GEOCHEMISTRY OF GROUND WATER IN AND AROUND DELHI.

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BY

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CERTIFICATE

The work presented in the dissertation entitled "Geochemistry of ground water in and around Delhi" was carried out at the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi.

This work has not been submitted in part or full for any other degree and diploma anywhere else.

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CONTENT

ABSTRACT

Mineral-water equilibria and control of lithology on concentration of different ions in ground water in Delhi region were explored in this work. 15 water samples from different localities representing diverse lithology and 4 water samples from Yamuna river, pond and abandoned mine had been collected 3 times in 1977 namely in January, June and September, approximately corresponding to peak winter, summer and monsoon season.

For detailed stdy winter data choosen because, firstly they give average quality of water and secondly to restrict large expansion of workmkeeping in view scape of M.Phil. dissertation and availability of time.

Control of lithology has been observed for all ions except for phosphate, limited control was observed in case of chloride, potassium and calcium. These ions are found maximum in sand dunes but in alluvium and quartzite then concentration is not appeared to be governed by lithology. Excellent control of lithology was seen in case of bicarbonate, sulphate, silica sodium and magnesium.

Phase diagrams study based on water chemistry indicated that dolomite or aragonite and huntite are likely to be precipitated depending upon the types of carbonate mineral assemblages choosen for theoretical interpretation.

In the similar manner different silicate system hinted gibbsite, kaolinite and K-feldspar are likely to be precipitated when K-silicate system considered, in case of Na silicate system montmorillonite, kaolinite and quartz and when magnesium system considered chlorite are likely to be precipitated in the state of saturation.

Finally, the presence of kaolinite and quartz is confirmed from weathered product of a pegmatite mine near Masudpur village by x-ray diffractograph.

CHAPTER :: I

INTRODUCTION

It was said by our late Prime Minister Pt. Jawaharlal Nehru that nature writes her story in books of stones and rocks (Nehru, 1976), This statement of Nehru is perfectly true but recent researches have proved that story of nature is not only limited to stones and rocks but also to waters. The role of water in human affairs is needless to emphasize. Water plays dominent role in many geological processes and this role was recognised since the birth of geology. The role is evident from weathering of rocks, water as powerful transporting medium of sediments and mineralizing solutions, precipitation of minerals from water particularly evaporites etc. The more interesting part is developed much later particularly in 1960s known as mineral-water equilibrium study. This branch is based on chemistry of water.

In precise words, mineral-water equilibrium study refers to the study of interaction between water and host rocks. Changes brought about by host rocks in chemical composition of water and finally precipitation of minerals from the water. In last 15 years or so our knowledge of chemical behaviour of minerals at ordinary temperature in contact with water has increased tremendously through experimental and theoretical hydrogeochemistry. The mineral-water equilibrium study requires the knowledge of geology, chemistry and physics. In other words it is interdisciplinary in nature. By theoretical analysis it can be predicted successfully which minerals are in equilibrium with water or are likely to form if saturation of water takes place. The theoretical prediction in most cases has been supported by actual experimental or field findings.

Previous Work

There are various aspects of geochemical investigation of water for example chemical quality study, pollution study, drinking, agricultural and industrial water quality study, water-mineral equilibrium study etc. Water-mineral equilibrium study has been done in various environment where it is found like ground water, springs, rivers, lakes, estuaries and oceans. Here an attempt is being made, in brief, to illustrate the progressof mineral-water equilibrium study. The various aspects of hydrogeochemistry were explored by the following works: Gibbs (1965), Garrels (1965), Garrels and Mackenzie (1967), Handa (1966, 67, 72), Holman (1968), Harries and Adams (1966), Jacks (1973a,b), Jayaraman (1977), Kramer (1968), Krauskopf (1967), Livingstone (1963), Raymahasay (1970), Subramanian (1974), Subramanian and d'Anglejan (1976) and Subramanian and Dalavi (1977).

Harris and Adams (1966) suggested that water acquire its constituents from various sources like atmospheric fall out as dust, salt particles from sea, volcanic debris, reaction during ground water recharge and mineral dissolution and the release of solute during chemical weathering. There are various factors which govern the concentration of ions in water life parent rock-type, climate, topography, and vegetation. Jacks (1973,b), Harris and Adams (1966) and Handa (1967) suggested role of parent rock type would be imporative and besides above mentioned following factors are also important nature of soil, micro organism, permeability and transmissibility of rocks mixing of two or more aquifers of role of man in changing the ground water regime.

Weathering is the major source of ions in ground water, though precipitated water contains some ions by interaction with the atmospheric gases (Barner, 1971, Mason, 1966). Out of physical, chemical and organic weathering processes, chemical weathering is of paramount importance, it is also taking place in very arid climates (Thornbury, 1954). Chemical weathering of igneous rocks have been investigated by various authors: Garrels (1965), Goldich (1938, in Thornbury, 1954), Harriss and Adams (1966), Jacks (1973,a) and Kramer (1967); as igneous rocks contain large number of primary minerals of different composition. Goldich's (1938) conclusion was confirmed by these authors that sequence of disintegration would be plagioclase - biotite - K-feldspar and quartz means plagioslase would disintegrate at faster rate in comparison to biotite, K-feldspar and quarts, beside this sequence of weathering, these investigators also developed the concept of water-mineral reaction and gave firm footing to this. Kramer (1966) comes to conclusion from study of granite, limestone and orthoquartzite and chert terrain that kaolinite will be the first formed mineral and the formation of kaolinite will be enhanced by rise of temperature, pressure and more advanced weathering. He also reported stable mineral assemblages of these rocks. Krauskopf (1967) by experimental study supported that first formed mineral will be kaolinite. Garrels (1965) has speculated an entire sequence of weathering product in igneous rocks, he has drawn conclusion if HCO_3^- concentration is about 100 ppm SiO_2, Ca^{++} and pH will be high based on field and experimental observation, in the above situation simultaneous precipitation of montmorillonite and kaolinite will take place, in next step silica concentration declining as it is consumed by these minerals and pH and HCO_3^- concentration start increasing and at 200 ppm HCO_3^- calcite will precipitate if reaction proceeds further the dissolved CO_2 will be consumed up and would form sodic montmorillonite and substitution begins Mg^{++} for Al^{++} as by increasing their content of K^+, Na^+, Mg^{++} and pH, Ca^{++} and SiO_2 concentration would diminish slightly, zeolite might begin to form, new kaolinite would tend to disappear and final assemblage would ~~tend to disappear and final assemblage would~~ be primary minerals plus zeolite and montmorillonite. He finally draws conclusion that clay is function of degree of weathering and as weathering proceeds silica started coming out more and more out of different minerals. Kranskopf (1967) expected besides above minerals chlorite, gippsite and ellite. Gibbs (1967) concluded that percentage of minerals in sediments like mica, illite, quartz, plagioclase will be controlled by relief and physical weathering processes and presence of montmorillonite will be controlled by calcic rocks and a combination of low relief and chemical weathering.

The releasing ions to solution is also investigated thoroughly, both major and minor ions. In case of silica, ions are released from alkali ion minerals like plagioclase (Garrels, 1965; Handa (1966) and Harriss & Adams (1966). Experimental investigations on silica ions was done by Kranskopf (1967). He found that solubility of silica varies with its different form, at room temperature quartz is soluble upto 13 ppm and forming weak silicic acid (H_4SiO_4). In case of amorphas silica or silica gel solubility can go upto 120 ppm. He also investigated the role of pH, the solubility of silica is constant below pH of 9 at ordinary temperature and it increases rapidly above 9 pH in colloidal form. In ordinary ground water it is found between 10-60 ppm. The conclusion is drawn that silica is state of in-equilibrium either silica is supplied in less quantity or it is used up by organism.

In case of calcite interesting observations were made by Krauskopf (1967) and Jacks (1973,a). Kranskopf pointed out that calcite is more soluble in cold water and releasing more Ca^{++} ions. He finds out that solubility of calcite depends on the saturation of water with carbon dioxide, the CO_2 is more soluble in cold water hence more carbonic acid will form. This carbonic acid will dissolve more calcite and forms calcitibi - carbonate. Jacks (1973,a) observed that calcium concentration increases with salinity of the water and calcite will precipitate in quite saline water but in case of sea water instead of calcite aragonite is precipitated (Pettijohn,1957). Handa (1973) observes that pH 7 indicates free CO_2 gas present in the water, he attributed this to rapid circulation of water with result that insufficient time of contact between rocks and water or absence of calcium minerals in the rocks.

Regarding the other ions, Kranskopf (1967) suggested the sources of K^{+}, Na^{+} and Mg^{++} ions in water are feldspar, mica, amphibole, pyroxene of igneous rocks and various schists and gneisses of metamorphic rocks and sources of chloride and sulphate is either contamination of sulphate water and other waters or dry fall out particularly in coastal region.

Water-mineral equilibrium study in river water was done by various workers. Dalavi (1978), Garrels and Mackenzie (1967), Gibbs (1967), Hohman (1968), Jayaraman (1977), Livingstone (1963), Raymahasay (1970), Subramanian and Dalavi (1977). Most of their work related to construction of phase diagrams of different component, experimental verifications and theoretical findings and erosional study of catchment area.

Subramanian and d'Anglejan (1976) from the study of St. Lawrence estuary predicted that kaolinite, Mg-chlorite and microcline can be expected to be present in the sediment. They have confirmed the theoretical finding by x-ray mineralogical study of suspended sediment.

Handa (1972) actually observed the presence of kaolinite and k-mica in suspended matter of Ganga river, this observation was further confirmed by Jayaraman (1977) in his theoretical study of mineral-water equilibrium in Ganga river based on chemical data given by Handa. Dalavi (1978) both theoretically and experimentally reported presence of kaolinite in Yamuna river water. Subramanian (1974) on his study of St. Lawrence river predicted the presence of kaolinite but he did not confirm his observations by experimental study. Gibbs (1967), Kramer (1966) and Subramanian (1974) drawn conclusion that drainage basin characters are likely to reflect in river water chemistry. This type of study was based on soluble dissolved ions and suspended matters.

Raymahasay (1970) repprted, based on old government data the predominance of mechanical weathering over chemical weathering in Ganga river basin, but Jayaraman (1977) contradicted this and on the basis of carbonate equilibria study suggested chemical weathering will dominate over mechanical weathering.

Garrels and Mackenzie (1967) concluded from the study of chemical composition of springs and lakes of U.S.A. that compositions ~~of~~ ape consistant with a model which the primary rock forming silicates are altered in a closed system to a soil mineral plus solution in a st~~u~~eady state equilibrium with their minerals.

Water-mineral equilibrium study in case of ground water is also done by Garrels (1965), Harriss and Adams (1966), Jacks (1973) etc. Harriss and Adams predicted the presence of kaolinite and montmorillonite in the soil of granitic rocks and they also used the stability diagrams as a means of finding out maturity index of soil. Jacks (1973) in case of a South Indian district predicted kaolinite would be mainly present in water. Handa (1967) made the statistical geochemical ground water of study of Cuddalore district and drawn conclusion that ppm concentration of HCO_3^- increases with increase in salinity, in another study of West Bengal, Handa (1966) drawn conclusion that it is not essential that total dissolved salts and soluble cations should always increase with increase in their conductivity.

The ground water in Delhi region is traversing across various lithological formations of varying age and varying climate (Chapter II). Ground water of this area was investigated by various workers from different point of view. The important workers were Biswas, Das and Verma (1964), Paliwal et.al. (1976), Roy (1969), Sett (1964a,b) and Sett & Khanna (1969). The Yamuna river around Delhi was investigated by Dalavi (1978).

Roy (1969) in his study of North India briefly described the general ground water condition of this region. Biswas et. al. (1964) have investigated this area from quality rating of wells for irrigation purposes and they have measured the water-table, fluctuations in water-table and presented large number of partial chemical analysis of waters from different region. Sett (1964a,b) and Sett and Khanna's work included water-table study, water-logging problem of Northern and Western Delhi and partial analysis pf different places. Sett (1964,b) made comprehensive study of highly saline water of Farrukhanagar and Sultanpur area and reported 4 complete analyses. Biswas has observed rise in water table from .1 to .65 meter in this region and also discussed seasonal fluctuations in water table. Paliwal and Yadav (1976) made exclusive study of ground water from agricultural point of view and discussed the solubility of water and reported large number of partial chemical analyses.

It is clear from the above review of Delhi region that previous work consists of water table fluctuation, partial chemical analyses which are in turn interpreted in terms of quality from domestic and agricultural point of view and general and nature of water table.

Scope of present wofk

The present work consists of mineral-water equilibrium study in Delhi and part of Haryana State ground waters. In order to produce a generalized picture of the region water samples were collected from all the rock types in rough proportion of their aerial distribution and some water samples are also collected from exposed water bodies like river, pond and abandoned mine. Seasonal sampling of water from the same spot was also done to study the seasonal variation of water. Quality and its impact on mineral-water equilibria. But this work is confined to only winter samples because average water quality is available in this season and scope of M.Phil. dissertation and availabilityof time were other factors. It is believed, winter samples give average quality of water because there is no excessive evaporation of water as it happens in summer which causes higher concentration of ions in water and in rainy season there is much dilution of ions take place because of percolation of surface water. The quantitative determination of pH, conductivity, total dissolved salts and major ions were done in the laboratory.

The possible sources of sulphate, phosphate and chloride ions have also been explored in this work because these ions are usually not present in minerals.

CHAPTER :: II

GEOHYDROLOGY OF DELHI REGION

The area included in this work falls between 28°15' to 28°45' latitude and 76°45' to 77°30' longitude covers more than 3800 sq. km. shown in Fig. 1 (Sett, 1964). The important cities and towns of this area are Delhi, Faridabad, Gurgaon, Najafgarh, Farrukhanagar and Badarpur of Union Territory of Delhi and part of Haryana State.

Climate

According to Sett (1964) the most part of the area comes under semi arid type of climate and part of area particularly western region is having arid type of climate. The temperature varies between 6.3°C to 47.0°C while mean temperature is 24.8°C the lowest temperature is found in the month of December and January and highest in the month of May and June.

The rainfall in this region is erratic and average is about 55 cms per year. The major part of the rain fall takes place in the monsoon season and while a small part in December and January. Sometimes flooding also occur in this region in monsoon season.

The amount of rainfall and variation in temperature both daily and annual are likely to have substantial effect on the quality of ground water.

Topography

Topography is also one of the important geological factors which plays major role in the recharge of ground water. The ground water recharge is more if area is plain and it is less if area has high slope provided other factors remain the same like rock type, fractures, joints, fissures, vegetation, amount of rainfall and amount of evaporation.

The most part of the area is plain in nature composed of alluvium and part of area is composed of hills and sand dunes. Hills are prominent features of quartzite (Sett, 1964). Delhi Ridge is found in quartzite terrain, enters from NNW direction, is most important feature of the area and is also acting as water shed.

The Yamuna is the only perrenial river traverses in the NE part of the area and in fact entire area is part of Yamuna Drainage basin.

Geology of the area

This area is composed of different lithological formations of heterogeneous character and of quite different age. There are 3 important geological formations met in the area viz., Delhi Quartzite, Older and Younger Alluvium and Sand dunes. The geology and distribution of these formations are shown in Fig. 1. The important geological characters are condensed in Table 1.

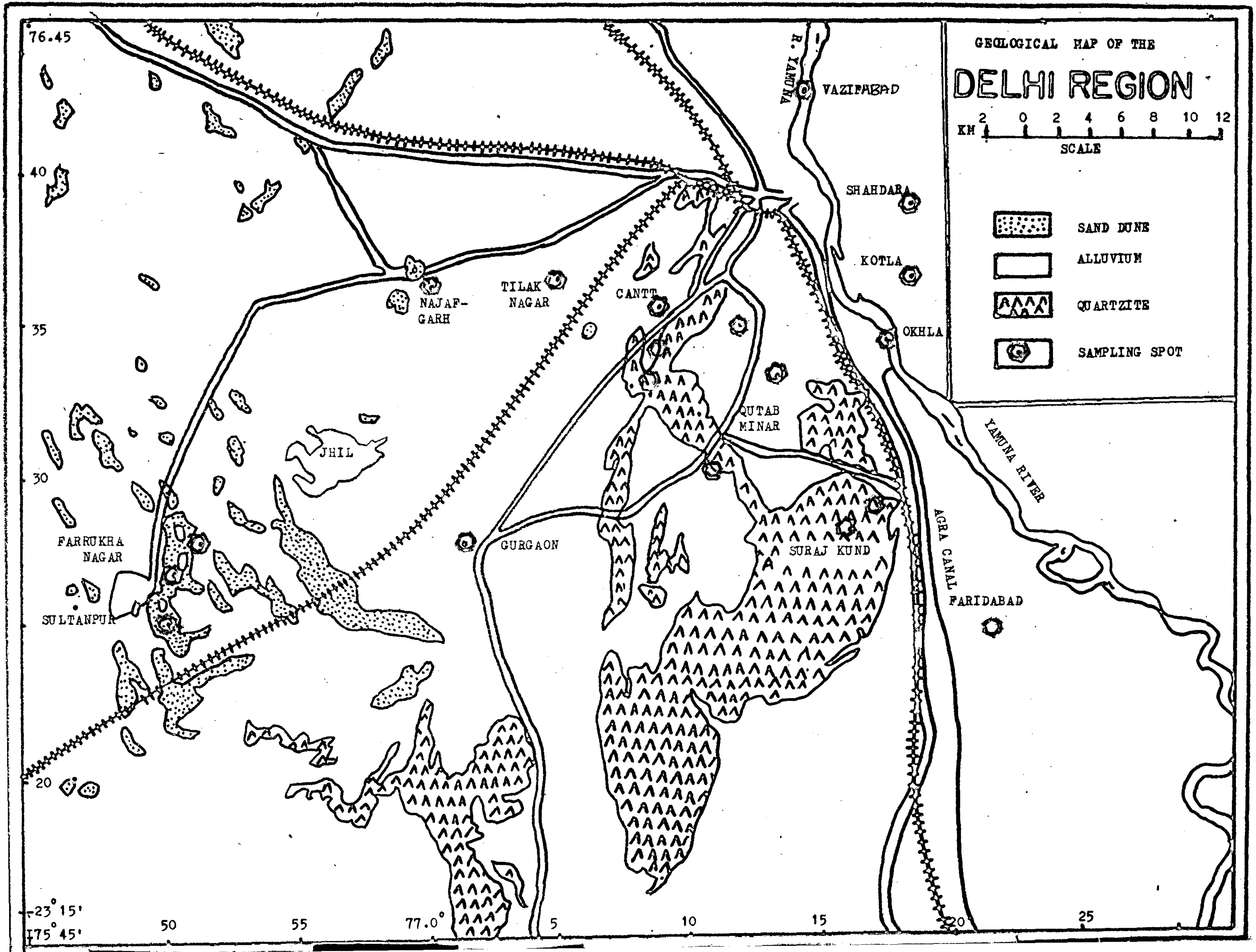

GEOLOGICAL MAP OF THE
DELHI REGION
KM 2 0 2 4 6 8 10 12
SCALE
SAND DUNE
ALLUVIUM
QUARTZITE
SAMPLING SPOT
R. YAMUNA
VAZIRABAD
SHAHDARA
KOTLA
OKHLA
TILAK NAGAR
NAJAF-GARH
CANTT
QUTAB MINAR
JHIL
FARRUKHA NAGAR
SULTANPUR
GURGAON
SURAJ KUND
AGRA CANAL
FARIDABAD
YAMUNA RIVER
76.45
40
35
30
20
23°15'
75°45'
50
55
77.0°
5
10
15
20
25

TABLE 1: GEOLOGY OF DELHI REGION (SUMMARISED FROM SETT, 1964)

S.No.	Name of the formations	Age of the formation	Nature of the formations	Special feature
1.	Eolean Sands	Recent	Developed in western part. It is well sorted fine to medium grain, consists of quarts, ferromagnesian minerals and mica flakes.	Sand dunes
2.	Newer Alluvium	Holocene	Found in eastern part, formed by stream laid sand, silt and clays grey in colour.	Sand is medium to coarse grained.
3.	Older Alluvium	Holocene	Formed by erosion and stream transport of bed rock debris and in part insitu weathering of bed rock material. Extensive distribution. Poorly sorted material.	Characterized by Kankars, calcium carbonate nodules which are found at the depth of 2.4 to 3 meters. Formed in the zone of soil water,
		Unconformity		
4.	Delhi Quartzite	Precambrian	Covers 25% of the area; compact, thickly bedded, very hard and bluish grey to pale grey in colour. Quartz grain has vitreous lustre and breaks with subchondroidal fracture.	Highly jointed. Locally intruded by the pegmatite veins particularly in Masudpur area and workable kaolinite deposit is another characteristic of pegmatite.

Occurrence of Ground Water

Ground water occurs in all the formations found in the area. In alluvium and sand dunes the ground water occurs in the interstices or pore spaces of the constituent grains lying with in the zone of saturation. Quartzite is very compact rock hence source of ground water in quartzite is joint and fracture plains which lie within the zone of saturation. The ground water occurs in water table condition means there is no impervious aquifer which could create artisian conditions on the surface. The slow recharge rate in sand dunes evident from patches of water logging suggests localised pocket of ground water. This observation is not confirmed (Sett, 1964).

Depth and Slope of Water Table

The principle source of recharge in the area is rain fall and to some extent partly downward a nd lateral percolation of the Yamuna water. Recharge of ground water is controlled by various factors as discussed in Chapter I, like amount of precipitation, nature of topography, nature of soil cover, rock type, cultivated area, amount of primary and secondary porosity like fractures and joints in the rock. The main sources of discharge of ground water are dug-well, tube-well, evaporation, springs and lateral movement of water to deeper depth.

The depth to water table varies from .11 to 31.51 meters below land surface in winter and 1.49 to 32.57 meters in the summer (Sett, 1964). It indicates seasonal fluctuation is very small. The probable season for this is water discharge is small because water quality in most part is unfit for domestic purposes and water requirement of the city is met by Yamuna. The water table is shallow in the sand dunes and alluvium and deep in quartzites. Sett and Khanna (1969) observed that nearly 84% of the well are having the water table within depth of 5 meters from the surface and nearly 49% wells are in the 2 meters. The water table gradient is also variable from place to place, it is .75 m/km at Farrukhanagar while .19 m/km in the north western part.

In localities, where water table is very shallow, the capillary fringe intercepts either land surface or approaches very near to it. In such cases in dry season salts are brought up on the surface by capillary action which forms an impermeable layer on surface or just below the surface which ultimately resulting into water logging. When water evaporates a salt layer forms on the surface, which is white gleastening in nature, is locally known as 'Reh'. Water logged patches are extensively developed between Farrukhanagar, Sultanpur and adjoining area. In the same localities 'Reh' layer is also observed in patches. The water logging is also caused by Kankar beds of carbonate of lime and magnesia, because Kankars are relatively impermeable (Biswas, 1965; Sett and Khanna, 1969).

CHAPTER :: III

METHODOLOGY

Sampling procedure

Proper sample collection is the main base of any scientific work and its importance is needless to be stated. There were 4 important parameters for sample collection had been taken into consideration, namely, time of sample collection, rock types, distance between two sample spots and source of sample.

Fluctuation in water quality over a period of year can be observed by only collecting the seasonal samples. Ideally in one year 3 times sampling shoud be done at the time of peak season, namely, winter, summer and monsoon. These samples will represent the impact of climate on quality of water. Seasonal sampling of selected area is also necessary because it is facing extream type of climate from chilly cold to scortching hot, in between monsoon sometimes result into widespread flood, therefore, samples were collected in January, June and September.

As stated in Chapter II that there are 3 important formations present and they have unequal geographic distribution. It is roughly calculated more than 70% area is covered by alluvium, about 25% area is covered by quartzites and rest by sand dunes and there is negligible occurances of pegmatite patches, besides these rock types. Yamuna is the perennial river flowing across the area and there are also some small permanent water bodies like ponds and water filled abandoned mines. The demand of this observation is that sample should be collected from each rock type and water bodies. A fair representation was given to this observation. Samples were also collected from Trans-Yamuna area (Shahdra and Kotla village) because this area is formed by newer alluvium, and there is possibility of [illegible] lateral percolation or movement of Yamuna water in this area because water table is very shallow in the region.

Samples were collected from different types of sources like tube-well, hand-pumps, dug-wells, Yamuna river, pond and abandoned mine.

In all, 19 samples were collected from the entire area: 4 from quartzites, 3 from sand dunes, 8 from alluviums and 4 from exposed water bodies. The sites of the different sample spots have been shown in Fig. 1 along with other details. The locality of the samples, rock types of the sampling site, source of sample and approximate depth of water table are summarised in Table 2.

Samples were collected from predetermined locality in one litre polythene bottles. First of all, clean bottles were washed twice with samples water and then it was dried and then fresh sample water was quickly filled in the bottle till the mouth. Care was also being taken to see that no air bubbles remain inside the bottles and after removing all air bubbles it was quickly sealed In the field diary, name of the locality, rock type and source

TABLE 2: SAMPLE SBOTS, DEPTH OF WATER TABLE, ROCK TYPE AND LOCALITY OF SAMPLE SPOTS

S.No.	Rock type	Name of the sample spot	Depth of water table in approx.mtrs	Source
1.	Delhi Quartzite	Jawaharlal Nehru University	12	Tube-well
2.		Badarpur	6 - 7	Dug-well
3.		Masudpur	15	-do-
4.		Mehrauli	18	-do-
5.	Alluvium	Shahdara (T.Yamuna)	2.5	Hand-pump
6.		Kotla Village(-do-)	2	-do-
7.		Tilak Nagar	2 - 3	-do-
8.		Gurgaon	10	Dug-well
9.		Lajpat Nagar	4	Hand-pump
10.		Najafgarh	5	-do-
11.		Faridabad	14	Tube-well
12.		Delhi Cantt.	7	Dug-well
13.	Sand Dune	Farrukhanagar	1.8	Dug-well
14.		Farrukhanagar	1.5	Hand-pump
15.		Sultanpur	1.5	Dug-well
16.	Exposed water bodies.	Okhla	Yamuna River	Surface of water bodies.
17.		Wazirabad	-do-	-do-
18.		Suraj Khund	Pond	-do-
19.		Pegmatite Mine	Abandoned Mine	-do-

were also noted down. Depth to water table was not measured in the field, it was taken from the work of Sett (1964a), who collected large number of samples from the entire area and also measured the actual depth to water table. Visual estimation was done in case of dug-well. It is desired that certain observations should be made on sampling spot itself like pH and alkalinity, however, because of lack of facility it could not be done in the field but as soon as samples were brought into laboratory, the desired observation was made immediately.

Laboratory study

Immediately after the samples were brought into the laboratory, pH, conductivity and alkalinity were measured. pH was measured by Philips portable pH meter, conductivity was measured by Systronics conductivity meter. Conductivity was measured in micromhos/cm^2. At the same time conductivity of standard solution in which known amount of soluble was dissolved was measured for drawing calibration curve at room temperature and pressure. From the help of this chart amount of total dissolved salt was calculated. Bicarbonate alkalinity was determined by titration procedure described in next paragraph.

The following major ions were quantitatively determined in the laboratory by standard methods, the ions are HCO_3^-, Cl^-, SO_4^{--}, PO_4^{---}, K^+, Na^+, Ca^{++}, Mg^{++} and SiO_2.

3 types of analytical techniques were used for quantitative analysis namely titration technique for HCO_3^-, Cl^-, Ca^{++} and Mg^{++}, flame photometer technique for Na^+ and K^+ and spectrophotometer technique for rest of ions. The brief description of adapted methods is as follows:

For tricarbonate ions, a known quantity of samples was titrated against .1 NHCl using methyl orange as indicator (Martin, 1968). Chloride was determined by titrating the known amount of sample against .22N $AgNO_3$ and potassium chromate is used as indicators (Martin, 1968). In case of calcium and magnesium standard EDTA technique was used. A N/50 EDTA solution was prepared along with two buffer solutions of 12 and 10.2 pH. First calcium was estimated with 3 cc buffer solution of pH of 12 by using murexide indicator. After doing this fresh sample was once again titrated for calcium and magnesium using eriochrome blue indicator and few drops of buffer of pH of 10.2 (American Public Health Association). Sodium and potassium was determined by Toshniwal flame photometer. Before actual sample processed in flame photometer, first calibration curve was drawn by taking the reading of standard samples ranging between 1 to 10 ppm of sodium and potassium concentration separately. The readings of actual samples were obtained after required dilution by double distilled water.

Sulphate silica and phosphate measurement was done by ECIL spectrophotometer by using standard method described in Golterman (1965). For all these analysis first standatd calibration curve were drawn by using samples of known concentration. Then actual samples were ran on the spectrophotometer with using different wavelength of light 420 mμ for sulphate, 530 mμ for phosphate and 820 mμ for silicate.

The data obtained in ppm are shown in Table 3.

Treatment of data

All the analytical results were converted into ppm. Then concentration of each ion was recalculated in terms of molality by using the formula

$$\text{molality (mi)} = \frac{\text{ppm} \times 10^{-3}}{\text{gram molecular weight}}$$

In next step ionic strength of the sample was calculated by formula described by Garrels and Christ (1965).

$$\text{Ionic strength (I)} = 1/2 \overset{n}{\underset{i=1}{}} \quad \text{mi} Z_1^{2}$$

mi = molality of individual ions

Zi^2 = charge of individual ions.

Activity coefficient can be calculated by two methods one is Debey-Huckel equation and another is Mean Salt Method. In case of ionic strength less than 0.1 as in ground water, fresh water, river water Debey-Huckel equation is used; if it is more than 0.1 as an

Table III: Analysis of Delhi Ground Water (Winter)

Date of sampling: 28 – 31 January 1977

S.No.	Name of the spot	Rock type	pH	Conductivity*	TDS	SiO_2	HCO_3	SO_4	PO_4	Cl^-	Na^+	K^+	Ca^{++}	Mg^{++}
1.	Yamuna Water at Okhla	-	7.35	580	530	85	244	48	12	47	75	28	26	36
2.	Yamuna Water at Wazirpur	-	6.9	540	485	102.5	219	56	17	31	48	28	56	16
3.	Surajkhund Pond	-	8.2	860	763	62	36	291	7	119	191	37	39	19
4.	Abandoned Mine near Masudpur	-	9.2	235	181	11.5	10	45	4	31	34	25	18	7
5.	Shahdara	Alluvium	7.1	2700	1807	108	66	430	9	31	750	54	257	145
6.	Kotla Village	-do-	8.2	1050	946	75	46	332	11	59	217	100	92	38
7.	Tilak Nagar	-do-	8.2	1515	1305	83	87	331	8	281	250	94	96	144
8.	Delhi Cantt.	-do-	7.05	800	700	118	54	278	7	31	146	96	32	41
9.	Najafgarh	-do-	7.5	1350	1118	58	73	416	9	172	225	125	53	38
10.	Lajpat Nagar	-do-	7.25	1400	1148	94	67	290	11	143.7	261	167	74	90
11.	Gurgaon	-do-	8.2	1120	958	113	59	206	16	81	190	56	96	49
12.	Faridabad	-do-	8.1	1000	858	94	37	331	15	62	153	83	55	20
13.	Farrukhanagar	Sand Dune	7.3	12000	7942	-	32	2531	10	1075	900	138	664	514
14.	Sultanpur	-do-	7.5	13000	8505	10	35	2313	12	2561	1620	247.5	718	278
15.	Farrukhanagar	-do-	7.6	7820	4615	59	39	663	15	2562	805	175	244	100
16.	Jawaharlal Nehru Univ.	Quartzite	8.0	810	574	121	48	200	7	62	83	42	103	16
17.	Masudpur	-do-	8.1	940	668	110	56	75	13	156	113	125	77	35
18.	Badarpur	-do-	6.85	1030	912	132.5	44	375	5	125	125	125	58	35
19.	Mehrauli	-do-	7.45	2810	2318	133	43	750	5	266	412	375	330	105

*Conductivity in micro mhos/cm^2. All other data are in ppm except pH.

example sea water whose ionic strength is 0.7 or super saturated brine Mean Salt Method is used (Garrels and Christ, 1965). The ionic strength of analysed samples were less than 0.1 hence Debey-Huckel equation was used which is as follows (Garrels and Christ, 1965):

$$\log \gamma_i = \frac{AZi^2 \sqrt{I}}{1+a^{\circ}B \sqrt{I}}$$

where r_i = activity coefficient

A, a°B = constant

Zi = charge of individual ions

I = Ionic strength.

The value of A, a°, B are the function of temperature. For dilute solutions the above equation modifies to

$$-\log \gamma_i = AZi^2 \sqrt{I} \, .$$

At 25°C and 1 atmospheric pressure the value of A is 0.5085 (Stum and Margon, 1970).

In next step activity of each ion was calculated by multiplying activity coefficient and molality of individual ions

$$a_i = m_i \gamma_i \, . \qquad a_i = \text{activity of ions.}$$

The activity value are converted into logarithmic value for plotting the data into stability diagram. All the values are shown in Table 4 and 5.

TABLE IV: CALCULATED VALUES OF log $pSiO_2$, log $\frac{K^+}{H^+}$, log $\frac{Na^+}{H^+}$, $pH-1/2pMg^{++}$ and $pH-1/2pCa^{++}$.

S.No.	Location	$pSiO_2$	$\log\frac{K^+}{H^+}$	$\log\frac{Na^+}{H^+}$	$pH-1/2pMg^{++}$	$pH-1/2pCa^{++}$
1.	Yamuna (Okhla)	4.3010	3.7	4.34	5.92	6.25
2.	Yamuna (Vazirpur)	3.0000	4.14	4.60	5.65	5.83
3.	Suraj Khund	4.7782	5.10	6.06	6.53	6.55
4.	Abandoned Mine	4.0792	5.97	7.85	7.30	7.39
5.	Shahdara	3.0792	4.10	5.50	5.76	5.75
6.	Kotla Village	4.9031	5.99	6.09	6.64	6.72
7.	Mehrauli	3.1461	4.59	4.60	6.07	6.21
8.	Tilak Nagar	4.9345	5.50	6.10	6.70	6.91
9.	Delhi Cantt.	3.1139	4.30	4.73	5.48	5.32
10.	Najafgarh	4.7782	4.55	5.15	5.71	6.05
11.	Lajpat Nagar	4.9412	5.00	5.43	6.07	5.93
12.	Gurgaon	3.0792	5.24	6.03	6.79	6.70
13.	Faridabad	4.9912	5.35	5.86	6.42	6.59
14.	Farrukhanagar (Hand-pump)	0	4.62	5.68	6.04	5.98
15.	Sultanpur	4.0000	5.25	6.3	6.18	6.07
16.	Farrukhanagar (Dug-well)	4.7782	5.15	6.1	6.23	6.32
17.	Jawaharlal Nehru University	3.1139	5.95	5.5	6.32	6.60
18.	Masudpur	3.4140	5.53	5.75	6.62	6.55
19.	Badarpur	3.1461	4.26	4.49	5.25	5.25

For carbonate system, it is necessary to have the value of ~~f~~ P_{CO_2} of each sample. It was calculated by the help of the following equation:

$$H_2O + CO_2 = H^+ + HCO_3^- .$$

At equilibrium

$$K = \frac{[H^+]\ [HCO_3^-]}{[H_2O]\ [CO_2]}$$

or

$$P_{CO_2} = \log[H^+]\ [HCO_3^-]\ -\log K.$$

K is the equilibrium constant. Its~~km~~ value is calculated theoretically; H^+ is the pH of water sample and HCO_3^- is the alkalinity of water sample measured in the laboratory. The value of P_{CO_2} is shown in Table 5.

For construction of stability diagram required free energy ~~f~~ value of each ions and minerals are taken from Garrels and Christ (1965).

TABLE V: CALCULATED VALUES OF P_{CO_2}, $\log Ca^{++}$, $\log Mg^{++}$ and $a\log Ca^{++}/aMg^{++}$.

S.No	Location	P_{CO_2}	$\log Ca^{++}$	$\log Mg^{++}$	$a\log Ca^{++}/aMg^{++}$
1.	Yamuna (Okhla)	-2.48	.00049	.011	.044
2.	Yamuna(Wasirabad)	-2.48	.00092	.0004	1.3615
3.	Suraj Khund	-3.57	.00051	.00046	.0453
4.	Abandoned mine	-5.6625	-3.3468	-3.5376	0.1903
5.	Shahdara	-2.32	.0021	.002	1.0212
6.	Kotla Village	-2.54	.0011	.00076	.1645
7.	Mehrauli	-2.83	.0033	.0017	.2878
8.	Tilak Nagar	-2.93	.001	.0026	2.5798
9.	Delhi Cantt.	-2.25	.00043	.00092	-1.6628
10.	Najafgarh	-2.38	.0039	.00084	.6665
11.	Lajpat Nagar	-2.7	.00064	.0014	-1.6628
12.	Gurgaon	-3.41	.0012	.001	1.0792
13.	Faridabad	-3.57	.00076	.00043	1.76
14.	Farrukhanagar (Hand-pump)	-2.86	.0023	.003	.8842
15.	Sultanpur	-2.81	.0023	.0014	.2148
16.	Farrukhanagar (Dug-well)	-3.0	.0027	.0018	.1761
17.	Jawaharlal Nehru University	-3.27	.0016	.00044	.4848
18.	Masudpur	-3.34	.0011	.00034	.1461
19.	Badarpur	-2.23	.00062	.00062	1.0

CHAPTER LL IV

ANALYSIS AND INTERPRETATION

Hydrogeochemistry has many field of investigation. Its various aspects are total dissolved salts (TDS), total suspended material (TSM), possible reaction between ground water and host rocks, mineralogy of suspended material, quality of ground water for different purposes. The Delhi ground water is lacking in suspended material. Therefore it was not investigated.

Total Dissolved Salts (TDS)

The hydrogeochemistry of TDS was examined by various authors both in case of ground water and river water. The important workers are Garrels and Mackenzie (1967), Gibbs (1970), Grove (1972), Handa (1967), Jacks (1973), Jayaraman (1977), Kramer (1967) and Subramanian (1976). Their combined observations suggest that there are various factors which control the ultimate composition of ground water or river water like nature of rock type, climate, process of weathering, underground movement of ground water, pH of water and water-mineral equilibrium. Groves (1972) comes to the conclusion that humid tropical weathering of basic rock yields a large amount of dissolved load, while Kramer (1967) has drawn conclusion that pH, silica and partial pressure of carbon dioxide in water are important factors in the formation of clay minerals. Same conclusion was drawn by Garrels (1967). Initial pH of water would be 5 when it enters into soil zone because CO_2

content of soils of igneous rocks is 10-100 times more than atmospheric content. In advance stage of reactions ~~the~~ certain new minerals like kaolinite, montmorillonite and calcite form along with increase in pH of water.

Jacks (1973) in a similar study drawn conclusion in case of ground water of igneous rocks that composition of soil atmosphere and rate of infiltration determine the initial acidity of the water and ultimately final composition ~~[illegible]~~ and he made quantitative estimation of release of bicarbonate ions from different minerals when react with waters of different pH. Subramanian <u>et al</u> (1976) come to the conclusion that correlation can be expected from water composition of a river with rock types of water shed area.

TDS is generally contributed by major ions found in water (Handa, 1972). The major ions are Ca^{++}, Mg^{++}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{-}, SiO_2. The determination of TDS through conductivity is not accurate because uncharged ions like SiO_2 and uncharged organic materials found in water do not help in estimation of conductivity, the property of conductivity of water is confined to charged ions only. TDS in investigated area varies from 180 ppm to 8505 ppm. TDS is very high in sand dunes, 8505 - 4615 ppm. Comparatively in alluvium, TDS is much less, 1807 - 700 ppm, and from alluvium to quartzite, 2318 - 774 ppm, it is still less. The TDS in exposed water bodies is also variable from 763 ppm in

Suraj Khund,is 530 ppm in Yamuna at Okhla, 485 ppm at Wazirabad and 181 ppm in Masudpur abandoned mine water. The variation of TDS in different rocketype is due to change in climate from arid to typical, different solubility of minerals, different porosity and permeability of the rocks, different dlay minerals, which are found in the water having capacity to absorb the ions from water and role of external factors like application of fertilizer in agricultural field, recharge of stagnant polluted water etc.

Abandoned mine water is showing very small TDS. It is probably kaolinite is absorbing ions from water while at Suraj Khund water is stagnant and perhaps clay minerals are not playing any important role. In the Yamuna river, TDS has increased from upstream to downstream. It is because of addition of industrial and city affluents added into it.

pH

Alkaline water is dominating in the area. Ouf of 19 pH analysis, two belong to acidic pH, rest water is alkaline (Table III). The Yamuna water when enters into city at Wazirabad showing pH 6.9 while at the end of city at Okhla it shows pH 7.35. The change in pH can be attributed to addition of large amount of city and industrial affluents and "intense photosynthesis can lead to alkaline Condition in a stream due to removal of carbon dioxide in sunlight by green plants" (Klein, 1977, 183pp), this quotation is also applicable to Yamuna as it has on both sides and on river bed heavy plantation.

The Badarpur ground water is also showing acidic character with pH 6.5 the probable explanation for it is rain water contain high amount of $\bar{SO_4}$ ions as thermal power house is situated here and percolation of it through fertilizer applied field. The dissolution of fertilizer could be cause of slightly acidic water.

The rest samples have shown pH from 7.05 to 8.2. The pH of the ground water is governed by equilibrium system operating in water. There are two major systems - carbonate and silicate systems - usually operate in water. The pH, whether acidic or alkaline, is determined by the fact which system is dominating over which. Since most of the samples are showing alkaline pH. It means, silicate system is dominating over carbonate system.

High alkaline pH 9.2 is shown by Masudpur abandoned mine-water and mine sediment analysis has revealed presence of kaolinite, it is possible here that kaolinite might have trapped some cations like HCO_3^- , SO_4^{--} , PO_4^{---}, Cl^- etc. (Grim, 1947).

Silica (SiO_2)

The quantity of silica is fairly high in water, it varies from 58 - 133 ppm, exceptions have been found at Sultanpur 10 ppm, Farrukhanagar no silica and Masudpur abandoned mine 11.5 ppm. The high amount of silica indicates water is saturated with respect to both quartz and amorphous silica (Krauskopf, 1967).

In quartzites, silica varies from 100 - 132.5 ppm. It was expected because Delhi quartzite at many places has been thickly weathered along joints and bedding planes. Intercalations of argellaceous beds have also been noted (Paliwal et al, 1976). The high amount of silica in alluvium may be due to mixing of quartzite and alluvium water and breakdown of feldspar of the alluvium. At the contact of alluvium and quartzite, high silica content is noted at Delhi Cantt (118 ppm) indicating possibility of mixing of quartzite and alluvium water.

In sand dunes silica is low because it is composed of loose sands and dissolution of silica is extremely slow process, therefore, sand dunes do not contain large amount of silica. The absence of silica at Farrukhanagar indicate possibility of recent recharge of ground water. Therefore no dissolution of silica is possible. At Masudpur abandoned mine silica is probably consumed in the formation of kaolinite found in the mine sediment.

Bicarbonate (HCO_3^-)

Various possible sources of bicarbonate ions have been investigated by different authors.

Atmospheric CO_2 reacts with water and form weak carbonic acid, this carbonic acid on disintegration produces hydrogen and bicarbonate ions according to the reaction

$$H_2O(l) + CO_2(g) \quad = \quad H_2CO_3(l) \qquad (1)$$

$$H_2CO_3 \quad = \quad H^+ + HCO_3^- \qquad (2)$$

when carbonic acid attacks limestone it forms on hydrolysis bicarbonate ions

$$CaCO_{3(s)} + H_2CO_{3(l)} = Ca(HCO_3)_{2(s)} \qquad (3)$$

$$Ca(HCO_3)_2 = Ca^{++} + 2\,HCO_3^- \qquad (4).$$

The carbonic acid also breaks down certain minerals like albite and releases various products in solution (Garrels, 1965):

$$2NaAl\,Si_3O_8 + 2\,H_2CO_3 + 9\,H_2O = \underset{(Kaol)}{Al_2Si_2O_5OH} + 4\,H_4SiO_4 + 2Na^+ + 2HCO_3^- \qquad (5)$$

Another reaction in which montmorillonite has been formed along with bicarbonate was investigated by Feth (quoted in wedepohl, 1970)

$$6(Na,Ca)\,AlSi_2O_8 + 6CO_2 + 18H_2O = 3\underset{(mont.)}{Na_{.66}Al_{2.66}\,Si_{3.33}O_{10}(OH)_2} + 2Ca^{++} + 2Na^+ + 6H_4SiO_4 + 6HCO_3^- \qquad (6).$$

Berner (1971) has experimentally demonstrated the production of bicarbonate ions from partial or complete decomposition of organic waste

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O \qquad (7)$$

$$CO_2 + H_2O \simeq H + HCO_3 \qquad (8).$$

Subramanian (1976) also explored possibility from waste of petrochemical industry and coal industry under anaerobic conditions

$$2CH_2O + SO_4^{--} = 2HCO_3^- + H_2S_{(g)} \qquad (9)$$

or

$$2CH_2O + SO_4^{--} = H_2CO_3 + HS^- + CO_2 + H_2O \qquad (10)$$

The high bicarbonate concentration was recorded in the Yamuna water 244 ppm at Wazirabad and 219 ppm at Okhla while in ground water it is less than 90 ppm. Three rock units show distinct character, low bicarbonate (32-39 ppm) in sand dunes, medium concentration (44-56 ppm) in quartzite and (37-87 ppm) in alluvium.

The bicarbonate concentration in Yamuna is much higher than world's average river water which is 58.4 ppm. (Livingstone, (1963). The probable reasons for these are firstly in its upper reaches, it is flowing over the Krol limestone terrain (Manickam, 1978). Secondly large amount of city and industrial affluents added into it during its course as area is highly populated. Olaniya et al (1976) has reported in case of Chambal river at Kota by addition of affluents of an industry bicarbonate concentration rise sharply from 122 ppm to 540 ppm.

High bicarbonate in alluvium can be accounted by the fact that it contains feldspar, calcite and clay minerals which yield bicarbonate on weathering according to reactions 3 - 6 and it is also possible that trapped organic material may also give bicarbonate according to reactions 7 and 8. The bicarbonate ions may also form from weathering of Kankars which is extensively found in alluvium. In quartzite and sand dunes which are apparently do not contain any calcereous minerals in large quantity, get their bicarbonate by percolation of water or on weathering of feldspar or calcereous mineral reaction number 5 - 6 and also mixing of alluvium water with their ground water.

Chloride(Cl^-)

The Delhi ground water is unpleasant in taste in many areas.~~duexis~~ This is due to high amount of chloride ions present in it. Chloride is found highest in sand dunes where it ranges from 1075 to 2562 ppm in alluvium 31-282 ppm and 61-156 ppm in quartzite. On the basis of this, it can be said that chloride content is far higher in sand dunes than quartzite or alluvium.

As carbonate the chloride content of Yamuna river is much higher than world average river water 7.8 ppm (Livingstone, 1963). While in Yamuna it is 47 and 31 ppm at Wazirabad and Okhla respectively. Similar data were obtained for Ganga river also at Varanasi by Agarwal et al (1976). He reported average content is 33.2 ± 7 ppm. The high concentration can be explained by the fact everyday large amount of city and industrial affluents are added into the river which must be causing this. The waste of paper, chemical, textile and soap industries are important.

Sands of sand dunes region is ultimately derived from Rann of Katch. In dry months wind blown sands come from there via Rajasthan to Haryana. It is composed of quartz, feldspar, hornblonde, gypsum, calcite and salt particles (Wadia, 1978). The chloride salt particles of sand on interaction with rain water dissolve immediately, therefore, chloride ions in sand dune is much higher.

The high variation, 31-282 ppm, in alluvium probably accounted by the fact releasing of pore waters from alluvium, mixing of Yamuna water, infiltration of water from agricultural field when chlorine is used as insecticide and pesticide as well as small amount of chlorine is associated with phosphatic fertilizer. Fuhermo (1926) (in Wedepohl, 1970) found high chloride in ground water of agricultural field and uncontaminated water from non-agricultural area was having .7 to 7.7 ppm. Fuhermo (1926) (in Wedepohl, 1970) observation supports high chloride content of rural area water.

The chloride ions might also be derived from leaching shale, alluvium which contain 234.7 ppm chloride (in Wedepohl, 1970).

Quartzite contains 38.3 ppm chloride (Wedepohl, 1970). High chloride concentration at Masudpur 156 ppm, Badarpur 125 ppm and Mehrauli 266 ppm can be explained by the facts that these localities are surrounded with vast agricultural field and large amount of fertilizer and insectiside and pesticide are applied every year to them. Therefore, because of percolation of water from these fields might be carrying chloride ions from fertilizer and other chemicals.

Sulphate

Sulphate ions have various sources.~~like~~ Sulphur is found in number of primary minerals like pyrite, gypsum, galena, chaleopyrite, sphelerite, anhydrite, barile and native sulphur. It is believed, sulphate in water originated from sulphide of the rocks (Davis and De Weist, 1966). The chief source of sulphate in sedimentary rocks are gypsum, anhydrite and pyrite. The breakdown of these minerals yield sulphate ions

$$FeS_2 + 2H_2O + 3O_2 = 2H_2SO_4 + Fe^{++} \qquad (11)$$

$$CaSO_4 + H_2O = CaO + H_2SO_4 \qquad (12)$$

$$H_2SO_4 = 2H^+ + SO_4^{--} \qquad (13).$$

The weak sulphuric acid formed from the above reaction also yield sulphate when it attacks block shales which contain pyrite and marcasite (Mason, 1966). The sulphuric acid in atmosphere is derived from dust particle of sulphur, oxidation of SO_2 and H_2S gas, burning of coal and oil.

Coal contains.5 to 5 % sulphur (Francis, 1960) in the form of pyrite and marcasite. It will give on burning SO_2 which later on convert into H_2SO_4 according to reaction

$$2SO_2 + O_2 \qquad 2SO_3 + 2H_2O \qquad 2H_2SO_4 \qquad (14).$$

The coal ash contains upto 20% pyrite which on dissolution gives sulphate in water (Francis, 1960). Hesketh (1974) has reported, unpolluted atmosphere contains .001 to .01 SO_2 and polluted .02 -2 ppm.

This SO_2 of the atmosphere convert into H_2SO_4 according to reaction number 14. Seinfeld (1975) suggested that H_2S gas formed by decay of organic matter, which react with atmospheric ozone gives SO_2 and water and ultimately sulphuric acid.

$$H_2S + O_3 = H_2O + SO_2 \qquad (15).$$

The river water and rain water contain an average 11.2 and 2 ppm of sulphate (Wadepohl, 1970).

Sulphate concentration in ground water is extremely variable in quartzite 75 - 750 ppm alluvium 200 - 831 ppm and sand dones 665 - 2531 ppm.

The average sulphate ion of world river water is 11.2 ppm while in Yamuna it is 56 ppm at Wazirabad and 48 ppm at Okhla indicating discharge of industrial waste into river. It could be also because of animal and man sewage. Sulphuric acid is also used in large quantity by almost all chemical based industries and their solid and liquid waste contain large amount of soluble sulphate (Sinha et al, 1978). Olaniga et al (1976) have measured sulphate ions of Chambal river before it enters into Kota, is having 11.0 ppm and when it leaves Kota around 115 ppm.

The other low values of sulphate are found at Masudpur 75 ppm only. The probable reason for this area is totally barren from agricultural and industrial points of view.

In sand dunes at Farrukhanagar and Sultanpur, sulphate contents are 2531 and 2313 ppm respectively. Here it can be expected that gypsum and anhydrite of sands are releasing the sulphate ions into water on weathering. In other cases, variation ranges from 200-750 ppm in all rock types. It can be explained by the fact that alluvium may contain some sulphate minerals, which on breakdown release sulphate ion in water, the area is highly industrial and intensive modern agriculture is being done here so their waste when leached by surface water and on percolation surface water carried sulphate ions downward. Alluvium also contain some organic material which on decay yields sulphate ion in water. Moreover, in this area there are two coal based thermal power house at Indraprastha and Badarpur. Their gaseous waste bound to contain SO_2 and ash contains pyrite which according to reaction 11 will yield sulphuric acid. However, there is strong possibility of mixing of ground water from different rock type particularly in quartzite because the water is deep in comparison to water level found in alluvium as ground water moves from higher water level to lower level area.

Phosphate (PO_4^{---})

The contributions of phosphate in ground water are phosphatic minerals of rocks, sedimentary phosphate beds, decay of organic material like coal, petroleum, plants, bones, fertilizers and waste waters (Davis & De Weist, 1960, Wedepohl, 1970).

.001 - .1 ppm phosphorous is reported from coal (Francis, 1960).

Phosphate is minor constituent of ground water but in Delhi ground water its concentration is very high. It ranges from 4-17 ppm. The probable reason for high detection of phosphate is silica interferes in phosphate analysis (Golterman, 1971), and silica was not removed from water before analysis of phosphate. It is expected phosphate might have come from fertiliser or percolation of industrial waste water and decay of plant and animal waste.

Sodium and Potassium

These two ions show similar chemical properties. The primary sources of sodium in water are weathering of plagioclase, pyroxene, hornblende, evaporite minerals. Rain water contains 2 ppm Na, industrial and domestic discharge are other important sources. Common sources of potassium are product formed by weathering of orthoclase, microcline, biotite, leucite and other potassium bearing minerals and rocks like granite, syenite, arkose, mica schist etc. Besides these potash fertiliser is another source of potassium. Rain water contains .1 ppm potassium.(Davis & De Weist, 1966).

Fournier (1973) investigated the following reactions at higher temperature.

$3/2$ K-feld + H^+ = $1/2$ K-mica + K^+ + 3 quartz. (16)

3 Albite + $2H^+$ + K^+ = K-mica + $3Na$ + 6 Quartz.(16a).

Reactions 5 and 6 are also releasing sodium in water,

In sand dunes highest amount of sodium has been noted. The two samples of Farrukhanagar yield the value 805 and 900 ppm while at Sultanpur 1620 ppm sodium ions. This difference may be explained by the fact Farrukhanagar is a residential area from there continuous discharge of water for different purposes have been observed while Sultanpur is barren area from where no water discharge is observed for any purpose, therefore, here there is only intake of ions in water while at Farrukhanagar because of discharge concentration of sodium is not possible. The source for Na ions here seems holite grains of sands and weathering of plagioclase to minor extent.

The Yamuna river at Wazirabad and Okhla showing 48 and 75 ppm sodium this is again higher than world's average river water tissue which is 6.3 ppm. The possible reasons are additional industrial and domestic affluents or weathering of river bed. The range of sodium in different rock type varies between 113 - 412 ppm. It is higher in alluvium and lower in quartzite. Higher value in alluvium is apparant from the fact it contains clay and feldspar which on weathering yield sodium ions. One extremely high value of sodium is found in Shahdara, where it is 750 ppm. It may be possible here that trapped pore water might contributing to high value of sodium, because it is made up Younger Alluvium which is not yet fully compacted and this area is not fully developed so large scale percolation of domestic and local waste is also possible.

One low value of 83 ppm was recorded in case of Jawaharlal Nehru University quartzite. This area is situated at higher elevation so mixing of other ground water is not possible and secondly it is free from industrial and agricultural activity.

High amount of potassium is recorded in sand dunes between 138 - 247 ppm while intermediate in quartzite 125 - 375 ppm except 42 ppm at JNU and 54 - 167 ppm in alluvium.

The high amount of potassium in sand dunes and quartzite when they do not contain any potassium minerals, may be because they are lacking clay minerals which are found in zone of saturation. Clay minerals readily capture anion from water and since no clay is found in them therefore, potassium content is bound to be higher in them, however, reverse is the case of alluvium it is dominently made up of clay which can easily absorb potassium ions of water hence reducing potassium content of water (Grim, 1947). The other reason is application of potassic fertilizer in agricultural field which will yield large number of potassium ions to water on leaching.

Calcium and Magnesium (Ca^{++} and Mg^{++})

Calcium and magnesium, like sodium and potassium, show similar chemical properties. They are found in quite abundance, 5.17% CaO and 3.76% MgO by wt. found in the earth crust.(Mason, 1966). There are various minerals of these ions like calcite, magnesite, dolomite, anhydrite, gypsum, feldspar, pyroxenes, amphiboles etc.

Calcium is an essential constituent of bones (Wadepohl, 1970, Davis and De Weist, 1970).

Equation numbers 4, 6, 12 and 15 are responsible for calcium ions in water. Calcium is also supplied by fertilizers, it is used for removal of alkalinity of soil. In rain water contains calcium and magnesium .1 to 10 and .1 or more ppm respectively Wadepohl, 1970).

The Yamuna water is again showing high amount of calcium at Wazirabad 56 and at Okhla 26 ppm when compared with world's average figure 15.1 ppm. It is because in its upper reaches it flows over limestone and weathering of river bed in alluvium area might be also adding calcium ions in Yamuna river water.

It is higher in sand dunes, but there is also considerable variation from 244 and 664.at Farrukhanagar and 718 ppm at Sultanpur. The high amount of calcium is derived from weathering of gypsum, feldspar and anhydrite minerals. The variation in two samples of Farrukhanagar is probably because of application of calcium in agricultural field where it might have gone down along with percolated water while other sampling spot is situated in residential area of village.

The two other high values of calcium have come from Mehrauli 330 ppm in quartzite and 257 ppm at Shahdara in Alluvium. At Mehrauli it may be because of application of calcium in agricultural field and at Shahdara may be due to breakdown of feldspar or calcereous minerals or nearby aby undetected source which is giving high content to surface water which is immediately percolating downward.

The rest value of calcium is ranging from 55 - 103 ppm both in quartzite and alluvium. Alluvium is characterised by calcereous nodules which are dominently made up of calcereous matter. The nodules are formed by capillary water just beneath the surface. In quartzite calcium ions appear to have come from alluvium.

Magnesium shows clear trend with respect to rock type. It varies from 100 - 514 ppm in sand dune, 20 - 145 ppm in alluvium and 16 - 35 ppm in quartzite.

The high concentration of magnesium in sand dune probably is owing to dissolution of salts of magnesium which might have come along with sand and small quantity of hornblonde may give magnesium added with high evaporation rate so concentration of magnesium automatically increases.

Highly saline water of Farrukhanagar and Sultanpur areas

The western part of the area is characterised by numbrous patches of sand dunes of small hight and sandy flat area. Sand appears to have come from Rajasthan (Sett, 1964). In sand dune area water is highly saline, at one time even salt industry was flourishing here. The reasons for highly saline water are low rain fall, high temperature, high evaporation and salt particle in sand which are readily soluble when come in contact with water. The secondary reasons are sproidic distribution of vegetation, high porasity of sand and negligible discharge of water. Sett (1964) speculated water of this area is as salty as sea water and he presented four chemical analysis of water from different localities, their present analysis is contradicting with analysis of Sett (1964). On inquiry it was found that highly saline water is available only when wells are dewatered at least 3 or 4 times after doing this real saline water comes into wells. It may be because of high rate of evaporation leading to precipitation of salts from water thus reducing salinity of water and mixing of fresh rain water with well water as salinity of rain water is extremely low thus salinity of well water is bound to reduce.

The soil of this area is also saline as apparent from white patches seen on the surface when temporary water logged area dries up during dry months of the year. These white patches shine during day time their thickness is variable but always less 5 millimeter. This white substance is soluble in water. The salinity of soil is also evident from the fact certain crops cannot be grown here, like wheat, sugarcane etc.

MINERAL-WATER EQUILIBRIUM STUDY

The use of phase diagram was first done in the study of crystallization behaviour of magma, later on phase diagrams were used in other branches of geology but their application in hydrogeochemistry is hardly two decades old. The various uses of these diagrams are listed by different workers (Kramer, 1967 and Jacks, 1973). They can be used in relating the actual condition to equilibrium model, secondly, lack of fit of equilibrium model.prediction suggests further investigations of data. Thirdly, organisation of system for generalization and simplification of emperical water chemistry data (Kramer, 1967). On the applied side these diagrams can be used successfully for prediction of which clay mineral will be formed in existing condition through rock-water reaction, these clay minerals have tremendous importance in stability of engineering structure like dam, tunnel, highway etc. because someclay minerals have got property of swelling when they come in contact with water and this property varies among different clay minerals (Grim, 1947, Jacks, 1973a).

minerals

Theoretically, diagrams are constructed by using free energy and then balanced the appropriate reaction.and free energy of minerals. In most of the cases theoretical prediction was successfully confirmed by X-ray diffractograph of suspended sediment (Subramanian, 1976), but in some case experimental findings do not support theoretical prediction, this is attributed to the facts that chemical kinetics is ignored here (Berner, 1971). Berner cites an example that in sea water where calcite is found to be in saturation while theoretical prediction is suggesting dolomite would form when carbonite system is considered.

The carbonate and silicate system are two major systems because most minerals formed by reaction between rock and water under normal condition belong to either of these two families, various phase diagrams have been constructed by using different parameters. In this work an attempt is made to study the above system as this work was confined to investigation of major ions only.

Carbonate System ($CaO-MgO-CO_2-H_2O$)

This system is restricted to important minerals of calcium and magnesium carbonate. Here the phase boundary between different minerals are derived from thermodynamic properties of the minerals on the assumption that equilibrium is developed in the carbonate minerals which are related with this system are calcite, dolomite, brucite, magnesite, aragonite, hydromagnesite. The reactions between two mineral phases expected at equilibrium are (Garrels and Christ, 1965) dolomite and calcite

$$CaCO_3 + MgCO_3 + Ca^{++} \rightleftharpoons 2\ CaCO_3 + Mg^{++} \qquad (19)$$

Calcite and dolomite

$$2CaCO_3 + Mg^{++} = CaMg(CO_3)_2 + Ca^{++} \qquad (18)$$

Dolomite and Magnesite

$$CaMg(CO_3)_2 + Mg^{++} = 2MgCO_3 + Ca^{++} \qquad (19)$$

Magnesite and Hydromagnesite

$$4MgCO_3 + 4H_2O = Mg_4(CO_3)_3(OH)_2.3H_2O + CO_2 \qquad (20)$$

Calcite and Brucite

$$CaCO_3 + Mg^{++} + 2H_2O = Mg(OH)_2 + Ca^{++} + CO_2 \qquad (21)$$

Dolomite and Brucite

$$CaMg(CO_3)_2 + Mg^{++} + 2H_2O = 2Mg(OH)_2 + 2CO_2 + Ca^{++} \qquad (22)$$

Dolomite and Hydromagnesite

$$2CaMg(CO_3)_2 + 2Mg^{++} + 4H_2O = Mg_4(CO_3)_3(OH)_2.3H_2O + Ca^{++} + CO_2 \qquad (23)$$

Hydromagnesite and Brucite

$$4Mg(CO_3)_3(OH)_2.3H_2O = 4Mg(OH)_2 + 3CO_2 \qquad (24)$$

It is clear from the above reactions that Ca^{++}, Mg^{++} and partial pressure of CO_2 are playing dominant ~~role~~ in carrying out the reaction, in fact these reactions are function of a Ca^{++}/aMg^{++} and P_{CO_2}. The equilibrium constant (K) for these reactions can be calculated by using the principle described below.

$$aA + bB = cC + dD \qquad (25)$$

$$K = \frac{(C)^c \ (D)^d}{(A)^a \ (B)^b} \qquad (26)$$

where A and B are reactant and C and D are products formed by the reaction of A and B; a, b, c and d are the numbers of molecules participated in the reaction, K is equilibrium. Suppose this principle is applied in case of reaction number (17) between calcite and dolomite

$$K_1 = \frac{\left[Ca\ Mg\ (CO_3)_2\right]\ \left[Ca\right]^{++}}{\left[Ca\ CO_3\right]^2\ \left[Mg\right]^{++}} \qquad (27)$$

Making assumption that for pure substance the activity is unity, at their standard state (Garrels and Christ, 1965), the K_1 reduces to

$$K_1 = \frac{Ca^{++}}{Mg^{++}} \qquad (28)$$

Here K_1 is independent of PCO_2. Calcite and dolomite are assumed as pure mineral species.

The exact value of K_1 is calculated by using Gibb's free energy of reaction as follows:

$$\triangle F^{\circ}_{r} = \text{Free energy of productants} - \text{Free energy of reactants} \qquad (29)$$

For reaction (1)

$$= (-520.5) + (-132.18) - 2(-269.78) + (-108.99)$$

$$\triangle F^{\circ}_{r} = -4.13\ \text{KCal.}$$

K_1 value is calculated by the equation

$$\triangle F^{\circ}_{r} = -RT\ \ln K$$

on simplification (30)

$$= -1.364\ \log K.$$

Putting the calculated value of F_r in the above equation, the value of log K_1 comes out to be for the above reaction.

$$-4.13 = -1.364 \log K_1$$

$$\text{or} \quad \log \frac{Ca^{++}}{Mg^{++}} = K_1 = 3.027 \qquad (31)$$

This value represents the chemical boundary between calcite and dolomite and can be represented as a line parallel to ${}_pCO_2$ axis at a distance of 3.027.

In this way the value of equilibrium constant (K_2) is calculated for reaction between dolomite and magnesite (reaction No.19) which is also a function of Ca^{++} and Mg^{++}

$$\log \frac{Ca^{++}}{Mg^{++}} = \log K_2 = 3.6 \qquad (32)$$

The reaction between magnesite and hydromagnesite and hydromagnesite and Brucite are function of partial pressure of CO_2 only. The equilibrium constant for reaction 20 becomes

$$K_3 = \frac{[Mg(CO_3)_3(OH)_2 \cdot 3H_2O] + [{}_pCO_2]}{[Mg\ CO_3]^4 + [H_2O]^4} \qquad (33)$$

Again assumption is made, as previous, activity of pure solid and liquid is unity. The above equation reduces to

$$K_3 = {}_pCO_2 \qquad (34)$$

The free energy of above reaction is calculated as

$$\Delta F^\circ_r = (-108.3)+(-92.31)-4(-246)+4(-56.69) = 10.16 \text{ KCal}$$

As $\quad \Delta F^\circ_r = -1.364 \log K.$

The value of K_3 comes to

$$\log \rho CO_2 = \log K_3 = -7.44.$$

This value represents a boundary line between hydromagnesite and magnesite at a distance 7.44 parallel to Ca^{++} / Mg^{++} axis.

For other reactions equilibrium constants (K) are calculated in the above manner and values are plotted against the either ρCO_2 or Ca^{++} / Mg^{++} axis.

The method of calculation of partial pressure of carbon dioxide (ρCO_2) is already discussed in Chapter III.

The Value of ρCO_2, log $a Ca^{++}$, log $a Mg^{++}$ and log $a Ca^{++}/a Mg^{++}$ is given Table IV.

These values of activities are plotted in the standard diagram. The original boundary of Carpenter's diagram (Garrels and Christ, 1965) of carbonate system was modified by Dalavi (1978) as Carpenter's diagram was based on wrong calculations. This diagram is shown in Fig. 2. From diagram No. 1, it can be predicted that dolomite is the only phase to be expected in the state of saturation, it means when minerals precipitation would start in ground water, the dolomite would precipitate as mineral in case of calcite and dolomite system is considered.

But if the system aragonite and huntite is considered, ~~majority~~ most of the points fall in arogonite region while the 6 analyses fall in huntite region. Out of these 6 analyses, 4 belong to alluvium

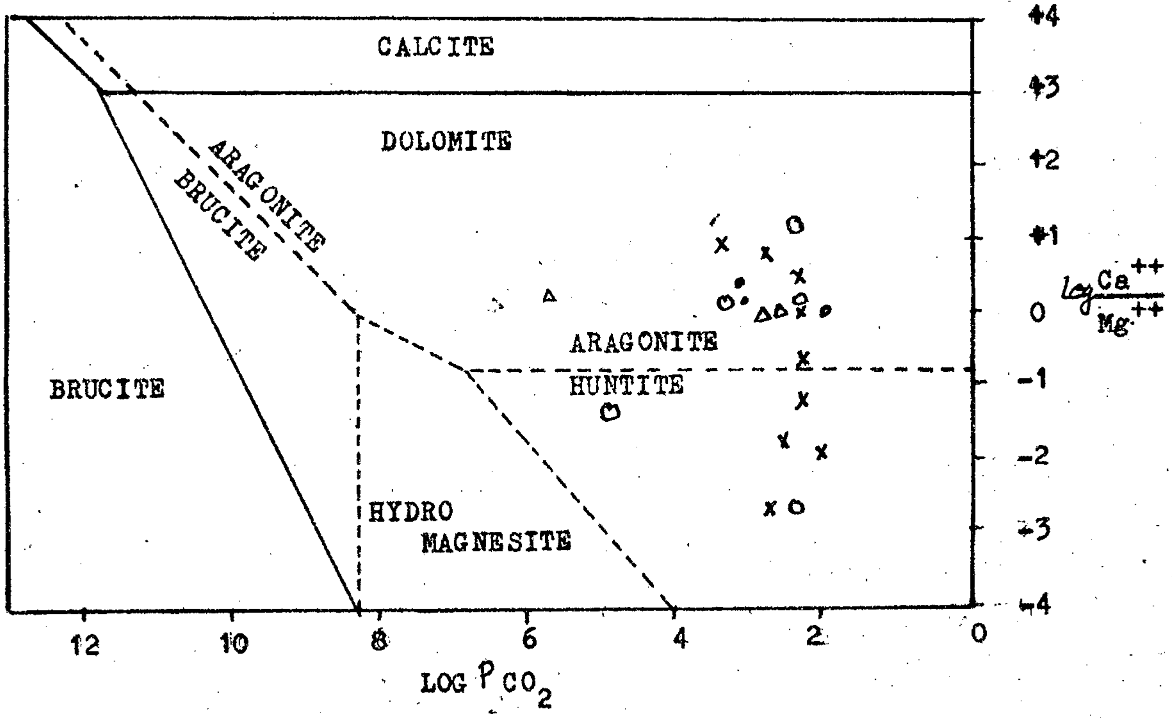


Fig. 2 - CARBONATE SYSTEM

SYMBOL

EXPOSED WATER BODIES O

ALLUVIAM X

QUARTZITE ●

SAND DUNE △

and 2 exposed water bodies while all quartzites sand dunes and partial alluvium and exposed water bodies fall in aragonite region.

This prediction can be confirmed if suspended matter is available in ground water by doing X-ray analysis. It can be found out which mineral is present in suspended matter. The other confirmation for this prediction is that soil is containing calcereous nodules known as 'Kankars', this nodules can be formed only when capillary water is in state of super saturation. The exact mineralogy of Kankar is not investigated hence it is very difficult to say that Kankar is made up of which minerals. The X-ray analysis was also not carried out because ground water was lacking the suspended matter.

The carbonate system was investigated by other workers also (Berner, 1971; Dalavi, 1978; Jayaraman, 1977). The dolomite presents difficulty because it is not the primary mineral, it is formed by substitution. Dalavi (1978) Based on carbonate system reported the presence of dolomite in the state of saturation in the Yamuna river. Jayaraman (1977) also reported the presence of dolomite in the Ganga river in the State of saturation thereby he confirmed the actual finding of Handa (1972).

SILICATE SYSTEM

Silicate system is explored extensively by different authors (Dalavi (1978), Garrels and Christ (1965), Harris and Adams (1966), Jacks (1973b), Jayaraman (1977), Subramanian (1974), Subramanian et al (1976,77) and Kramer (1967). This system embraces large number of minerals both primary and secondary. All rocks are dominantly made up of minerals of silicate family except limestone, dolomite and carbonatites. This system has been investigated in all environments like ocean, estuary, delta, river, ground water and lakes. Subramanian et al (1976) using principle of Helgeson and Mackenzie (1970) plotted the data of water chemistry of St. Lawrence estuary on silicate phase diagram suggested Mg-Chlorite, solid ~~mt~~ solution of illite - montmorillonite, microcline, quartz and kaolinite can be expected in the sediment. Kramer (1967), Garrels (1967), Garrels and Christ (1965), Garrels and Mackenzie (1967) and Mackenzie and Garrels (1967) have used these diagrams for different environments using different parameters.

In case of India stability diagrams had been used by Dalavi (1978), Jayaraman (1977), Jacks (1973b) and Subramanian and Dalavi (1977). Dalavi (1978) and Jayaraman (1977) used these diagrams in case Yamuna and Ganga river study and they predicted different minerals are likely to be present in the sediment. Dalavi has also done experimental verification of his theoretical finding while

Jayaraman supported the actual finding of Handa (1972). Jacks (1973,b) predicted the presence of different minerals in the ground water of Coimbatore District of Tamil Nadu. Then he made study by dividing silicate system into 4 sub-systems.

Considering the large number of minerals found in silicate system it is ~~very~~ impossible to represent all the minerals by taking two parameters. Therefore, this system was divided into 3 sub-systems.

1) K_2O - Ak_2O_3 - SiO_2 - H_2O System
2) Na_2O - Al_2O_3 - SiO_2 - H_2O "
3) MgO - Al_2O_3 - SiO_2 - H_2O " .

1) $K_2O - Al_2O_3 - SiO_2 - H_2O$ System

The minerals which are making this system are K-feldspar, K-mica, gibbsite and kaolinite. The expected reactions in this system are

K-feldspar = K-mica

$$3KAlSi_3O_8+2H^++12H_2O = KAl_3Si_3O_{10}(OH)_2+6H_4SiO_4+2K^+ \qquad (35)$$

K-mica and gibbsite

$$2KAl_3Si_3O_{10}(OH)_2+2H^++18H_2O = 3Al_2O_3\ 3H_2O+2K^++6H_4SiO_4 \qquad (36)$$

K-feldspar and kaolinite

$$2KAlSi_3O_8+2H^++9H_2O = H_4Al_2Si_2O_9+2K^++4H_4SiO_4 \qquad (37)$$

Kaolinite and Gibbsite

$$H_4Al_2Si_2O_9+5H_2O = Al_2O_3.3H_2O+2H_4SiO_4 \qquad (38).$$

Expecting the equilibrium between above set of reaction and water the equilibrium constant for each reaction can be determined as done in carbonate system. For example the equilibrium constant (K) for K-feldspar and K-mica (35)

$$K_4 = \frac{[K^+]\ [H_4SiO_4]^3}{[H^+]} \qquad (39)$$

The chemical boundary for this reaction will be provided by the following equation

$$\log K_4 = 4.9 = \log \frac{[K^+]}{[H^+]} + 3 \log [H_4SiO_4] \qquad (40)$$

For K-mica and gibbsite (36)

$$K_5 = \frac{[K^+]\ [H_4SiO_4]^3}{H^+} \qquad (41)$$

$$\log K_5 = -7.6 = \log \frac{[K^+]}{[H^+]} + 3 \log [H_4SiO_4] \qquad (42)$$

In the same manner equilibrium constants for other reactions are calculated. The activity-activity plot of this system is shown in Fig. 3 using the variable $\log [K^+] / [H^+]$ and $\log H_4SiO_4$. The data from Table III are plotted in the diagram No. 3.

Widely scattered points attract attention immediately. They are distributed in K-feldspar kaolinite and gibbsite. This indicates K-feldspar kaolinite and gibbsite will precipitate in state of super saturation.

On the close scrutiny of diagram, it is revealed that all samples of alluvium fall in gibbsite region except of Shahdara and

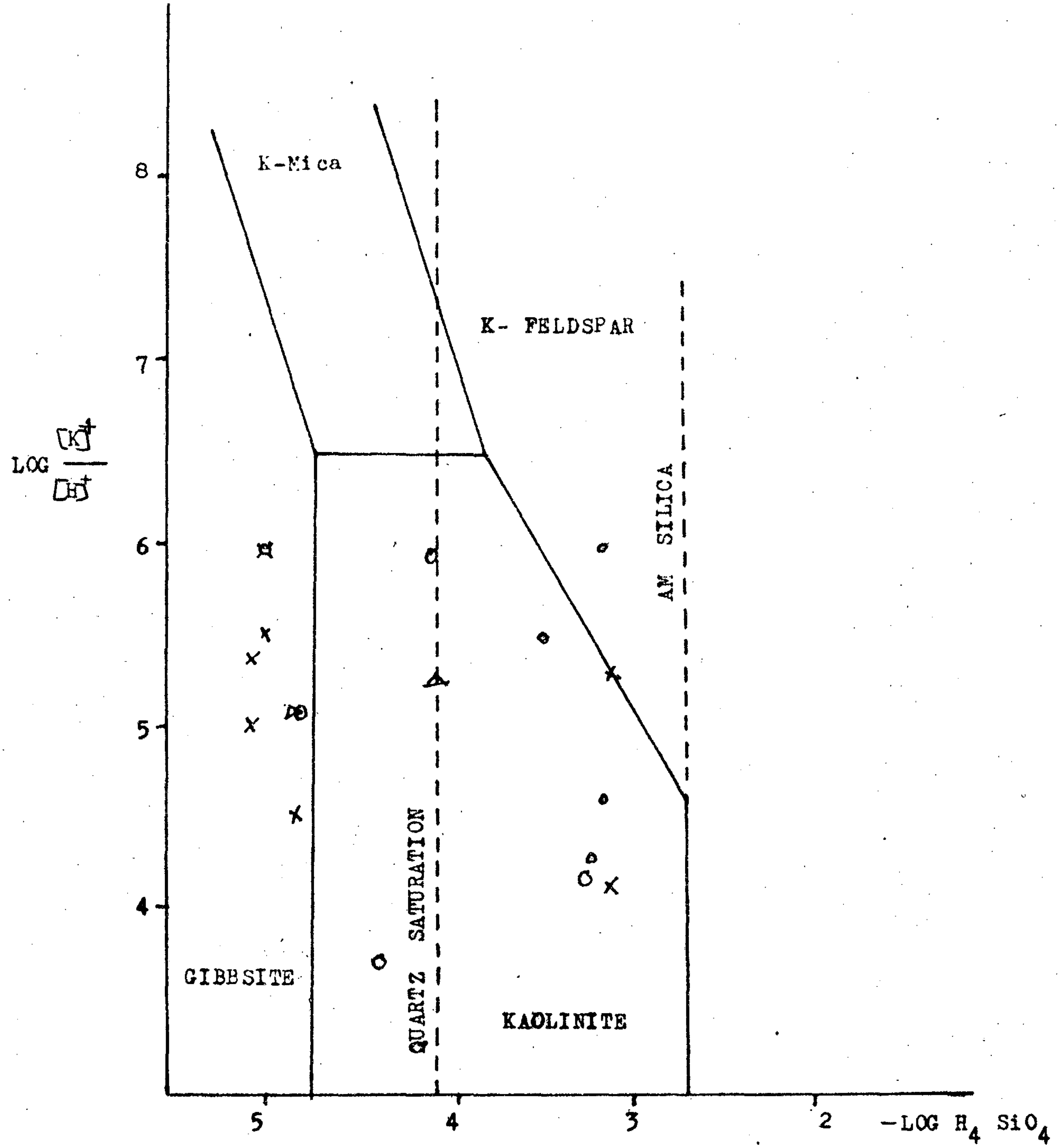


Fig. 3 - K_2O - Al_2O_3 - SiO_2 - H_2O System

SYMBOL	
EXPOSED WATER BODIES	O
ALLUVIAM	X
QUARTZITE	●
SAND DUNE	△

Delhi Cantt., which fall in kaolinite and feldspar area. The analysis of quartzites fall in kaolinite and K-feldspar region it was expected because gibbsite is pure hydrons alluminium oxide mineral and quartzite is lacking in alumina. The JNU sample falls in K-feldspar region while others in kaolinite region. In case of sand dune one sample falls in kaolinite of Sultanpur and other in gibbsite region just near the boundary of gibbsite and kaolinite. The samples of Yamuna water fall in kaolinite field. This observation is in conformity with Dalavi (1978) who has also studied Yamuna water and reported kaolinite both by phase diagrams and x-ray analysis of suspended matter. This observation is also matching with conclusion of Garrels and Mackenzie (1967) that river water sample will fall in kaolinite region, in case of Ganga river. Jayaraman (1977) has also drawn similar conclusion.

2) $Na_2O - Al_2O_3 - SiO_2 - H_2O$ System

The representative minerals of this system are albite, montmorillonite, kaolinite and quartz. The reaction among these minerals are as follows (Garrels and Christ, 1967).

Albite and Montmorillonite

$$7NaAlSi_3O_8+6H^++20H_2O \rightleftharpoons 6Na^++10H_4SiO_4+3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 \quad (43)$$

Montmorillonite and kaolinite

$$6Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2+23H_2O \rightleftharpoons$$
$$7Al_2Si_2O_5(OH)_4+6H^++8H_4SiO_4+6Na^+ \quad (44)$$

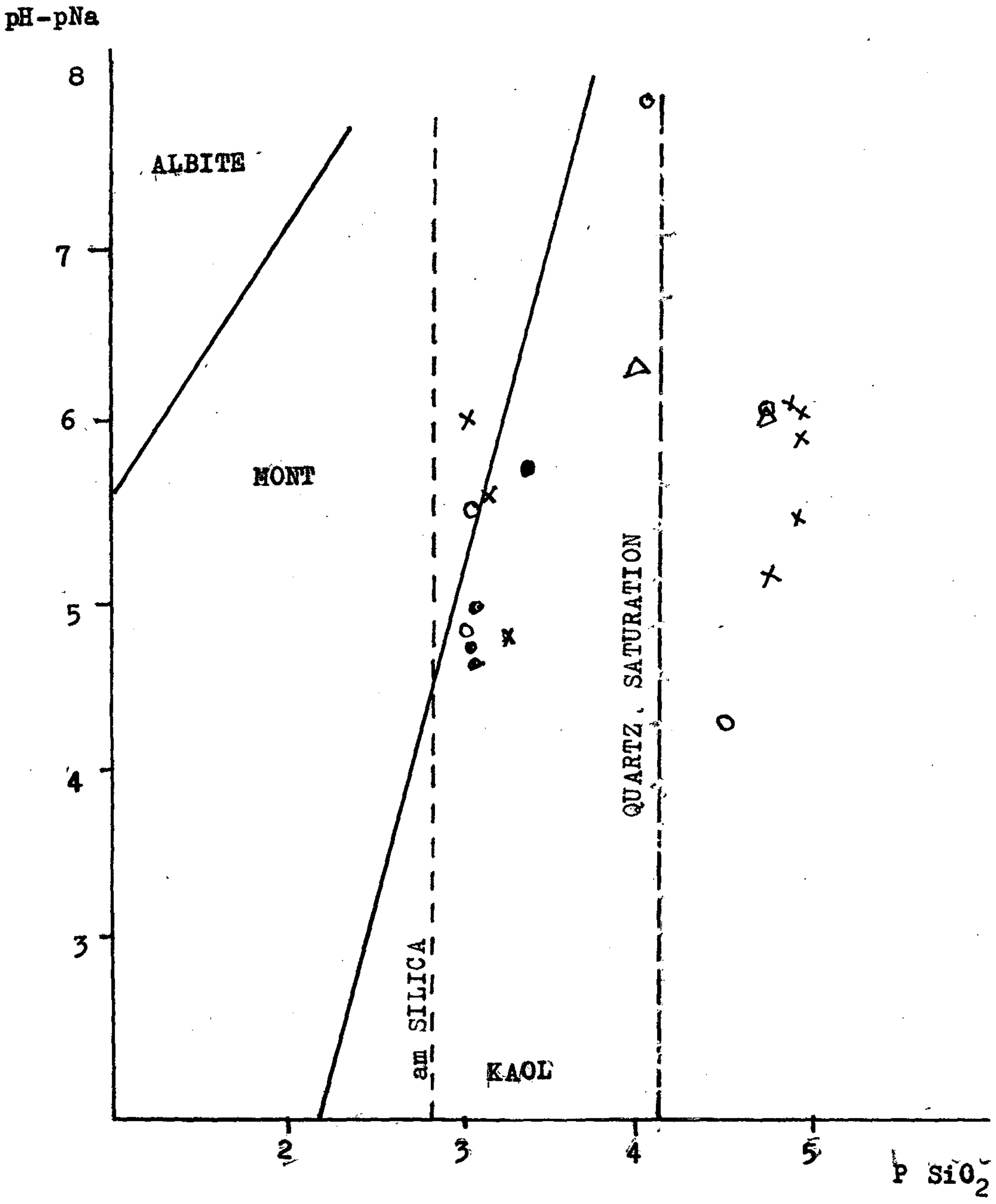


Fig. 4 - Na_2O - Al_2O_3 - SiO_2 - H_2O System

Symbol	
Exposed Water Bodies	○
Alluviam	×
Quartzite	●
Sand Dune	△

The other possible reaction in this case is between kaolinite and quartz. The equilibrium diagram used here is developed by Jacks (1973) based on the above reactions (Fig. 4). The analysis of Fig. 4 indicates present work falls in montmorillonite, kaolinite and quartz region. 5 alluvium analyses fall in quartz region. One each in kaolinite and montmorillonite. The samples of quartzite fall in montmorillonite and kaolinite region while the samples of exposed water bodies are scattered in all the 3 regions. No sample is falling in albite region.

3) 3 - MgO - Al_2O_3 - SiO_2 - H_2O System

The main minerals involved in this system are kaolinite and chlorite according to reaction 45

2Kaolinite + 6 magnesium = Mg-Chlorite + 2 aluminium

$$2H_4Al_2Si_2O_9 + 6\ Mg^{++} = Mg_6(OH)_8Si_4O_{10} + 2Al^{+++} \qquad (45)$$

Using two parameters $pH\text{-}1/2\ P_aMg$ and $_pSiO_2$ Jacks (1973b) has drawn the phase diagram for magnesium silicate system. On the same reproduced diagram (Fig. 5) the different values of above parameters (Table III) have been plotted. It is found that all points are concentrating in Mg-Chlorite region. The observation indicates Mg-chlorite is likely to form in the state of saturation. The Badarpur analysis is only falling on the line of kaolinite and Mg-chlorite.

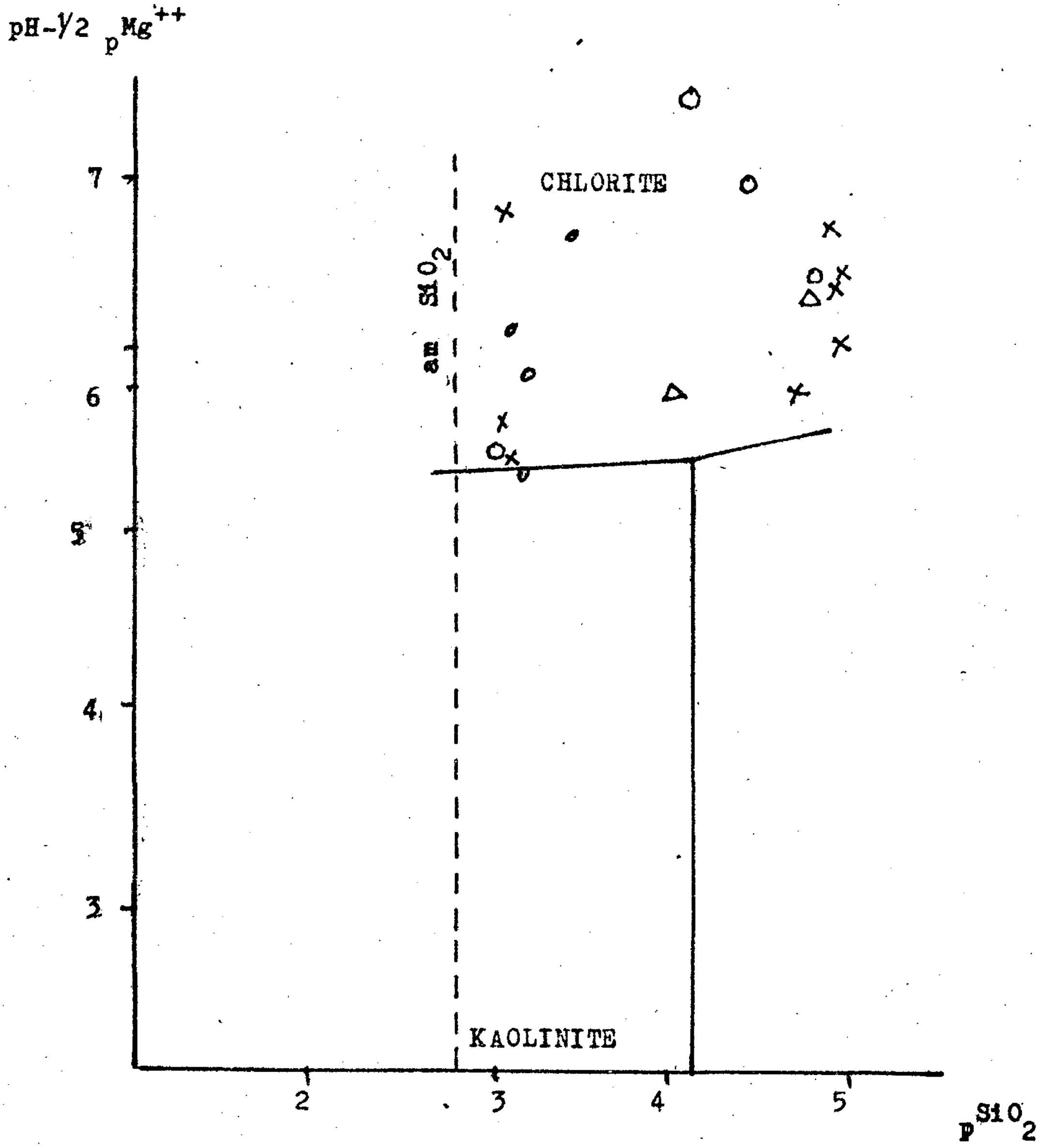
X-ray study of sample

As mentioned, ground water is free from suspended matter. So x-ray analysis of the samples could not be done but in case of Masudpur abandoned mine, large amount of mine sediment as weathering product was available and it was assumed that entire product has come from pegmatite. This was of clay partide size. This mine sediment on x-ray analysis confirmed the presence of kaolinite as predicted by the silicate phase diagram. Two peaks were obtained at 3.36°A and 7.18°A which are indicating presence of pure kaolinite and small amount of quartz in sediment. The x-ray diffractograph pattern is shown in Fig. 6. The presence of quartz was predicted by sodium silicate system.

Dalavi (1978) has also done x-ray study of Yamuna sediment and he found illite along with kaolinite and quartz.

Soil mineralogy has been determined by various authors by x-ray. Ray Chaudhury, 1952 (in Paliwal _et al_, 1976) investigated first soil mineralogy of this region. He found chlorite, illite and kaolinite, later on Das, 1958 (in Paliwal, 1978) reported kaolinite and illite. Dhar (1968) (in Paliwal _et al_, 1976) indicated the possibility of montmorillonite, illite and kaolinite and high carbonate content in soil.

These soil mineralogy data are exactly matching with theoretical prediction of author of kaolinite, chlorite and K-feldspar. Therefore, there is good agreement in the theoretical finding and



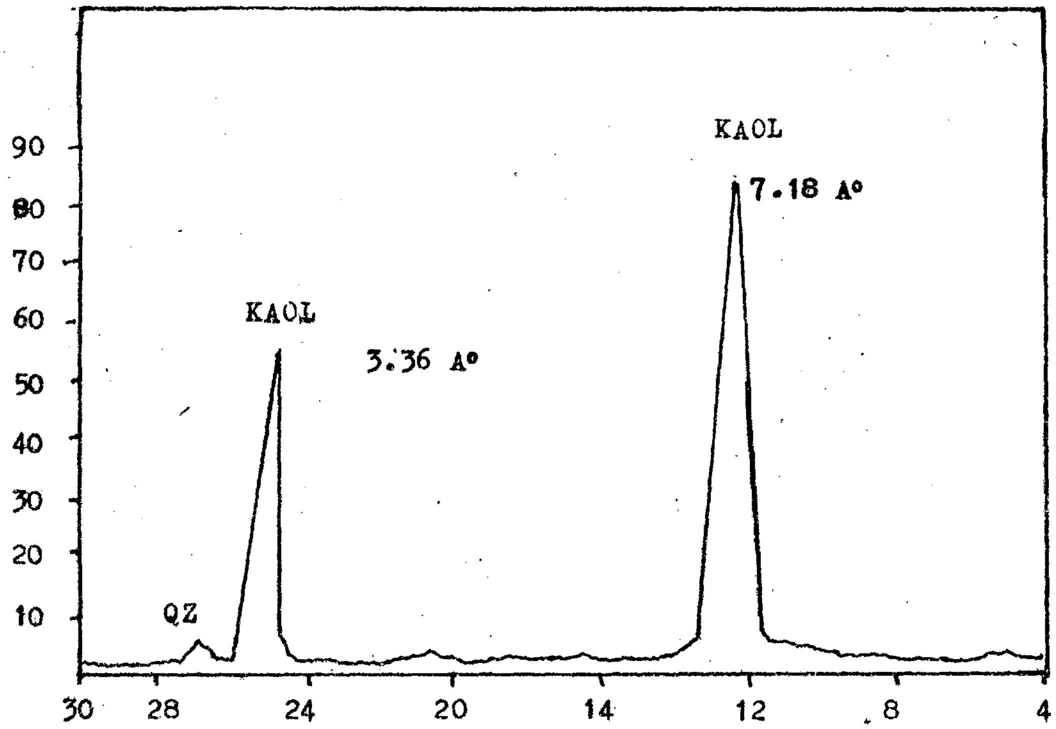
MAG-SILICATE STABILITY DIAGRAM

	SYMBOL
EXPOSED WATER BODIES	○
ALLUVIAM	×
QUARTZITE	●
SAND DUNE	△

Fig. 5

experimental analysis of soil mineralogy, mine sediment and Yamuna water.

Since illite was not the component of phase diagram, therefore, it was not predicted. The carbonate system does not require any verification because presence of carbonate minerals is shown by 'Kankars' found in the alluvium. Mineralogy of Kankars is so far not investigated. Therefore, it cannot be said conclusively that Kankars are made up of dolomite, aragonite or huntite or not.



X-RAY DIFFRACTION PATTERN

Fig. 6

CONCLUSION

The present work carried out on Delhi ground water has shown contradiction in reported value of chemical analysis given by different workers (Sett, 1964a,b; Biswas et al, 1969). The analytically determined data have shown less concentration of ions in monsoon sample and high concentration in summer. Silica is always found to be saturated in ground water both in quartz and amorphous silica. This silica has been released from chemical and physical weathering of area. Physical weathering is more significant in Sultanpur, Farrukhanagar areas while chemical in rest of the areas.

The water quality is found to be highly variable from rock to rock and even in the same rocks from one place to another place. This indicates large scale mixing of ground water of two aequifer. The highest salinity is shown by Sultanpur-Farrukhanagar samples but comparatively less by alluvium and quartzite. Considerable impact on ground water quality is made by fertilizers, industrial and domestic waste.

Very good control of lithology was observed in the case of following ions: silica (maximum in quartzite and minimum in sand dunes), bicarbonates (maximum in alluvium and minimum in sand dunes). Here it is expected large scale transfer of bicarbonate ions from alluvium to quartzite, sulphate is maximum in sand dunes and minimum in quartzite. Same is observed in case of chloride. The higher concentration of particular ion in a particular rock-type is due to the fact that rock was rich in that ion and minimum concentration in particular rock-type indicates impoverishment of that mineral which releases that ion in the rock.

A loose control of lithology was observed in case of potassium, chloride and calcium between alluvium and quartzite. Their concentration is such that no definite conclusion can be drawn about their relationship with the rock-type.

Phosphate has not shown any control because it is not primary constituent of any rock met in the area. Moreover, in phosphate analysis silica interference is also suspested. Its presence in ground water can be attributed to percolation of surface water from agricultural field when phosphate is used as fertilizer.

Carbonate system has shown presence of dolomite in the state of saturation when calcite-dolomite system is considered and aragonite and huntite, when aragonite-huntite system is considered. The presence of carbonate minerals is evident from widespread distribution of Kankar in alluvium (Sett, 1964) which was formed in the state of saturation by capillary action of water.

The predictions of different silicate phase diagrams have been successfully correlated with x-ray analysis of mine-sediment, Yamuna sediment (Dalavi, 1978) and soil mineralogy (Paliwal _et al_, 1976), Phase diagrams have shown presence of kaolinite, quarts, gibbsite, montmorillonite and chlorite. Paliwal (1976) has reported that kaolinite, quartz, illite and chlorite. Since illite phase was not considered in phase diagrams, therefore, it is yet to be verified by theoretical study. But in the light of other predictions it can be speculated that it would also be present in the phase diagrams.

Yamuna river has shown marked departure from world's average data of Livingstone (Wadepohl, 1970). It can be assured here that since it is passing through readily soluble rocks limestone and alluvium before it enters into Delhi, therefore, it contain high dissolved load and then the entire area is highly populated which is producing high domestic and industrial affluents dumped into water which is another major factor for high dissolved load. In fact load carried by Indian rivers are much higher than the other rivers of the world (Subramanian <u>et al</u>., 1977).

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