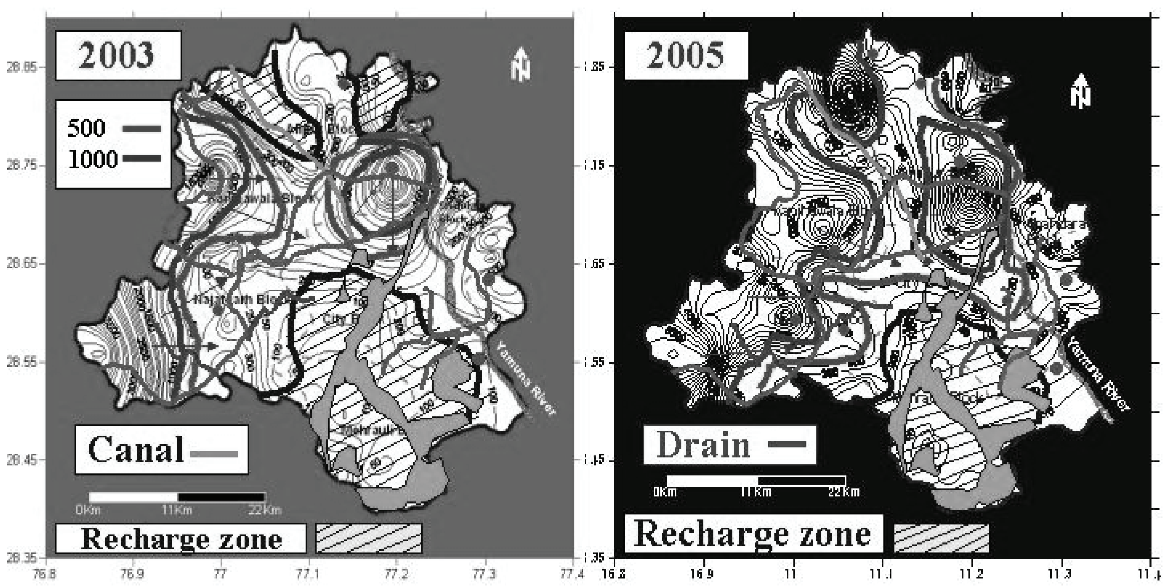

Figure – 2 AQUACHEM Model of High Chloride (mg/l) Plumes Dynamics in Groundwater of Delhi Region. Groundwater is moderately to highly saline, with lateral extension of high salinity plumes towards the central urban parts along specific flowpaths, induced by withdrawal not in balance with recharge.

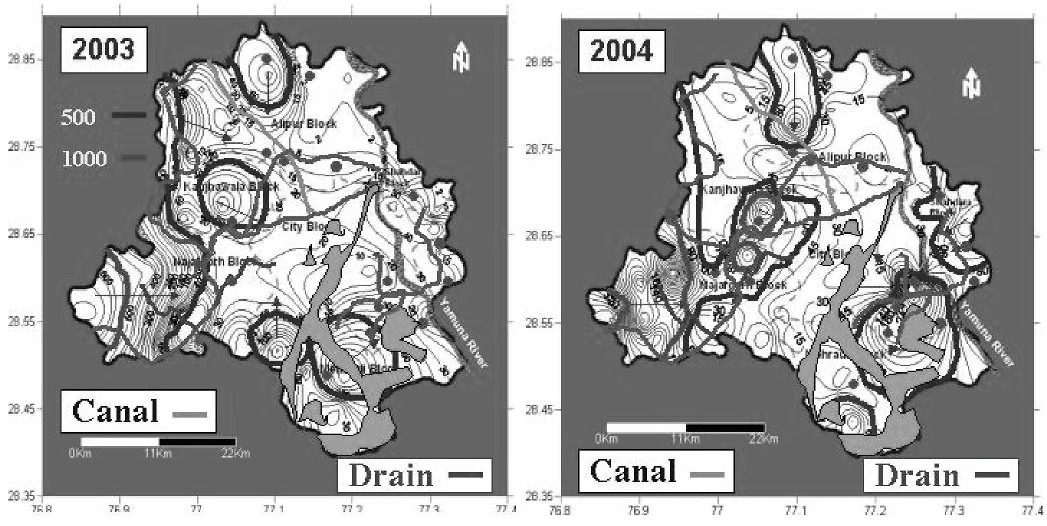

Figure – 3 AQUACHEM Model of High Nitrate (mg/l) Plumes Dynamics in Groundwater of Delhi Region

On a regional scale good positive straight-line relationships between groundwater Cl and $\delta^{18}O$ (Figure- 4) indicate multiple source of high salinity groundwater mixing with good quality water along two or more visualized specific flow pathways, due to changes in the hydraulic heads (Datta et al, 1996), induced by indiscriminate pumping. Except in southern parts, eastern parts and City area, significant variation in groundwater chloride with almost no change in ^{18}O isotopic composition suggests salinity increase contributed by vertical infiltration of chloride containing chemicals in soil with rainwater or irrigation water. The lateral flow water also carries contaminants alongwith it through specific flow-pathways (Datta et al, 1996), influenced by mixing and the extent of the hydrodynamic zones (as indicated by small isotopic gradients).

Identification of sources of recharge based on major ion chemistry

AQUACHEM based major-ion trilinier diagrams (Figure-5) indicates that the groundwaters have different chemical compositions, viz., Ca-Mg-HCO_3; Na-Ca-HCO_3-Cl; Mg-Na-HCO_3; Na-HCO_3; Na-Cl-HCO_3; Na-Mg-Cl; Na-Cl and Ca-Mg-Cl. While, Calcium bicarbonate water is originated as rainfall-derived recharge, over decades to centuries, Calcium-sodium bicarbonate water, are more likely derived from recharge of rainfall that carried saline water mixing alongwith. Since, the clay mineralogy of the area indicates presence of 60% to 80% Illite (Datta and Tyagi, 1996), which apparently is highly resistant to weathering process, the abundance of (Ca+Mg) in most of the groundwaters in the Delhi area can be attributed to mainly carbonate weathering, as observed from earlier studies (Datta and Tyagi, 1996). Presence of 'Kankar' carbonates in the alluvial sediments and occurrence of metamorphosed dolomitic limestones in Delhi Aravalli rocks could favour this process.In addition to this, the groundwater chemistry seems to be significantly affected by the dissolution of concrete materials. Additional Ca2+ may be released to groundwater by corrosion of subsurface concrete materials such as building foundations and basements.

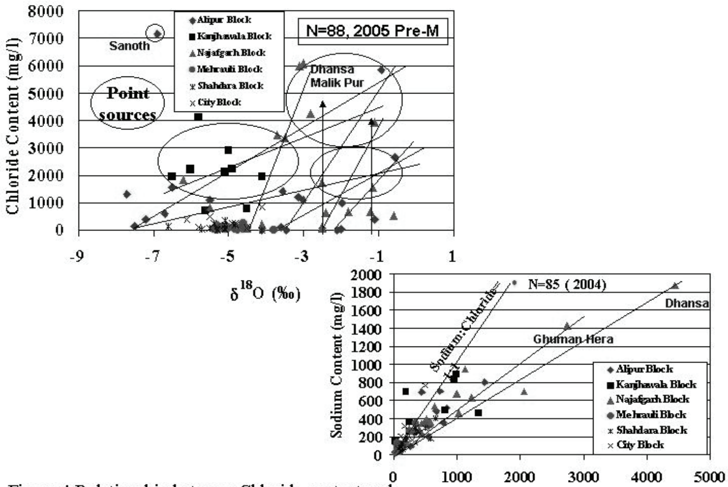

Figure-4 Relationship between Chloride content and d18O and Sodium content in groundwater of Delhi

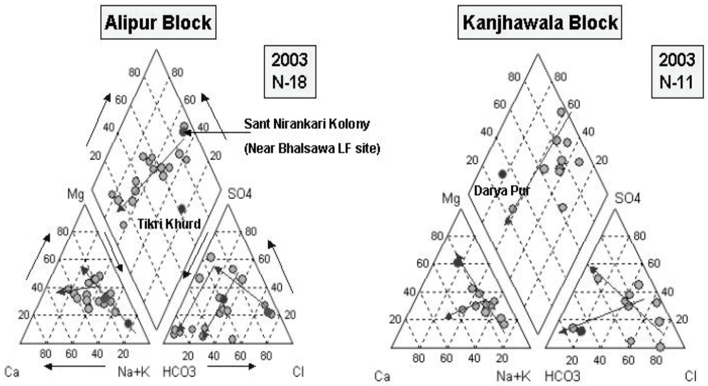

Figure-5 AQUACHEM Model of Chemical Composition of Groundwater in Delhi Area

Very highly saline waters (EC>10000 µmhos/cm) are of Na-Cl type. Moderately saline groundwaters (EC: 3000-6000 µmhos/cm) are of Na-Mg-Cl type. However, sodium shows no correlation with salinity (Electrical conductivity). Highly correlated linear trend between Na and Cl (Figure-4) indicates mixing of two groundwater bodies with different end member composition (i.e. fresh and saline). It is interesting to observe that in every year, most of the groundwater samples lie below the equiline in the scatter diagram of Na vs. Cl, suggesting influence of anthropogenic activities. Groundwaters with low SO_4 and high Cl probably indicates localized SO_4 reduction. The very high Cl and SO_4 concentrations in some of the groundwaters may be related to the long history of evaporation and to oxidation of reduced sulphur gases from land in the relatively lower elevations of flood plain regions, (Datta and Tyagi, 1996). Further the possibility of contribution from anthropogenic sources can not be ruled out.

In ground water of the northwestern and southwestern parts, Sodium-chloride water might have been acquired by mixing with a large component of relict saline water in the deep aquifers (60-200ft) during geologic time. Calcium-magnesium-bicarbonate-sulfate water genesis may be due to longer periods of weathering in contact with aquifer sediments. The groundwaters, plotted on the trilinear diagram on a mixing line between Calcium-sodium bicarbonate and Sodium-Chloride waters, represent the continuum between rainfall-driven recharge, and relict saline water. The ground waters with mixed cation- bicarbonate and mixed-cation bicarbonate-chloride water, found in surface water or shallow ground water, represent mixtures of various waters (Figure-6). In contrast, mixed-cation bicarbonate water with "depleted" stable isotopic signature, were found both very shallow (15 ft) and relatively deep (60 ft or greater). The deeper mixed-cation bicarbonate water might have evolved by geochemical interactions with aquifer sediments. Ternary diagrams of the major cations and major anions show that agricultural land use produces calcium-sulfate type water due to liming and the application of fertilizers. Residential land use produces water more enriched in sodium and either chloride or bicarbonate, due to an increased contribution of road salt, and in part to the elevated levels of these ions in sewage plumes.

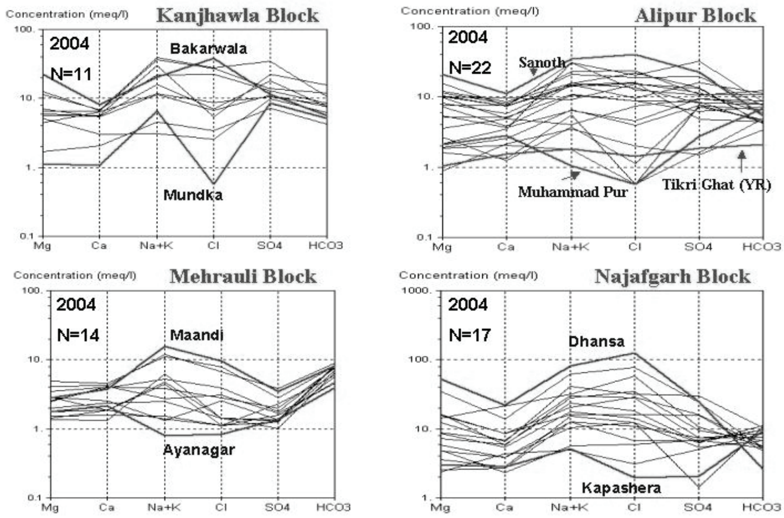

Figure-6 AQUACHEM Multi-Component Model of Groundwater Intermixing

Concluding remarks

The study establishes that groundwater has become more vulnerable to contamination and isotope studies should be conducted as part of comprehensive geohydrological and hydrochemical 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. Further systematic research is needed on hydrogeologic characteristic of the groundwater flow under natural and stressed conditions, dynamics of groundwater contaminants, and its linkage with spatial and temporal variability in concentration, depth variation in contaminants level in relation to well structure and casing conditions, denitrification potential of soil and geohydrology in limiting contamination. Iso-concentration maps of contaminants levels in groundwater should be prepared and revised time to time, in relation to the changes in landuse pattern. The scope of this study has broader significance, since urbanization can place similar pressures on the water resources worldwide.

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