AN ABSTRACT OF THE THESIS OF

Meer T. Husain for the Master of Science Degree in Earth Science Presented on June 20,1991.

TITLE : Geochemistry of Nitrate in Groundwater in Kansas.

ABSTRACT APPROVED : _Delwayne Backhus_

COMMITTEE MEMBERS : Dr. David C. Schroeder, Chairman

Dr. James S. Aber

Prof. Paul Johnston.

Ground water pollution in Kansas by nitrate has occurred for many years, but its chemistry in aquifers is still not well known. Some wells in Nemaha, Chase and Harvey Counties have shown a disappearance in nitrate accompanied by an increase in dissolved iron, suggesting a natural nitrate reduction process.

The main purposes of this study are to describe the chemical reactions of nitrate in ground water and to identify the geological factors controlling the reactions. In order to examine the purposes of this study both Flow tests and Beaker tests were carried out with the minerals pyrite and siderite with nitrate and synthetic ground water solutions. The Beaker tests revealed reduction of nitrate by pyrite. The tests indicated that pyrite particle <0.125 mm size are able to reduce nitrate. The tests also revealed that after 74 and 51 days, total reduction of nitrate in Preliminary beaker test no. 2 and Final beaker test no. 2 were 78.6 % and 10 % respectively. The reaction between NO_3^- and FeS_2 mineral is not a direct one. It took place after a lag time. The reaction is most possibly catalyzed either by bacteria or by freshly precipitated $Fe(OH)_3$.

The nature of the reduction of nitrate by pyrite closely corresponds to the iron and nitrate relationship in alluvial aquifer in Harvey County, glacial drift aquifer in Nemaha County, High Plains aquifer in Harvey County, Chase and Council Grove Group aquifer in Chase County and Pleistocene aquifer in Nemaha and Chase Counties. This phenomenon suggests that the reduction of nitrate in ground water in Kansas is also controlled by pyrite. The presence of pyrite in aquifers in Kansas can be supported by two indirect evidences: pyrite occurs in rocks of all ages in Kansas (Buchanan, 1989) and the variation of SO_4^{2-} concentrations in relation to iron and nitrate concentrations in the aquifers of the study areas.

The reduction of nitrate by pyrite in ground water conditions can not be fully justified because the tests were carried out by pure minerals. In order to obtain detailed information regarding the rate of reduction of nitrate and reaction between nitrate and pyrite in actual ground water conditions, a scheme of experiments has been proposed.

GEOCHEMISTRY OF NITRATE IN GROUND WATER IN KANSAS

A Thesis

presented to

the Division of Physical Sciences

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Earth Science

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by

Meer T. Husain

June, 1991

DeWayne Backhus

David C. Schroeder

Approved for the Major Department

Faye N. Vowell

Approved for the Graduate Council

ACKNOWLEDGEMENT

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Various sources of nitrate are known. In Kansas, according to most investigators, livestock feeding operations and fertilizers are the principal sources of nitrate pollution. Metzler (1958) suggested the following possible sources of nitrate in ground water.

1. Nitrogenous organic matter of animal origin, especially liquid and solid waste such as manure and sewage.

2. Nitrate formation in normal agricultural soils.

3. Nitrate fixation by legume crops.

4. Organic and inorganic fertilizers to enrich the soil.

5. Decay of vegetable matter.

6. Buried organic materials in sediments, peat deposits.

7. Nitrate deposits in geological formations.

8. Nitrogenous industrial wastes.

9. Oxidation of atmospheric nitrogen during electrical storms.

The Nitrate - Iron Relationship:

Contamination of ground water by iron in Kansas is not as common as nitrate. However, high concentrations of iron some public water wells and observation wells do occur. Iron is an abundant and widespread constituent of rocks and soils. In sediments, it occurs in ferrous form in some species of minerals, such as pyrite (FeS_2), siderite

Well no. 1 in Nemaha County (Figs. 1 & 5) had a concentration of iron in each year lower than NO_2 and NO_3. In 1989, the highest iron concentration was 0.04 mg/L whereas the lowest NO_2 and NO_3 was 1.90 mg/L. In 1987 and 1988 the lowest iron concentration was < 0.01 mg/L where the NO_2 and NO_3 concentration was 8.10 and 4.86 mg/L.

Well no. 2 and 3 in Nemaha County (Figs. 1 & 6) showed very high concentrations of iron and low concentration of NO_2 and NO_3. In 1985, well no. 3 exhibited the highest NO_2 and NO_3 concentration of 1.5 mg/L and lowest iron concentration of 0.16 mg/L. The concentration of iron, and NO_2 and NO_3 in well no. 2 ranged from 1.3 to 2.0 mg/L and <0.01 to 0.03 mg/L whereas the iron and NO_2 and NO_3 concentration in well no. 3 ranged from 0.16 to 1.8 mg/L and < 0.01 to 1.5 mg/L.

Well no. 4 in Harvey County (Figs. 1& 7) had high concentrations of NO_2 and NO_3 and low concentration iron. The lowest concentration of iron (0.01 mg/L) was observed in 1985 and 1989 where the NO_2 and NO_3 concentration was 5.60 and 6.77 mg/L. The highest concentration of iron (0.07 mg/L) was observed in 1986 where the NO_2 and NO_3 concentration is 5.40 mg/L.

Well no. 5 in Harvey County (Figs. 1 & 7) showed very high concentration of iron and low concentration of NO_2 and NO_3. The lowest iron concentration (0.59 mg/L) was observed in 1986 where the NO_2 and NO_3 concentration was 0.19 mg/L. The highest concentration was 0.19 mg/L. The highest concen

Figure-1:   Observation well location map of Kansas

              showing the well locations of study   area

              in Nemaha, Chase and Harvey Counties.

Well No.   Local Identifier

    1.   02S12E26CDA 01
    2.   05S14E11ACC 01
    3.   04S13E35BBA 01
    4.   23S01W32BBC 01
    5.   24S03W26ADA 01
    6.   19S07E27CBC 01
    7.   19S08E20AAA 01
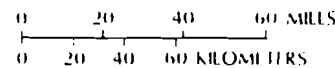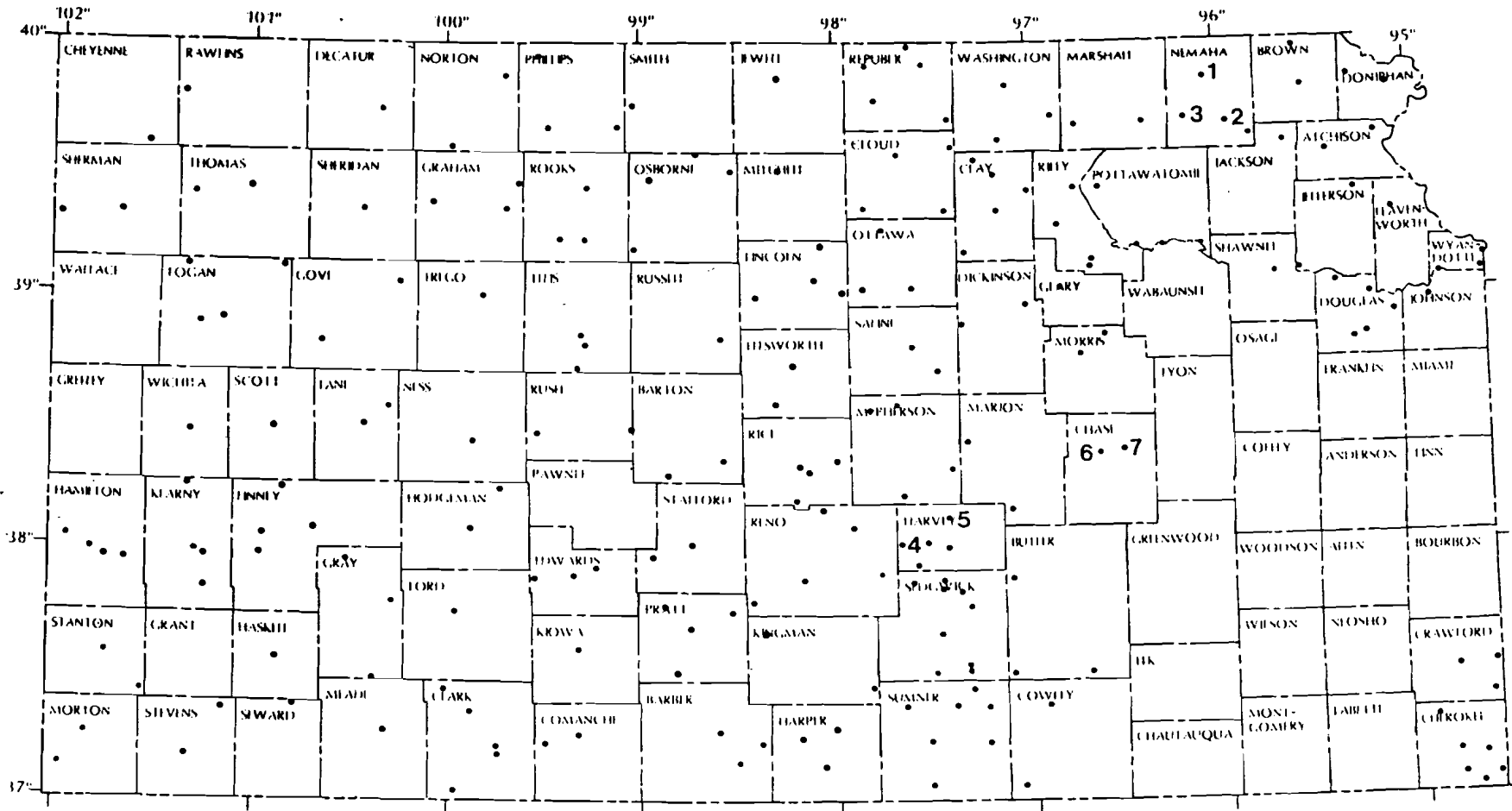
WELL LOCATION MAP

tration of iron (4.5 mg/L) was observed in 1987.

Well no. 6 in Chase County (Figs. 1 & 8) showed high concentration of iron (0.47 mg/L) in 1986 where the NO_2 and NO_3 concentration was 0.15 mg/L. The lowest concentration of iron (0.01 mg/L) was observed in 1988 where the NO_2 and NO_3 concentration was 0.22 mg/L. In 1985 and 1989, the highest and lowest concentrations of NO_2 and NO_3 were 5.10 mg/L and <0.01 mg/L, and the iron concentration was 0.03 mg/L.

Well no. 7 in Chase County (Figs. 1 & 8) revealed very low NO_2 and NO_3 concentration and very high iron concentration. The lowest iron concentration (0.01 mg/L) was observed in 1985 where the NO_2 and NO_3 concentration was 0.23 mg/L. The highest concentration of iron (3.4 mg/L) was observed in 1989 where the NO_2 and NO_3 concentration was less than 0.01 mg/L.

Pyrite and Siderite:

Before conducting the experiments it was assumed that under reducing condition, reduced form of iron - bearing minerals would go into solution and liberate iron. Accordingly minerals pyrite and siderite were selected for the experiments.

The chemical formula of pyrite is FeS_2. Pyrite is the most common sulfide mineral, also called fool's gold because of its yellowish golden color. It is a common accessory minerals in many igneous and metamorphic rocks. Under reducing condition pyrite forms in shale and coal deposits.

Pyrite is found in various crystal forms, such as the cube (001) where the three crystallographic axes are in equal length, pentagonal dodecahedron (210), or occasionally octahedrons (111). It may also forms granular or encrusting masses. In shale, coal and other sediments, small desmineted crystals and raspberry like aggregates are also found.
The hardness and specific gravity of pyrite are 6-6.5 and 5.02 respectively. Pyrite dissolves in water as Fe^{2+}, S^{2-} and S. FeS_2 ---> Fe^{2+} + S^{2-} + S, where Fe^{2+} and S^{2-} in crease the conductivity of water. The reduced form S^{2+} of sulfur in water is sometimes found as HS^- ions and or dis-solved undissociated H_2S.

$$S^{2-} + H_2O ---> HS^- + OH^- ---> H_2S + 2OH^-$$
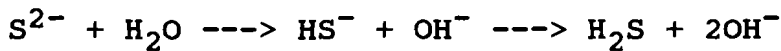
where reduced forms of sulfur and OH^- ions help to increase the pH of water. The oxidation reactions of H_2S and S pro-duce SO_4^{2-} ions, reduce nitrate, and decrease pH of water. The reactions are as follows :

$$H_2S + 2O_2 ---> SO_4^{2-} + 2H^+$$
$$5H_2S + 8NO_3^- ---> 4N_2 + 4H_2O + 5SO_4^{2-} + 2H^+$$
$$S + 3/2O_2 + H_2O ---> SO_4^{2-} + 2H^+$$
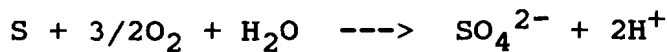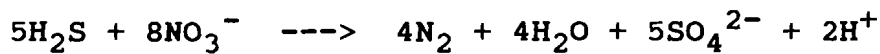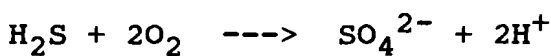
The oxidation of ferrous ions produced to form ferric ion, above pH values 3.0 precipitated as hydrated iron oxide and reduces nitrate and decreases pH of water.

$$4Fe^{2+} + O_2 + 4H^+ ---> 4Fe^{3+} + 2H_2O$$
$$5Fe^{2+} + 12H_2O + NO_3^- ---> 5Fe(OH)_3 + 1/2N_2 + 9H^+$$
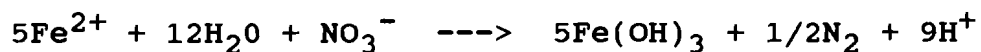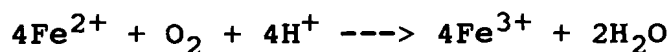
The ferric iron further dissolves pyrite minerals. The conversion of oxidized to reduced species of iron and sulfur

or vice versa are often associated with biochemical process-
es. In Kansas, pyrite occurs in coal deposits and in areas
where zinc and lead occurs. It is also found with gypsum in
the dark shale. Pyrite occurs in rocks of all ages in Kansas
(Buchanan, 1989).

The mineral siderite most commonly occurs as grains in
sedimentary iron formations where it is associated with
clays and various iron oxides, hydroxides and silicates.
Siderite is also found in metamorphic iron formations and in
carbonate rocks altered by iron bearing solutions. In igne-
ous rocks, it may be present in carbonatite and in fractures
and amygdules in basalts, diabase and andesite. Crystals of
siderite are usually rhombohedrons (1011), sometimes modi-
fied by a basal pinacoid (0001). The hardness and specific
gravity of pure siderite are 4-4.5 and 3.96. The chemical
composition of siderite is $FeCO_3$.In Kansas, pure siderite is
not found. The impure form is called iron claystone, found
as nodules, or whole beds in clays, shale and sandstone.

Purposes of Study:

The main purposes of the study are:
1. To describe the chemical reactions of nitrate in
   ground water.
2. To identify the geological factors controlling the
   reactions.

GEOLOGICAL CHARACTERISTICS OF AQUIFERS IN KANSAS

Kansas relies on both surface and ground water resources. The major water supply in the eastern part of the state is provided by river systems. In the western two third of the state, abundant ground water resources provide most of the water supplies. There are seven principal aquifers in Kansas, which can be divided into two groups. These are unconsolidated aquifers and consolidated aquifers. Unconsolidated aquifers include rocks of Cenozoic age. These are:

1. alluvial aquifer

2. glacial drift aquifer

3. High Plains aquifer

Consolidated aquifers consist of fine sandstone, limestone and dolomite. The principal consolidated aquifers in Kansas are as follows:

1. Great Plains aquifer

2. Chase and Council Grove Group aquifer

3. Douglas aquifer

4. Ozark aquifer

Unconsolidated Aquifers:

<u>Alluvial aquifer</u>:

The aquifer is widely but discontinuously distributed across the state. It consists of clay, silt, sand and gravel that were deposited in river valleys. Wells typically yield more than 500 gallons of water per minute in the Kansas,

Arkansas, Republican and Pawnee valleys. In other valleys, wells usually yield less than 100 gallon per minute. The aquifer is unconfined.

Glacial drift aquifer:

The aquifer is distributed over Nemaha, Brown, Doniphan, Atchison, Jackson, Jefferson, Pottwatomie and Wabaunsee Counties. It is composed of fine to course quartz sand, silt, clay, gravel and boulders, deposited under glacio-fluvial environment. Thickness and lithology slightly varies from county to county. The aquifer is unconfined and wells in the aquifer generally yield 10 to 100 gallons per minute.

High Plains aquifer:

This is a most important and most extensively used aquifer in Kansas. It covers nearly three-fourths of the Great Plains. It consists of thick unconsolidated fluvial and aeolian deposits of Tertiary and Quaternary age. Tertiary deposits mainly include the Ogallala formation. It is greenish gray, pink, red tan and ash color, massive to cross bedded, generally arkosic gravel, sand and silt. It contains limestone, volcanic ash, opaline sandstone and bentonitic clay. The maximum thickness of the formation is 350 feet. The aeolian sediments consist of fine sand, silt and clay. The aquifer is unconfined and wells commonly yield 500 to 1000 gallons per minute.

Figure-2: Aquifer map of Kansas showing the geographic
           distribution of aquifers in Kansas.

AQUIFER MAP OF KANSAS
AFTER USGS 1984

102°

95°
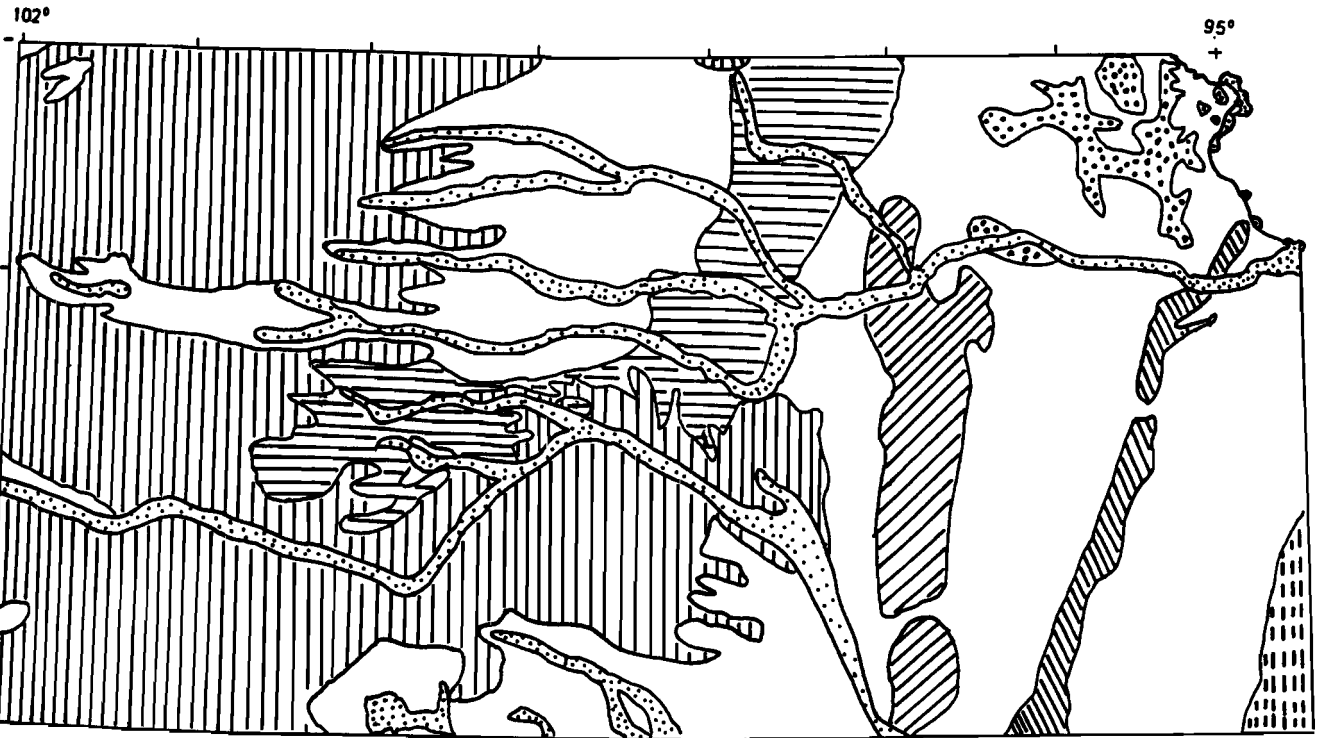
0   50   100 MILES

EXPLANATION

Alluvial aquifers

Glacial drift aquifers

High Plains aquifer

Not a principal aquifer

Great Plains aquifer

Chase and Council Grove aquifers

Douglas aquifer

Ozark aquifer

13

Consolidated Aquifers:

Great Plains aquifer:

The aquifer is a major source of water in the north eastern quarter and in the southern part of the great plains.It is unconfined and composed of Dakota and Cheyenne sandstone of Creataceous age. Cheyenne sandstone is white to buff to light gray, massive, mostly fine grained and partly cross bedded sandstone. It contains lenses of gray sandy shale, conglomerate and locally minor amounts of clay, siderite crystals, ironstone nodules and pyrite minerals.

Dakota formation occurs in north central and western Kansas. The formation consists of kaolinitic claystone, mudstone, shale, siltstone and interbedded and lenticular sandstone. It contains carbonaceous materials, lignite, and locally sandstone cemented with calcite or iron oxide. Grains or pellets of siderite are common in much of clay-stone and mudstone. The common well yields of the aquifer is 10 - 100 gallons per minute. Some wells in Finney, Ford and Hodgeman counties can yield more than 1000 gallons per minute.

Chase and Council Grove Group aquifer:

The aquifer is both unconfined and locally confined. It is composed of limestones of Chase and Council Grove Groups of Permian age. The common well yields of the aquifer is 10 to 20 gallons per minute. Chase group is composed of lime-

Pleistocene aquifer:

The aquifer consists of sand, silt, clay, gravel and chert of Pleistocene age. The well yield of the aquifer is very low. The aquifer is unconfined.

Study wells:

Seven observation wells in Nemaha, Chase and Harvey Counties represent the glacial drift, alluvial, High Plains, Chase and Council Grove Group and Pleistocene aquifers. Well no. 1 in Nemaha County penetrated the glacial drift aquifer. The total depth of the well is 54 feet. Well no. 4 and 5 in Harvey County represent the alluvial and High Plains aquifers. Wells penetrated a total thickness of 133 and 75 feet respectively. In Chase County well no. 6 penetrated the Chase and Council Grove Group aquifer. The total depth of the aquifer is 50 feet. Well no. 2, 3 in Nemaha County and well no. 7 in Chase County represent the Pleistocene aquifer (not a principal aquifer). The wells covered a total thickness of 65, 121 and 57 feet respectively.

The name of the aquifer, Pleistocene is so given so that it does not conflict with the other aquifers of Pleistocene age. The well numbering is given for the convenience of the study purpose.

Figure-3:   Line diagram of pH level in glacial drift
             aquifer   (well no. 1) and   Pleistocene
             aquifer (well no. 2 and   3) in Nemaha
             County, 1985 - 1989.

PH Level in Well #1, 2&3, Nemaha County

Legend: —■— Well #1 —✳— Well #2 —▲— Well #3
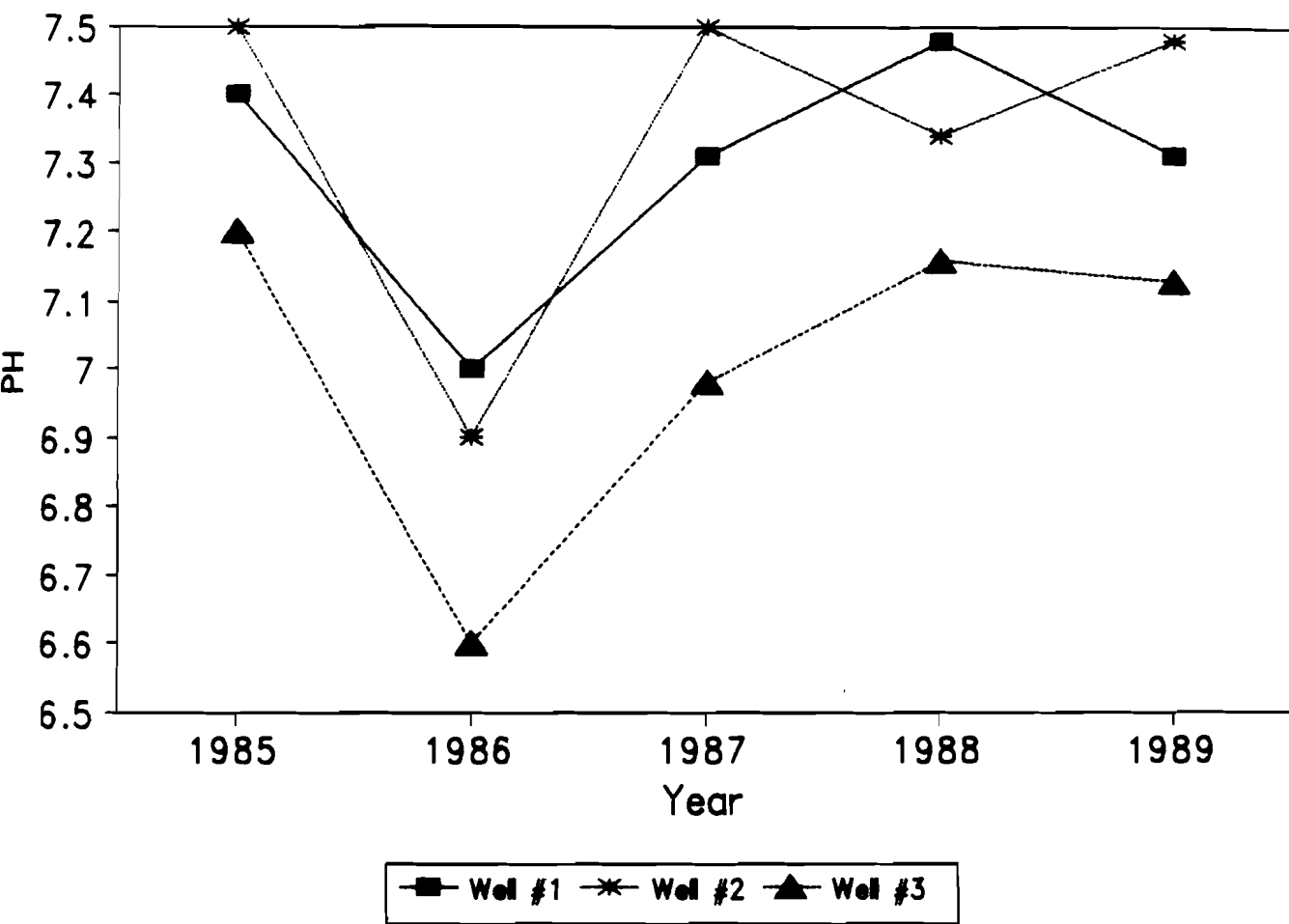
Figure-4:   Line diagram of pH level in   alluvial
            aquifer (well no. 4), High Plains aquifer
            (well no. 5) in Harvey County, Chase and
            Council Grove Group aquifer (well no. 6),
            and Pleistocene aquifer (well no.7) in
            Chase County, 1985 - 1989.

Figure-5: Line diagram of NO_2 + NO_3 and Fe concentration in glacial drift aquifer (well no. 1) in Nemaha County, 1985 - 1989.

Fe and NO2+NO3 Conc. in Glacial Drift Aquifer, Well #1, Nemaha County
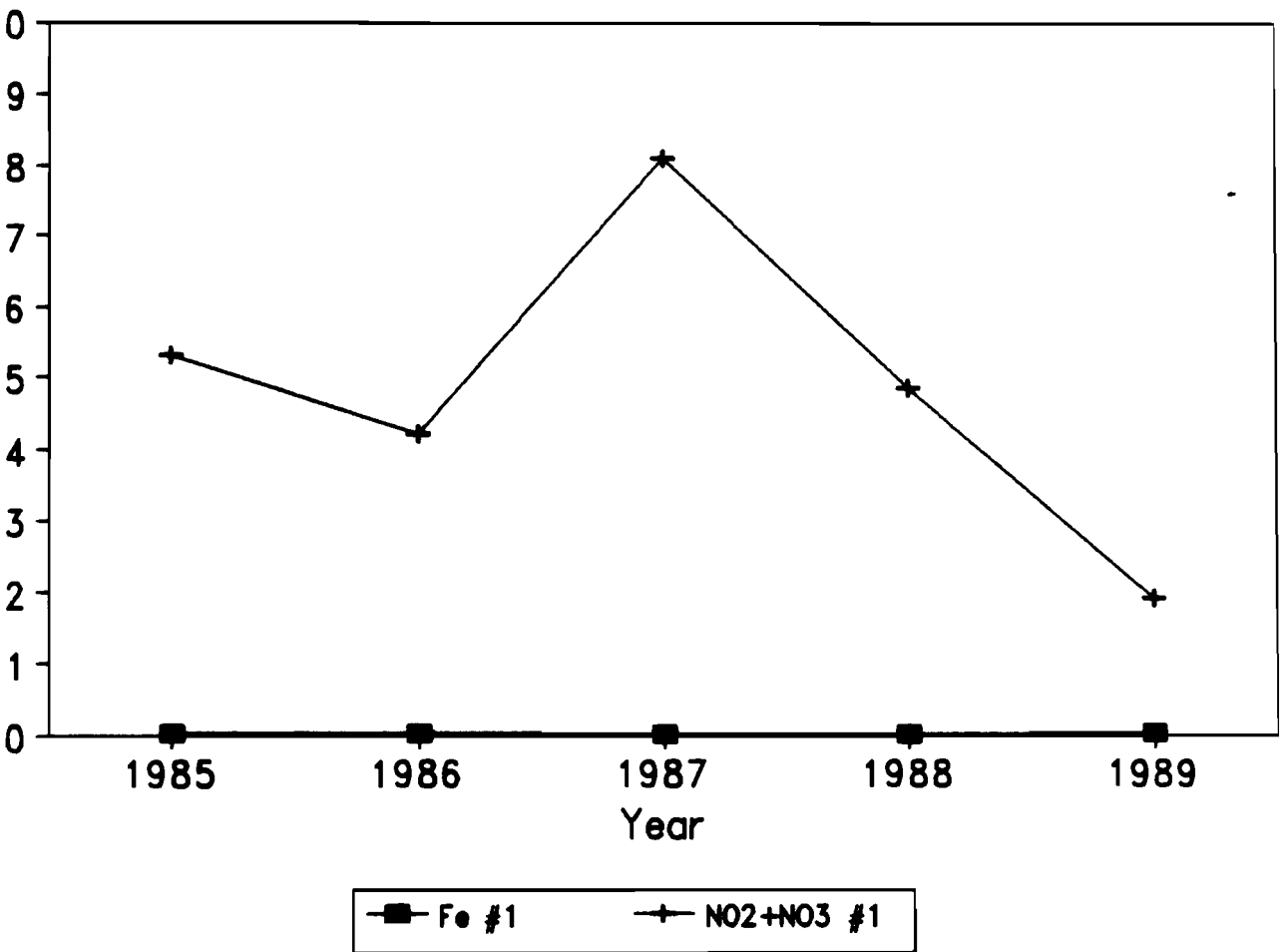
Fe and NO2+NO3 Conc. in Pleistocene Aquifer, Well # 2&3, Nemaha County
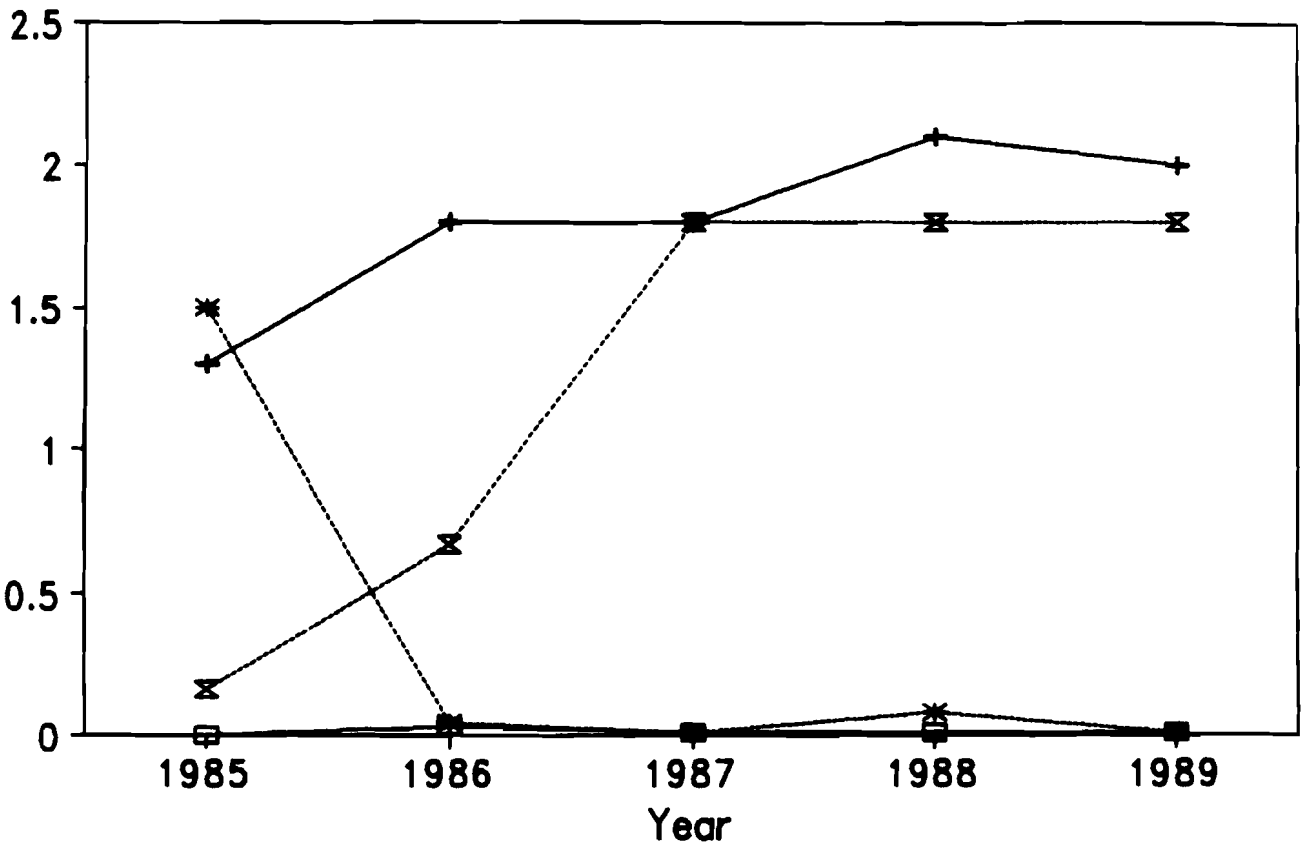
Legend: —+— Fe #2   —⊟— NO2+NO3 #2   —⊠— Fe #3   —✳— NO2+NO3 #3

Figure-7:   Line diagram of NO_2 + NO_3 and Fe concentra-
            tion in alluvial aquifer (well no. 4) and
            high Plains aquifer (well no. 5) in harvey
            County, 1985 - 1989.

Fe and NO2+NO3 Conc. in Alluvial & High Plains Aquifer, Well #4&5, Harvey County

Legend: + Fe #4   ■ NO2+NO3 #4   * Fe #5   □ NO2+NO3 #5

X-axis: Year (1985, 1986, 1987, 1988, 1989)
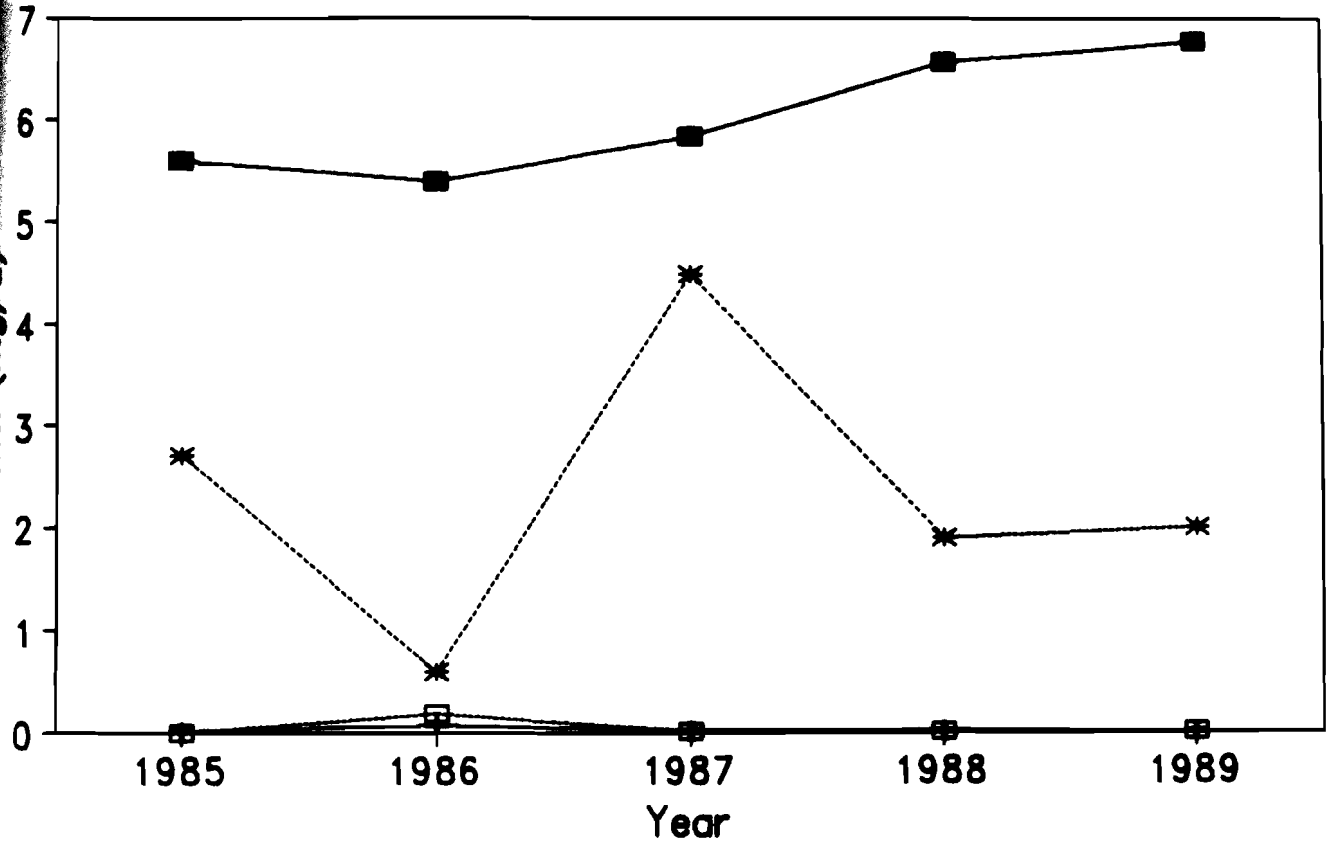
Figure-8: Line diagram of NO_2 + NO_3 and Fe concentra-
tion in Chase and Council Grove Group aquif-
er (well no. 6) and Pleistocene aquifer
(well no. 7) in Chase County, 1985 - 1989.

Fe and NO2+NO3 Conc. in Chase & Pleis-tocene Aquifer, Well #6&7, Chase County
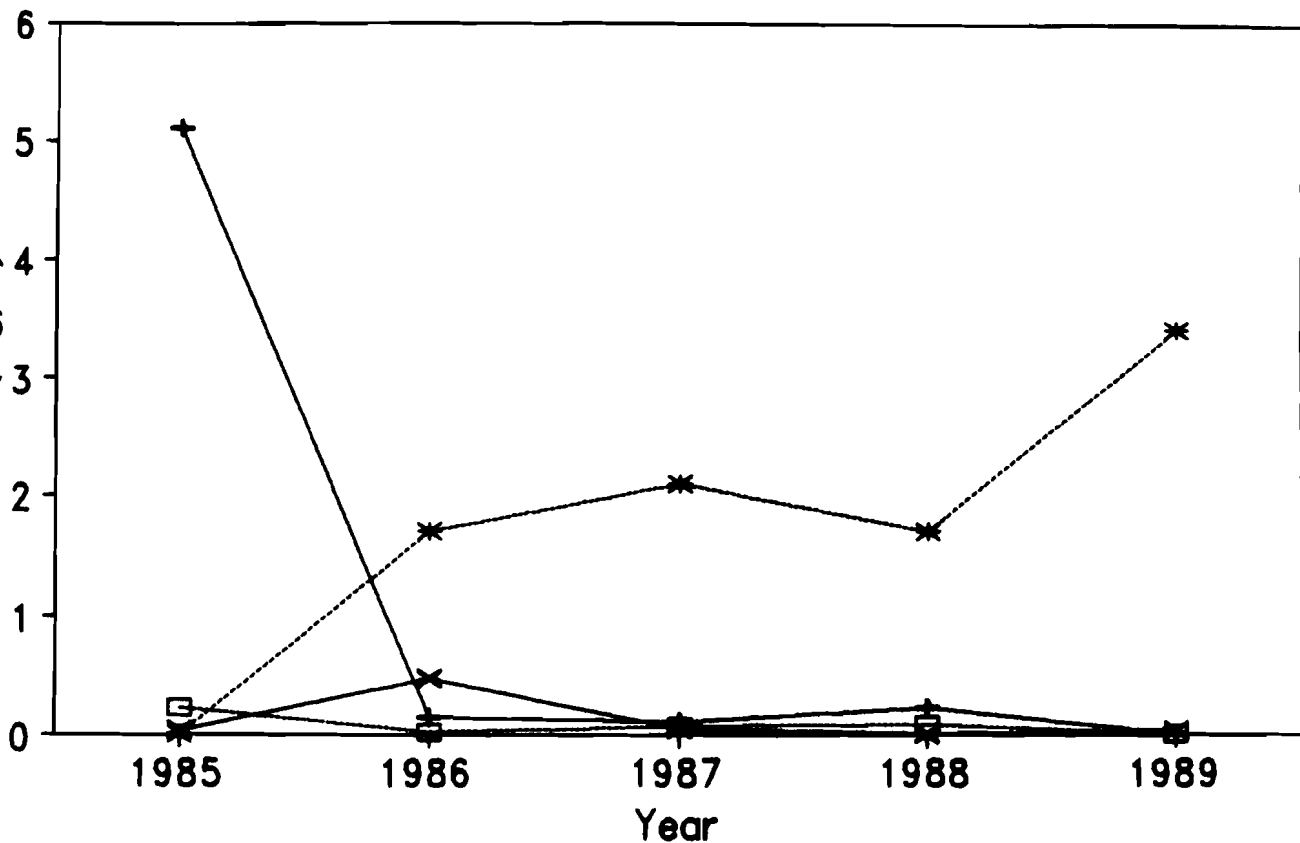
WATER QUALITY OF AQUIFERS

Water quality depends on type of precipitation, rock types, soil and organic materials, as well as chemical reactions. Generally ground water contains more dissolved solids than surface water. The high dissolved materials content of ground water is due to longer and more intimate contact of ground water with organic materials, soils, and rock particles of the aquifers. Lateral and vertical changes in water quality depends on type of porosity and permeability. Ground waters are less homogeneous than surface water, which tends to be less well mixed. Often cations are controlled by inorganic reactions and anions are controlled by organic reactions.

All of the aquifers in Kansas generally contain good quality of water. Dissolved solids are usually less than 1000 mg/L. Hardness of water varies from hard to very hard.

The alluvial aquifer in (well no. 4) in Harvey County showed that the water is very hard and total dissolved solids ranges from 157-340 mg/L (Fig. 9). Iron and nitrate concentrations range from 0.01-0.07 mg/L and 5.40-6.77 mg/L (Fig. 7). The water is calcium bicarbonate type (Fig. 13).

Water in glacial drift aquifer (well no.1) in Nemaha County occasionally exceeds secondary drinking water standard for total dissolved solids. Hardness varies from 390-480 mg/L (Fig. 10). Iron and Nitrate concentrations range from 0.01-0.04 mg/L and 1.98-8.10 mg/L (Fig. 5). The water is

Figure-9:   Bar diagram of hardness and total dissolved
            solids   of   water   in   alluvial   aquifer
            (well   no.   4),   and   High   Plains   aquifer
            (Well no. 5) in Harvey County, 1985 - 1989.

Hardness & TDS in Alluvial and High Plains Aquifers, Well #4&5, Harvey Co.
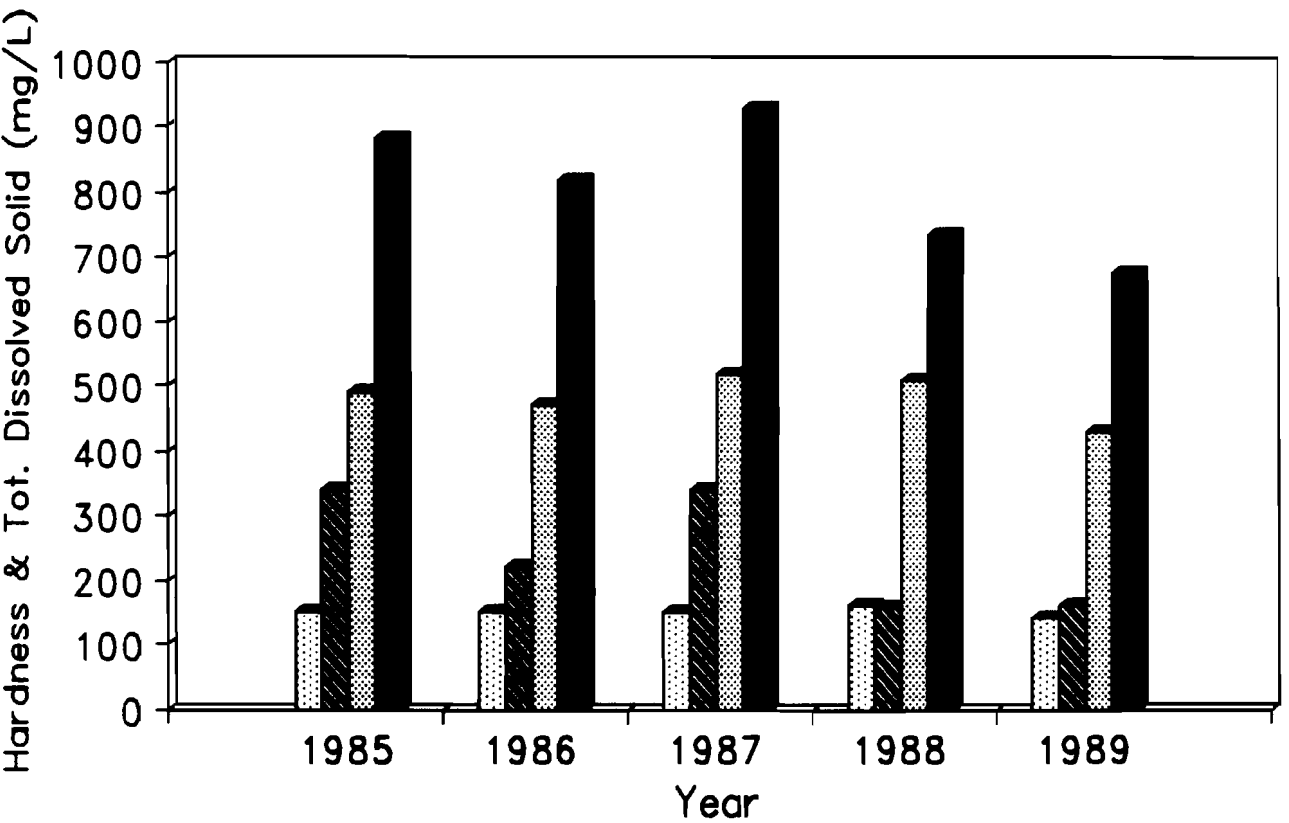
Bar chart showing Hardness & Tot. Dissolved Solid (mg/L) on the y-axis (0 to 1000) versus Year on the x-axis (1985–1989). Legend: Hardness Well #4, TDS Well #4, Hardness Well #5, TDS well #5.

Figure-10:   Bar diagram of hardness and total disolved
             solids of water in glacial drift aquifer
             (well no. 1), Nemaha County, 1985 – 1989.

Hardness and Total Dissolved Solids in Glacial Drift Aquifer, Well#1, Nemaha Co
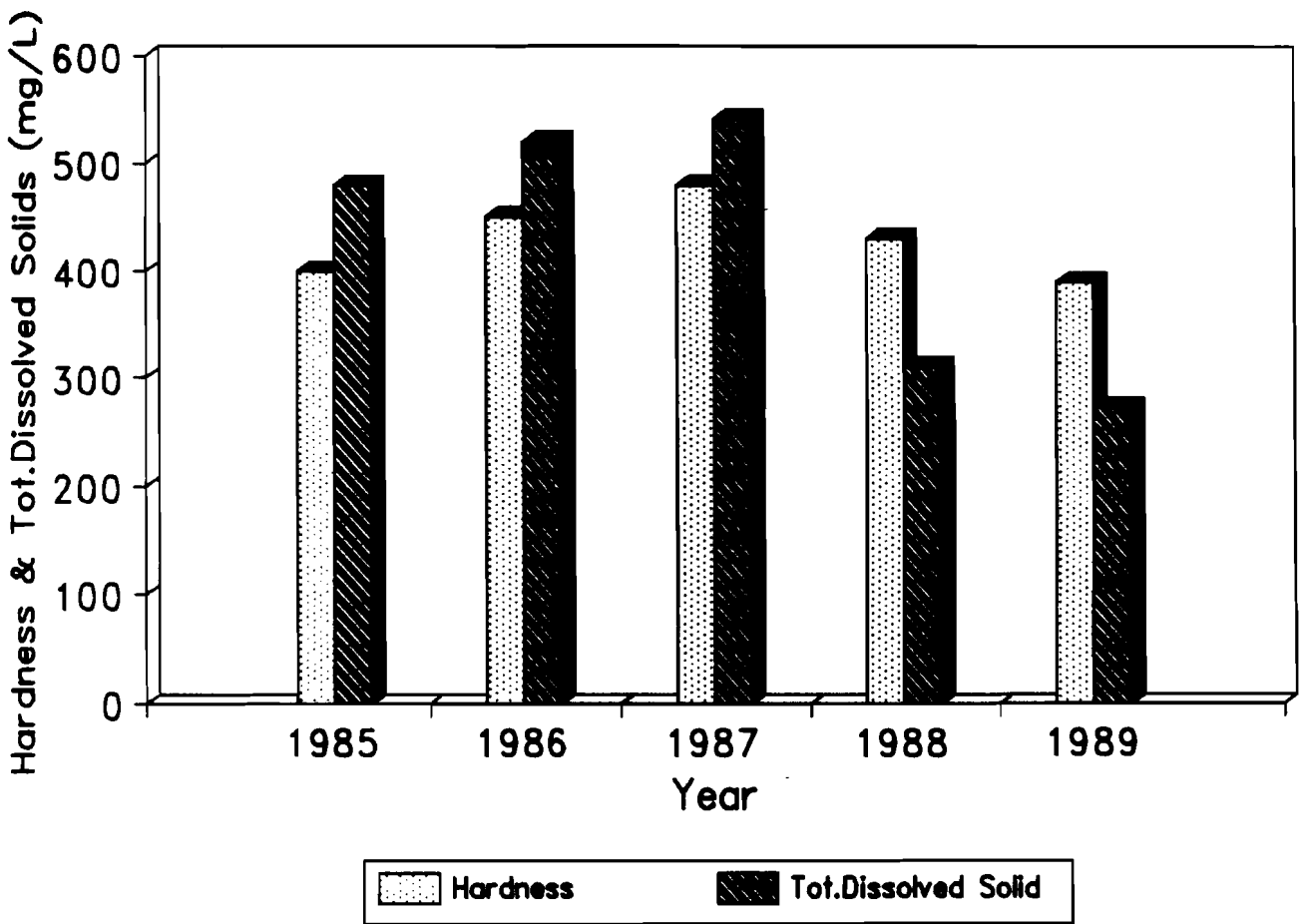
Figure-11: Bar diagram of hardness and total dissolved
            solids of water in Chase and Council Grove
            Group aquifer (well no. 6) and Pleistocene
            (well no. 7), Chase County, 1985 - 1989.

Hardness &TDS in Chase &Council Grove & Pleistocene Aquifer, Well#6&7, Chase Co

35
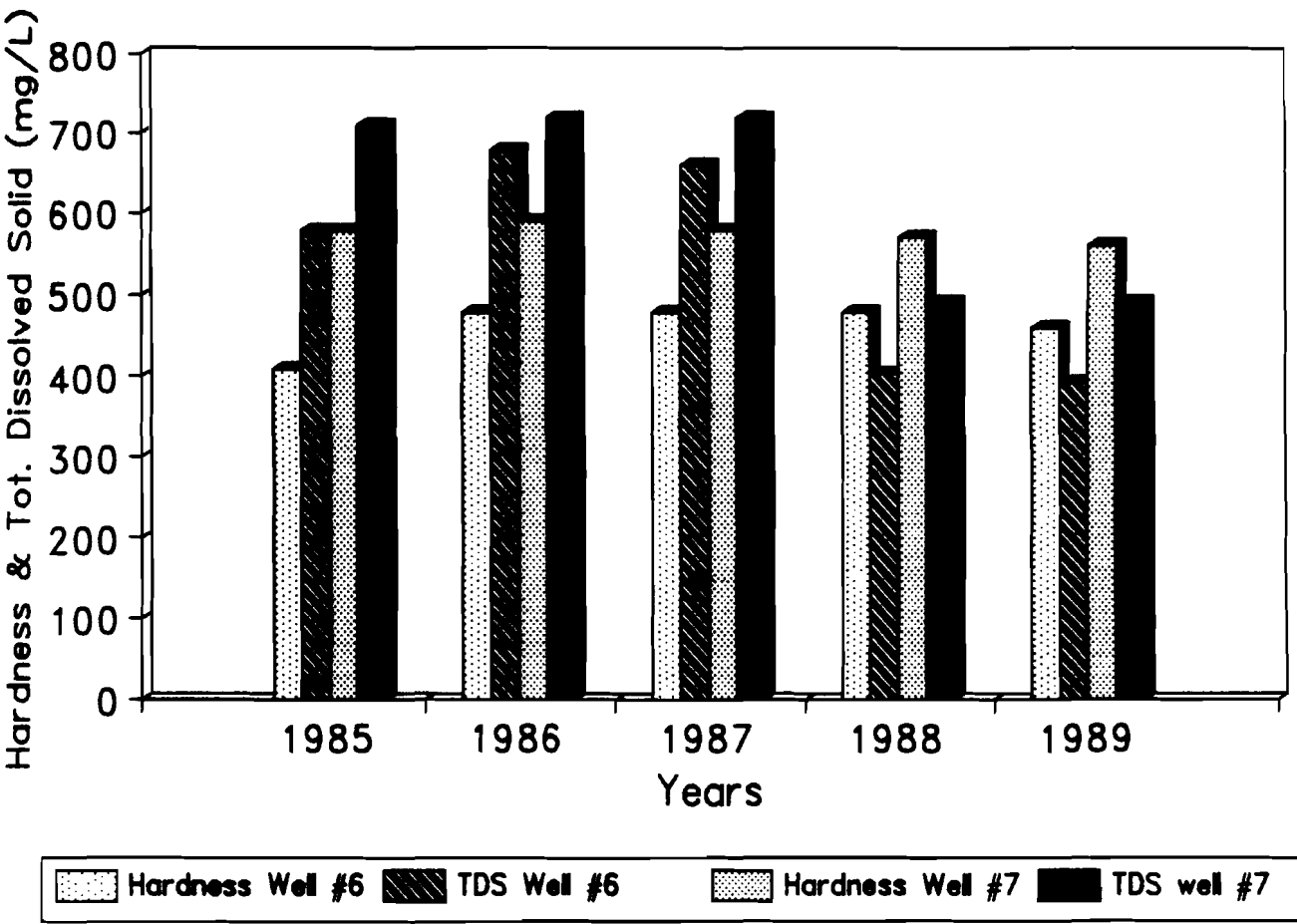
Figure-12: Bar diagram of hardness and total dissolved
            solids of water in Pleistocene aquifer
            (well no. 2 & 3), Nemaha County, 1985-1989.

Hardness & Tot.Dissolved solid in Pleistocene Aquifer, Well # 2&3, Nemaha Co.
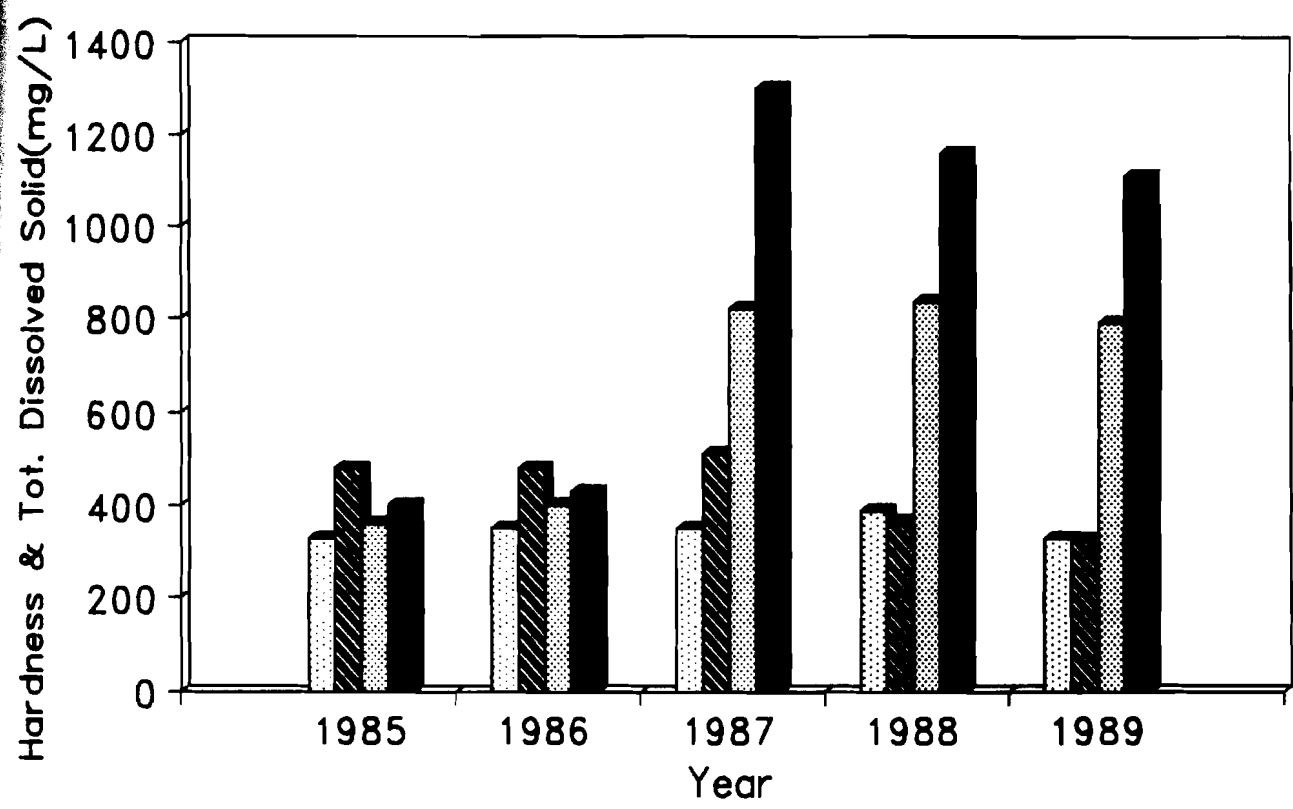
calcium bicarbonate type (Fig. 14).

The High Plains aquifer is the most productive aquifer in Kansas. Water in the aquifer in Harvey County (well no.4) is very hard. Total dissolved solids range from 676 - 930 mg/L (Fig. 9). Nitrate concentration is very low but iron concentration is very high (Fig. 7). The water is calcium bicarbonate and calcium sulfate mixed type (Fig. 15).

Water from Chase and Council Grove Group aquifer is suitable for most uses. Water in well no.6 in Chase county is very hard. Total dissolved solids range from 393 - 680 mg/L (Fig. 11). Iron concentration is generally low and nitrate concentration is below the limit of the primary drinking water standard for nitrate (Fig. 8). The water is calcium bicarbonate type (Fig. 16).

Water in Pleistocene aquifer is very hard. Total dissolved solids are usually below the secondary drinking water standard limit (Figs. 11 & 12). Well no. 3 in 1987, 1988 and 1989 has exceeded secondary drinking water limit for total dissolved solids. All of the wells indicate very low nitrate concentration and high iron concentration (Figs. 6 & 8). The water in well no. 2 is calcium bicarbonate type, well no. 3 is calcium sulfate type and well no. 7 is calcium bicarbonate type (Figs. 17, 18 & 19).

Figure-13:   Stiff diagram showing milliequivalents
              per liter of major cations and anions in
              water of alluvial aquifer (well no. 4),
              Harvey County, 1985 - 1989.

STIFF DIAGRAM
SCALE MEQ. PER LITER
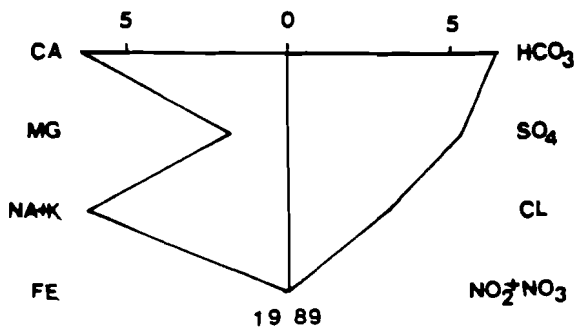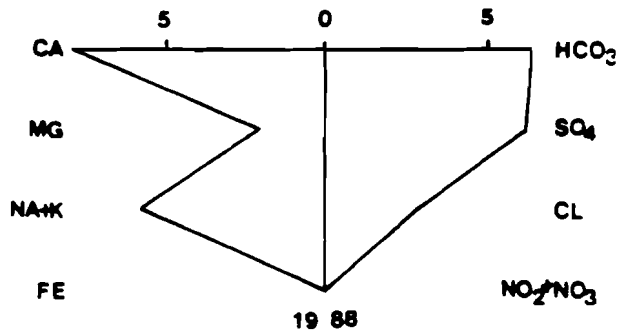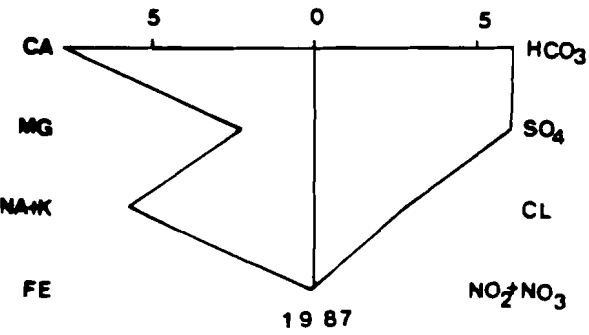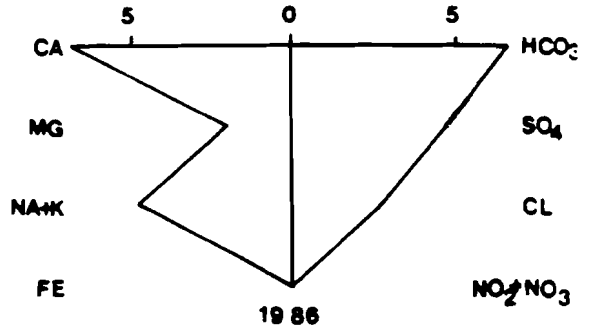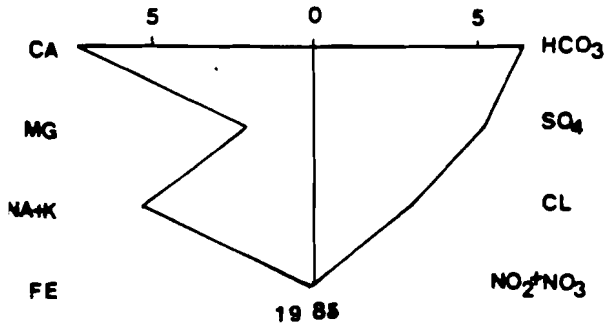
ALLUVIAL AQUIFER, WELL NO. 4
HARVEY COUNTY

Figure-14:   Stiff diagram showing milliequivalents

water   per   liter of major   cations   and

anions of water in glacial drift aquifer

(well no. 1) Nemaha County, 1985 – 1989.

STIFF DIAGRAM
SCALE MEQ. PER LITER
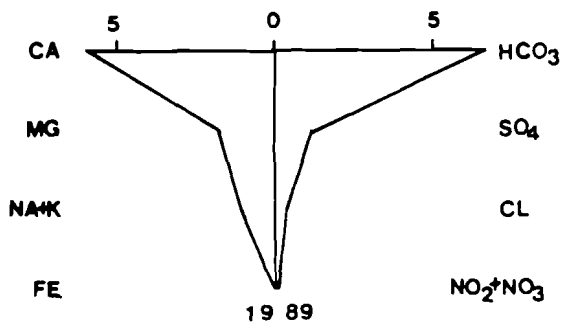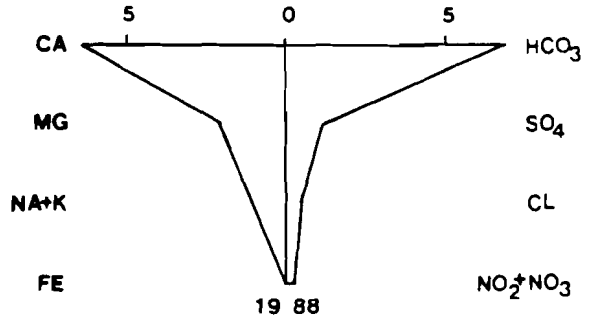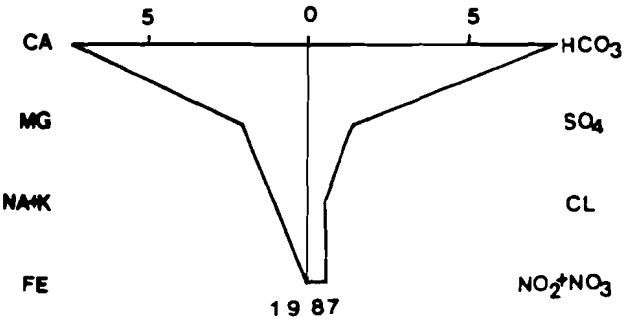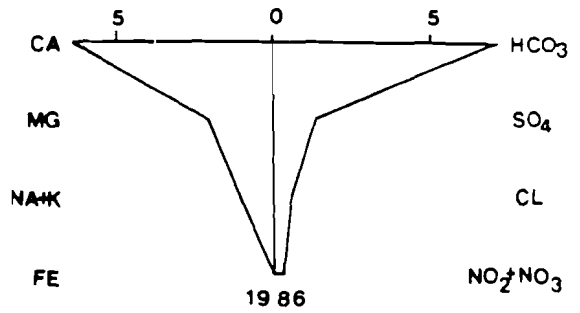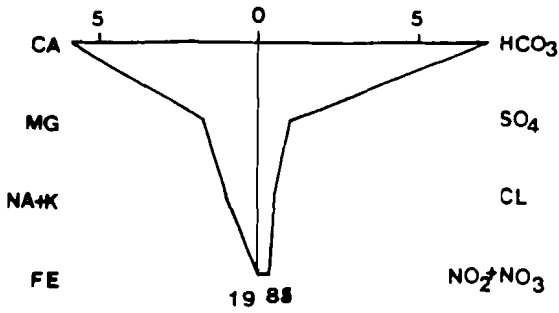
GLACIAL DRIFT AQUIFER, WELL NO. 1
NEMAHA COUNTY

Figure-15:   Stiff diagram showing major cations and
              anions of water in High Plains aquifer
              (well no. 5), Harvey County, 1985 - 1989.

STIFF DIAGRAM
SCALE MEQ. PER LITER

HIGH PLAINS AQUIFER, WELL NO. 5
HARVEY COUNTY

44
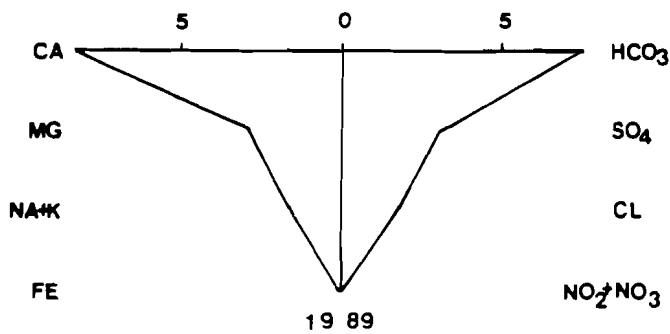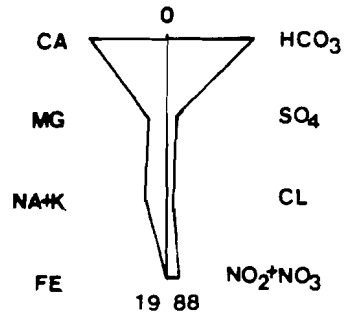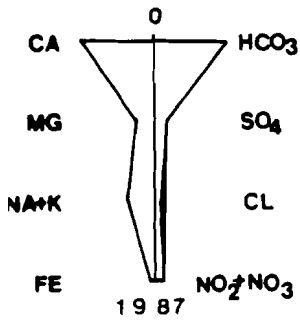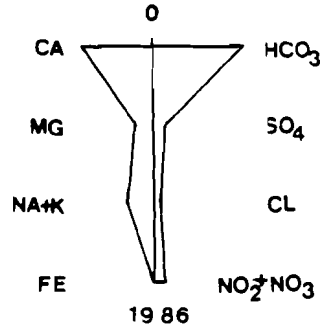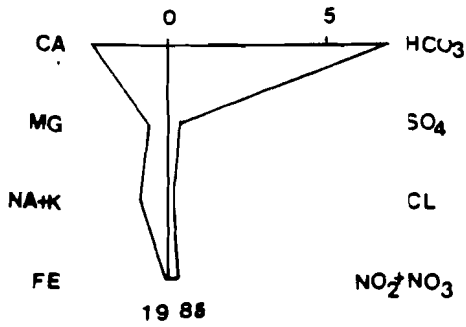
Figure-16:   Stiff diagram showing milliequivalents
              per liter of major cations and anions of
              water in Chase and Council Grove Group
              aquifer (well no. 6), Chase County, 1985
              - 1989.

STIFF DIAGRAM
SCALE MEQ. PER LITER
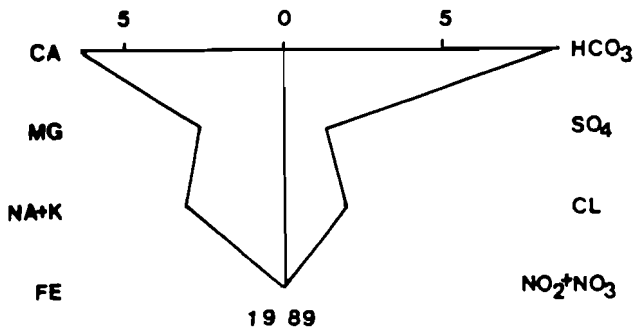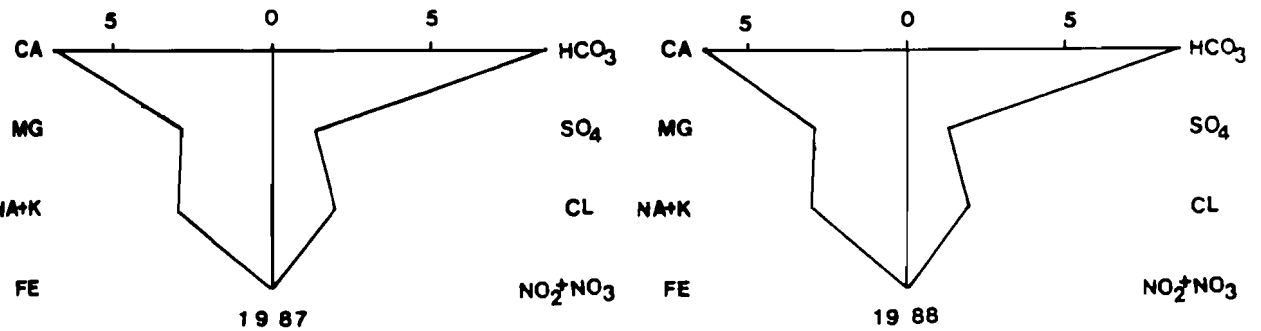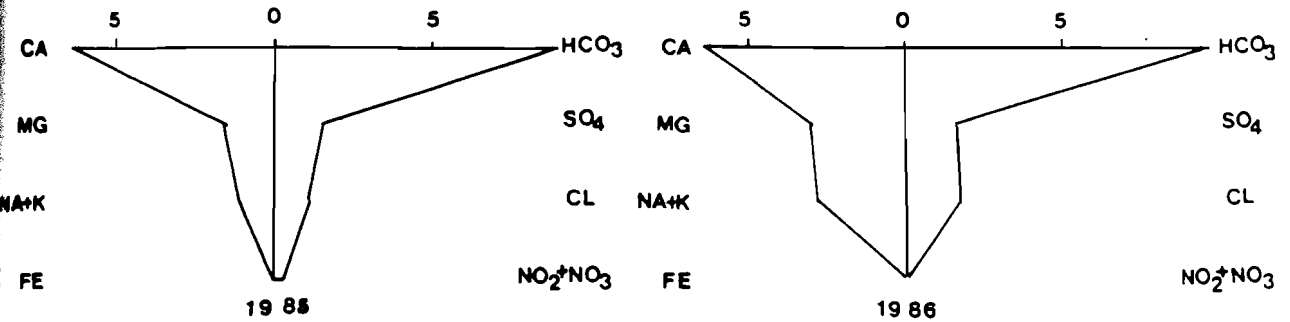
CHASE & COUNCIL GROVE GROUP AQUIFER
WELL NO. 6, CHASE COUNTY

Figure-17:   Stiff diagram showing milliequivalents
              per liter of major cations and anions of
              water in Pleistocene aquifer (well no. 2)
              Nemaha County, 1985 - 1989.

STIFF DIAGRAM
SCALE MEQ. PER LITER
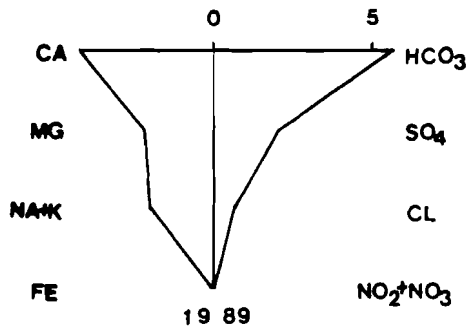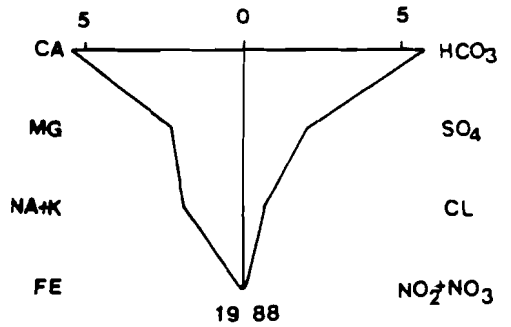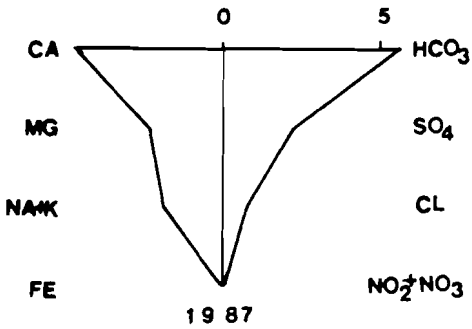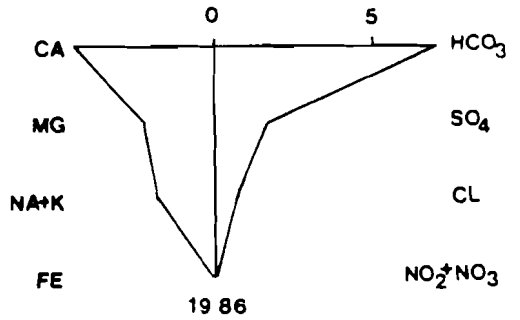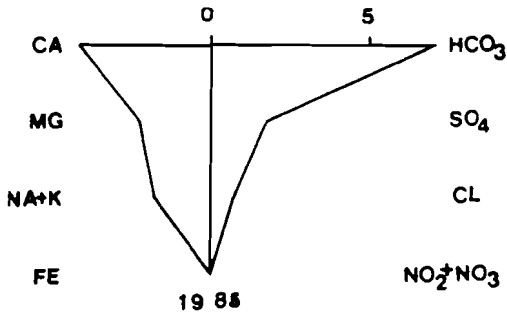
PLEISTOCENE AQUIFER, WELL NO. 2
NEMAHA COUNTY

Figure-18: Stiff diagram showing milliequivalents per
            liter of major cations and anions   of
            water in Pleistocene aquifer (well no. 3),
            Nemaha County, 1985 - 1989.

STIFF DIAGRAM
SCALE MEQ. PER LITER
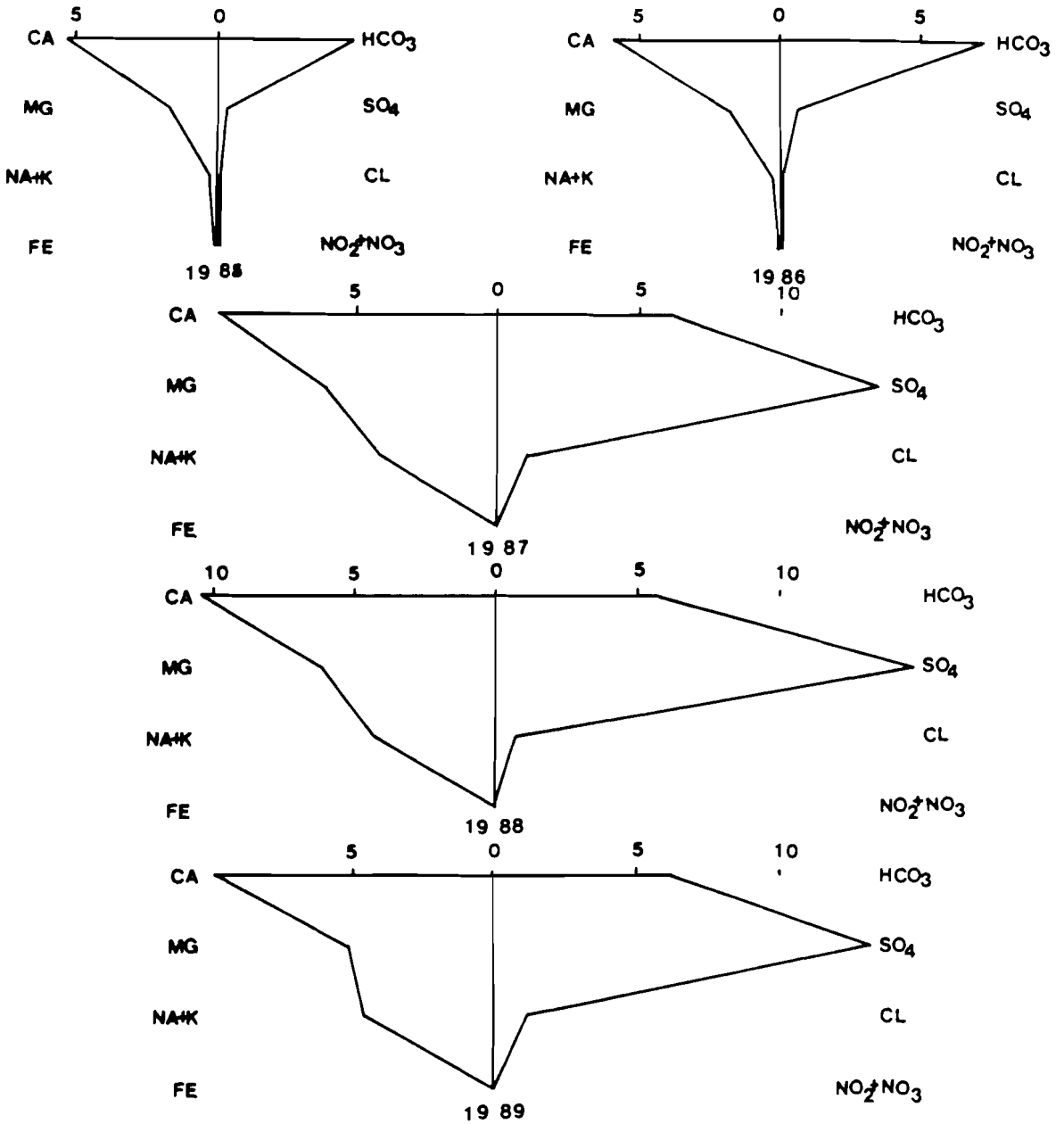
PLEISTOCENE AQUIFER, WELL NO. 3
NEMAHA COUNTY

STIFF DIAGRAM
SCALE MEQ. PER LITER
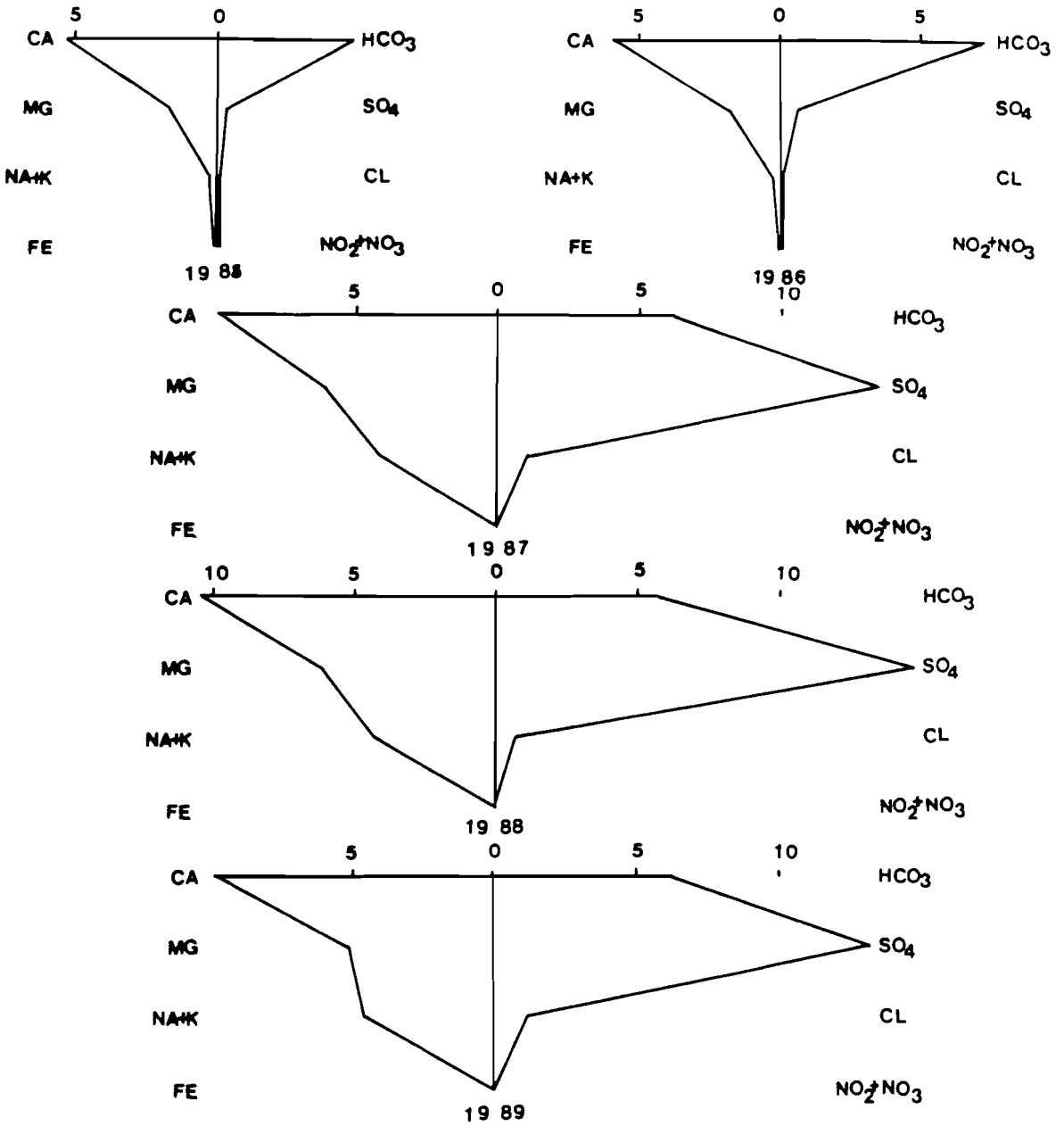
PLEISTOCENE AQUIFER, WELL NO. 3
NEMAHA COUNTY

Figure-19: Stiff diagram showing milliequivalents per liter of major cations and anions of water in Pleistocene aquifer (well no. 7), Chase County, 1985 - 1989.

STIFF DIAGRAM
SCALE MEQ. PER LITER
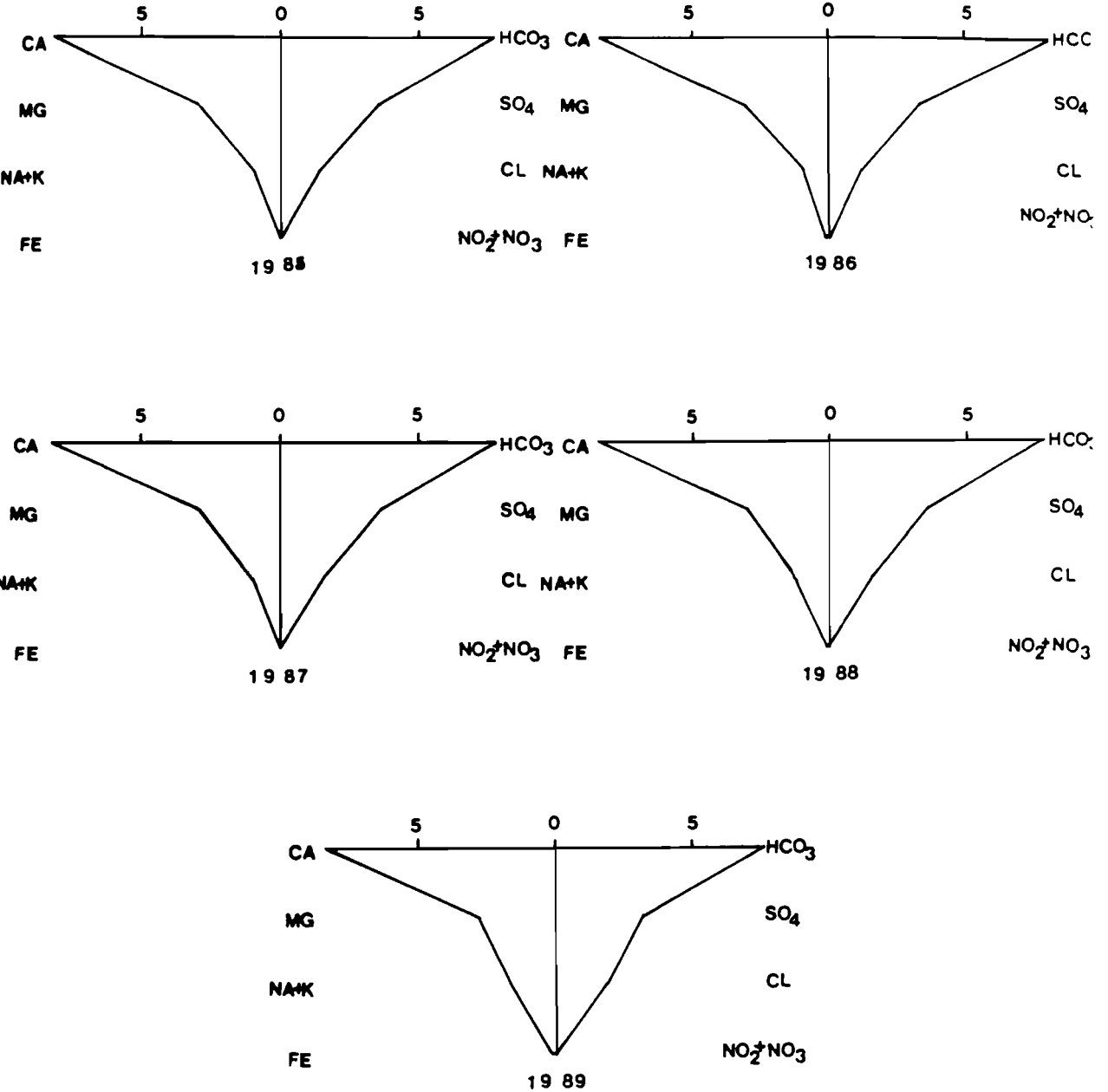
PLEISTOCENE AQUIFER, WELL NO. 7
CHASE COUNTY

EXPERIMENTAL

Nitrate determination was performed by direct UV screening method (Greenberg,1980). This is a simple, rapid and reliable method in the ultraviolet region. Nitrate absorbs UV radiation at 210 - 220 nm and Beer's law is usually obeyed at up to 4 mg/L. Positive interferences are removed by acidification. An empirical correction is made for water containing unsaturated organic compounds by subtraction of twice the absorbance at 275 nm from the primary absorbance at 220 nm. The absorbance at 275 nm is used to determine the presence, or absence of dissolved organic matter that could also show absorbance at the wave length selected for nitrate determination.

Iron concentration was determined by flame atomic absorption method. Iron absorbs at 248.3 nm and Beer's law holds up to 5 mg/L as linearity. The method is simple, rapid and reliable. Chemical interferences can be avoided by maintaining proper flame height and temperature.

Preliminary experiments include two different tests.

1. Flow Test

2. Beaker Test

Between the two experiments, only the beaker test provided positive results. On the basis of the preliminary investigations, the final tests, which are essentially beaker tests with some modified conditions, were completed.

Flow Test Method:

A.   Apparatus

Nitrate solution was passed through a column of reaction tube filled with granular pyrite. Samples were collected at the bottom of the tube. Absorbance of nitrate-nitrogen was measured at 220 nm by GCA / Mcpherson UV Spectrophotometer using a 1 inch path length quartz cell. The absorbance of iron was measured at 248.3 nm by Perkins Elmer 603 Flame Atomic Absorption Spectrophotometer.

B.   Reagents

1.   Pyrite particles, <0.50 - 0.125, <0.35 - 0.125, <0.35 and <0.125 mm sizes were used to fill the reaction column.

2.   Distilled, deionized water, stored in a glass bottle, was used for the preparation of all solutions.

3.   5.0 mg/L nitrate solution and 5.0 mg/L standard nitrate solution were prepared by diluting 25.0 ml of 100 mg/L stock potassium nitrate solution with distilled deionized water in a 500 ml volumetric flask.

4.   A blank solution was prepared by adding 500 uL, 3M hydrochloric acid to 25 ml distilled deionized water.

5.   500 uL and 300 uL, 3 M hydrochloric acid were added to 40 ml and 20 ml samples to keep the sample free from any positive interferences which might cause erroneous higher results in the analysis.

6. 2 ppm, 5 ppm and 10 ppm standards of iron solution were prepared by diluting 500 UL, 500 UL and 1000 UL iron solution from 1000 ppm stock iron solution to 250 ml, 100 ml and 100 ml volumetric flasks.

C.   Procedure

Two flow tests were performed by using different sizes of pyrite grains and 5 mg/L nitrate solution. The bottom 2/3 part of the reaction tube was filled with pyrite grains. The bottom opening of the tube was filled with a small amount of cotton so that it can hold the pyrite grains and filter the nitrate solution passing through the column. The samples were collected at the bottom of the tube using water suction apparatus which accelerated the flow of the solution through the column. The first Flow test was completed in two trials. After the first trial the column was filled with acetone to avoid any kind of contamination. The second trial was completed by flashing the acetone and washing the column with distilled deionized water.

The weight and grain size of pyrite and pH and conductivity of nitrate solution are as follows :

	Nitrate Solution		Pyrite Grains	
Test No	pH	Conductivity (umhos/cm)	Grain Size (mm)	Weight in (gms)
I.	4.95	47	<0.50 to 0.35	35
			<0.125	10
II.	4.60	47	<0.125	26

The same way the second test was completed. During the

test only 3 samples of 25 ml each were collected because of the reduced flow rate of the solution caused by the compaction of finer grains.

The absorbance of nitrate and dissolved organics was measured at 220 nm and 275 nm. The absorbance of nitrate standard solution (5mg/L) sample and blank absorbance were measured before each measurement. The absorbance at 220 nm and 275 nm were set at zero absorbance with the blank. Readings were made directly from the digital display screen. Concentrations were calculated by the following formulas.

Corrected absorbance = A_{220} nm $-(2)(A_{275}$ nm$)$

Unknown Concentration : $C_x = (C_s)(A_c)(x) / (A_c)(s)$

Where, C_s = Concentration of standard

x = Absorbance of unknown sample

s = Absorbance of standard sample.

Absorbance of iron was measured at 248.3 nm. Absorbance of standards and blank samples were measured before and after the measurement of unknown samples. The absorbance of blank was used to correct the absorbance of standards. Before each measurement, absorbance readings were set at zero absorbance after the aspiration. Readings were taken directly from the digital display screen. Concentrations of iron were calculated by the following formula.

C_x (mg/L) = $(A_x)(10$ mg/L$) / A_s$

C_x = Concentration of unknown

A_x = Absorbance of unknown,

A_s = Absorbance of standard

Preliminary Beaker Test:

A. Apparatus

Two beaker tests were conducted with pyrite and one was with siderite. The absorbance of nitrate was measured at 220 nm by using Direct UV screen method. The absorbance of iron was measured at 248.3 nm by using Flame Atomic Absorbance method (Greenberg, 1980).

B. Reagents

1. Pyrite grains of < 0.125 and <0.50 - 0.35mm sizes.

2. Distilled, deionized water, stored in a glass bottle, was used for the preparation of all solutions.

3. 5.0 (mg/L) nitrate solution and 5.0 (mg/L) stand-ard nitrate solution were prepared by diluting 25.0 ml of 100 mg/L potassium nitrate stock solution with distilled deionized water to a 500 ml volumetric flask.

4. A blank solution was prepared by adding 500 uL, 3M hydrochloric acid to a 25 ml distilled deionized water.

5. 300 uL, 3 mole hydrochloric acid was added to each 20 ml sample to remove any kind of positive interferences from the sources of sample itself.

6. 2 ppm, 5 ppm and 10 ppm standard solution of iron were prepared by diluting 500 uL, 500 uL and 1000 uL iron solu-tion from 1000 ppm stock solution of iron to 250 ml, 100 ml and 100 ml volumetric flasks.

C.   Procedure

Three beakers, 150 ml each were filled with 5.0 mg/L nitrate solution. In two beakers pyrite and in one beaker siderite were added and stirred for about two minutes. The beakers were covered by parafilm to prevent loss of solution from the evaporation and stored in dark place at room temperature. The samples were collected at seven days interval for the measurement of pH, conductivity and absorbance. The pH and conductivity of nitrate solution and grain size and weight of pyrite and siderite are as follows :

Test No	NO$_3$ soln.		Mineral	Weight(gms)	Grain size(mm)
	pH	Cond.(umhos/cm)			
I.	4.98	47	pyrite	20.14	<0.50-0.35
II.	5.0	47	pyrite	25.90	<0.125
III.	4.96	47	siderite	14.18	<0.50-< 0.35

Unfiltered 20 ml sample from each solutions were collected and 300 uL, 3M hydrochloric acid was added in each sample before measuring the absorbanc for iron and nitrate. The pH and conductivity were measured without adding hydrochloric acid. The absorbance and concentration for iron and nitrate were measured and calculated according to the standard methods and formulas as mentioned in the flow tests.

<u>Final</u> <u>Beaker</u> <u>Tests:</u>

A.   Apparatus

Two beaker tests were carried out with pyrite. Absorbance of nitrite-nitrogen was measured at 220 nm by using the direct UV screening photospectrometric method and absorbance of iron was measured at 248.3 nm by using standard flame atomic absorbance method (Greenberg, 1980).

B.   Reagents

1.   Pyrite grain of < 0.125 mm size was used.

2.   Distilled, deionized water, stored in a glass bottle, was used for the preparation of all solutions.

3.   5.0 mg/L nitrate solution was prepared by diluting 100 ml solution from 100 mg/L potassium nitrate stock solution with deionized water to a 2000 ml volumetric flask.

4.   Synthetic ground water solution was prepared by diluting 100 ml solution from 100 mg/L potassium nitrate stock solution and 1.683 grams sodium bicarbonate with deionized water to a 2000 ml volumetric flask.

5.   A 100 mg/L potassium nitrate stock solution was prepared by taking 0.7218 grams of potassium nitrate, dried in an oven at $105^{o}C$ for two hours, dissolving it in water and diluting with deionized water to 1000 ml volumetric flask.

6.   A standard nitrate solution (5.0 mg/L) was prepared by diluting 5 ml of 100 mg/L potassium nitrate stock

solution to a 100 ml volumetric flask.

7.   A blank solution was prepared by adding 500 uL, 3 M hydrochloric acid to 25.0 ml deionized water.

8.   2 ppm, 5 ppm and 10 ppm standard solutions of iron were prepared by diluting 500 uL, 500 uL and 1000 L of 1000 ppm stock solution of iron to 250 ml, 100 ml and 100 ml volumetric flasks.

C.   Procedure

Two, 2-liter Erlenmeyer flasks were used, one of which was filled with mineral pyrite and 5.0 mg/L nitrate solution. The other flask contained pyrite mineral and synthetic ground water solution. Each flask was placed on a magnetic bar to stirrer the solution continuously. Each flask was closed by rubber cork to prevent the loss of solution from evaporation. Samples were collected at 3 days interval for analysis. The pH, conductivity of nitrate solution and synthetic ground water solutions and weight and grain size of pyrite mineral are as follows :

| | Nitrate solution | | Pyrite grains | |
Test No	PH	Cond.(umhos/cm)	Weight (gms)	Grain size (mm)
I.	4.96	47	100	< 0.125
II.	8.1	-	25.5	< 0.125

20 ml filtered samples from each solution were collected and 300 uL, 3 M hydrochloric acid was added to each sample before measuring the absorbance for nitrate and iron.

The pH and conductivity of samples were measured without adding hydrochloric acid. The absorbance and concentration of nitrate and iron were measured and calculated in the same way of Flow tests and preliminary beaker tests.

RESULTS

Flow Test No. 1:

The test was performed on 02/01/91 and 02/06/91 with pyrite grains of grain size (0.50 to 0.35 and <0.125 mm) with nitrate solution (5 mg/L). Seven samples (40 ml each) were analyzed for the absorbance of nitrate and iron (Table -1), pH, concentration of nitrate and iron (Table - 2). The data indicated no significant change in pH, conductivity, nitrate and iron concentrations. This further indicated that no reaction took place during the test.

Flow Test No. 2:

The test was performed on 02/07/91 with pyrite (grain size <0.125mm) and with nitrate solution (5 mg/L). Three samples of 25 ml each were analyzed to measure the absorbance of nitrate, iron, (Table -3) and pH, concentration of iron and nitrate (Table -3). The test revealed similar type of results as in test no. 1.

The flow tests were abandoned with the assumption that the residence time of nitrate solution in the reaction column was too short to allow any significant reaction with pyrite minerals.

Table - 1

Absorbance of nitrate-nitrogen and iron

Flow Test No.1:

Sample No.	Abs. of NO$_3$	Abs. of NO$_3$	Abs. of Fe
1st. Trial	at 220 nm	at 275 nm	at 248.3 nm
1.	1.350	0.175	0.086
2.	1.417	0.055	0.005
3.	1.360	0.046	0.003
4.	1.400	0.044	0.003
5.	1.421	0.057	0.000
6.	1.995	0.750	0.001
7.	1.411	0.059	0.002
2nd. Trial			
1.	1.300	0.162	0.013
2.	1.309	0.088	0.003
3.	1.304	0.000	0.000
4.	1.283	0.071	0.002
5.	1.348	0.061	0.002
6.	1.298	0.069	0.003
7.	1.346	0.060	0.002

Abs. of NO$_3$ standard (5 mg/L)		Abs. of Fe standard at 248.3nm		
Abs.220nm	Abs. 275nm	10 ppm	5 ppm	2 ppm
1.125	0.005	0.211	0.121	0.048

Table - 2

pH, conductivity, and concentration of nitrate and iron

Flow Test No. 1:

Sample No.	pH	Cond.(umhos/cm)	Apparent NO$_3$ Conc. (mg/L)	Fe Conc. (mg/L)
1st. trial				
1.	4.7	88	6.00	4.07
2.	5.1	83	6.29	0.24
3.	5.1	71	6.04	0.14
4.	5.2	74	6.22	0.14
5.	5.25	76	6.31	0.00
6.	5.2	72	8.87	0.05
7.	5.2	69	6.27	0.09
2nd. trial				
1.	4.85	76	5.84	0.6
2.	4.85	68	5.88	0.14
3.	4.85	68	5.86	0.00
4.	5.00	66	5.76	0.09
5.	5.15	68	6.05	0.09
6.	5.10	68	5.83	0.14
7.	5.40	65	6.05	0.09

Table - 3

Absorbance of nitrate-nitrogen and iron

Flow Test No. 2 :

Sample No.	Abs. of NO_3 at 220 nm	Abs. of NO_3 at 275nm	Abs. of Fe at 248.3 nm
1.	1.396	0.063	0.000
2.	1.516	0.070	0.042
3.	1.612	0.079	0.071

Abs. of NO_3 standard 5(mg/L)		Abs. of Fe standard at 248.3nm		
Abs. 220nm	Abs. 275nm	10ppm	5 ppm	2 ppm
1.150	0.000	0.211	0.121	0.048

pH, conductivity, and concentration of nitrate and iron

Sample No.	pH	Cond.(umhos/cm)	Apparent NO_3 Conc. (mg/L)	Fe Conc. (mg/L)
1.	4.45	144	6.07	2.37
2.	4.95	132	6.59	2.00
3.	5.40	152	7.01	3.36

65

<u>Preliminary</u> <u>Beaker</u> <u>Test</u> <u>No.</u> <u>1:</u>

The test was conducted from 2/8/91 to 3/26/91. It was performed with pyrite (grain size : <0.50 - 0.125) and with nitrate solution of 5 mg/L. The data show an anomalous result (Table 4 & Fig. 20). On 3/8/91 a little reduction of nitrate occurred but later analysis showed no reduction of nitrate at all. The pH and conductivity gradually increased and reached to 6.4 and 709 (umhos/cm) on 3/26/91.

<u>Preliminary</u> <u>Beaker</u> <u>Test</u> <u>No.</u> <u>2:</u>

The test began on 2/8/91 and was completed on 4/23/91 with a significant change in nitrate reduction (Table 4 & Figs. 21 & 22). The test was carried out with less than 0.125mm size pyrite grains and with nitrate solution of 5 mg/L. pH data showed gradual increase till 4/5/91. On 4/12/91 and 4/23/91, the sample showed a little decrease in pH. On 4/12/91 and 4/23/91, the amount of sample was not adequate enough to measure the pH and conductivity. The final conductivity reached to 1057 umhos/cm. During the last three dates conductivity became very consistent. From 3/26/91 to 4/23/91, no reduction of nitrate occurred and the analysis showed a stable nitrate concentration of 1.07 mg/L.

<u>Preliminary</u> <u>Beaker</u> <u>Test</u> <u>No.</u> <u>3:</u>

The test began on 2/22/91 with the siderite and abandoned on 4/12/91. The analyses (Table 5 & Fig. 22) indicated no nitrate reduction. pH and conductivity values gradually increased. On 3/26/91, the sample showed very little nitrate reduction but later analyses showed no reduction of nitrate.

Table - 4

Absorbance of nitrate-nitrogen and iron

Preliminary Beaker Test No. 1:

Date	Abs. of NO_3 at 220 nm	Abs. of NO_3 at 275 nm	Abs. of Fe at 248.3 nm
2/15/91	1.463	0.053	-
2/22/91	1.415	0.036	0.005
3/8/91	1.229	0.020	-0.005
3/18/91	1.929	0.077	0.057
3/26/91	2.511	0.115	0.023

Preliminary Beaker Test No. 2:

Date	Abs. of NO_3 at 220 nm	Abs. of NO_3 at 275 nm	Abs. of Fe at 248.3 nm
2/15/91	1.962	0.053	-
2/22/91	1.525	0.127	1.101
3/8/91	1.017	0.144	0.885
3/18/91	0.476	0.077	0.039
3/26/91	0.273	0.076	0.023
4/5/91	0.243	0.074	0.023
4/12/91	0.247	0.082	0.023
4/23/91	0.248	0.115	0.011

	Abs. of NO_3 Standard		Abs. of Fe Standard at 248.3 nm		
	Abs. 220nm	Abs. 275nm	10 ppm	5 ppm	2 ppm
2/22/91	1.156	0.002	0.211	0.121	0.048
3/8/91	1.270	0.003	0.211	0.121	0.048
3/18/91	1.177	0.003	0.375	0.211	0.102
3/26/91	1.269	0.002	0.375	0.211	0.102
4/12/91	1.153	0.000	0.375	0.211	0.102
4/23/91	1.128	0.002	0.436	0.240	0.110

Figure-20:   Line diagram of pH, and concentration of
              Nitrate   and   iron in Preliminary beaker
              test no. 1, 46 days.

pH and Concentration of Nitrate & Iron
Preliminary Beaker Test No.1

Figure-21:   Line diagram of pH, and concentration of
            nitrate and iron in preliminary beaker
            test No. 2, 74 days.

pH and Concentration of Nitrate & Iron
Preliminary Beaker Test No.2

Figure-22:   Nitrate reduction diagram showing the pH,
             and concentration of nitrate in prelimi-
             nary beaker test no. 2, 74 days.

Nitrate Reduction
Preliminary Beaker Test No.2

Table - 5

Absorbance of nitrate-nitrogen and iron

<u>Preliminary</u> <u>Beaker</u> <u>Test</u> <u>No.</u> <u>3</u>:

<u>Date</u>	Abs. of NO_3 at <u>220 nm</u>	Abs. of NO_3 at <u>275 nm</u>	Abs. of Fe at <u>248.3 nm</u>
2/22/91	1.215	0.014	0.004
3/8/91	1.288	0.088	-0.016
3/18/91	1.217	0.010	-0.016
3/26/91	1.219	0.014	-
4/12/91	1.223	0.012	0.006

	Abs. of NO_3 standard		Abs. of Fe standard at 248.3 nm		
	<u>Abs.220nm</u>	<u>Abs. 275nm</u>	<u>10 ppm</u>	<u>5 ppm</u>	<u>2 ppm</u>
2/22/91	1.156	0.002	0.211	0.121	0.048
3/8/91	1.270	0.003	0.211	0.121	0.048
3/18/91	1.177	0.003	0.375	0.211	0.102
3/26/91	1.269	0.002	0.375	0.211	0.102
4/12/91	1.223	0.012	0.375	0.211	0.102

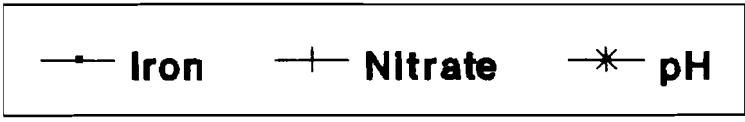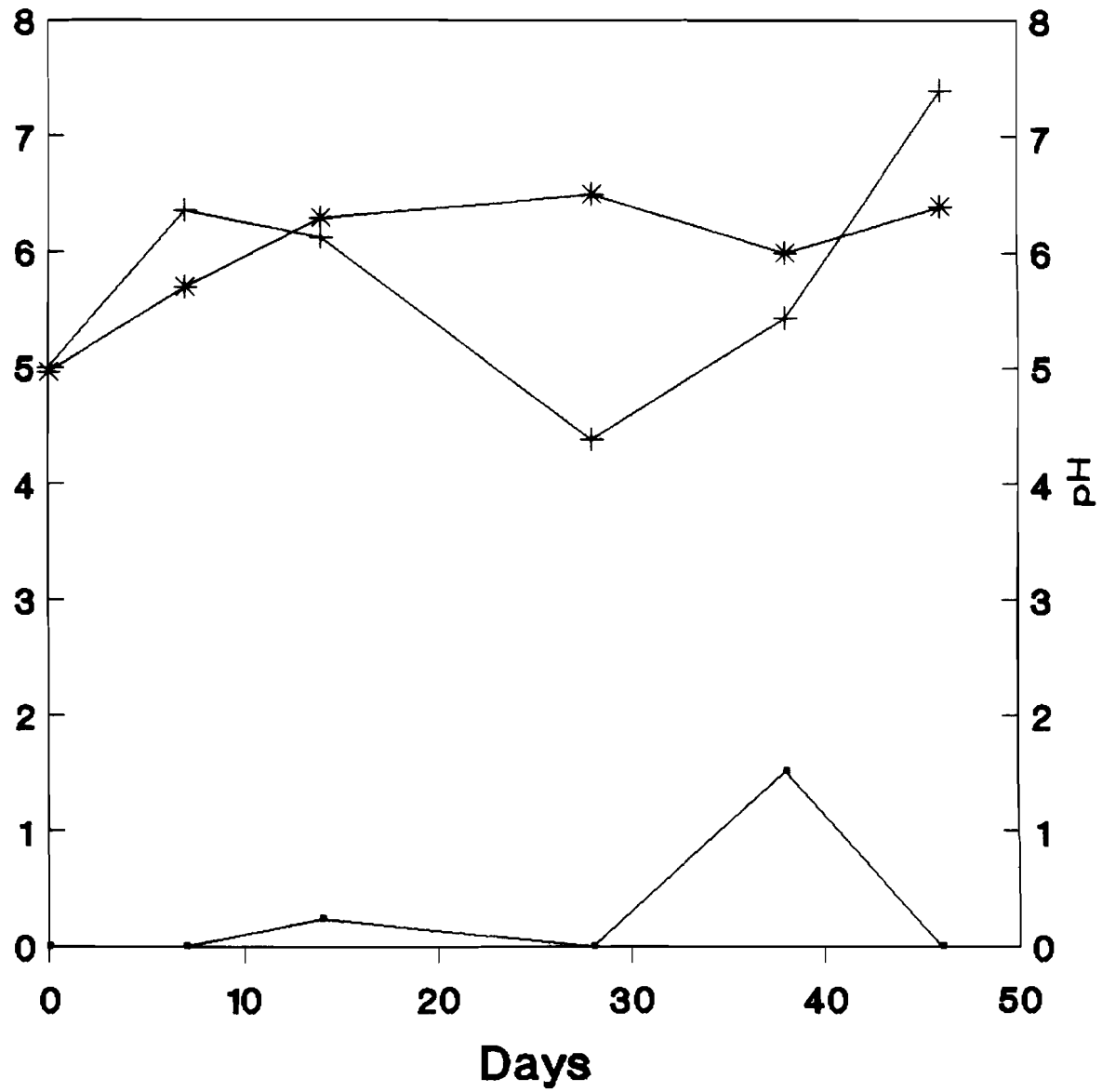Figure-23:   Line diagram of pH, and concentration of
             nitrate and iron in Preliminary beaker
             test No. 3, 56 days.

pH and Concentration of Nitrate & Iron
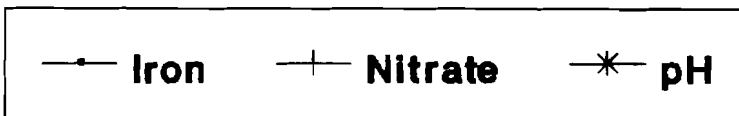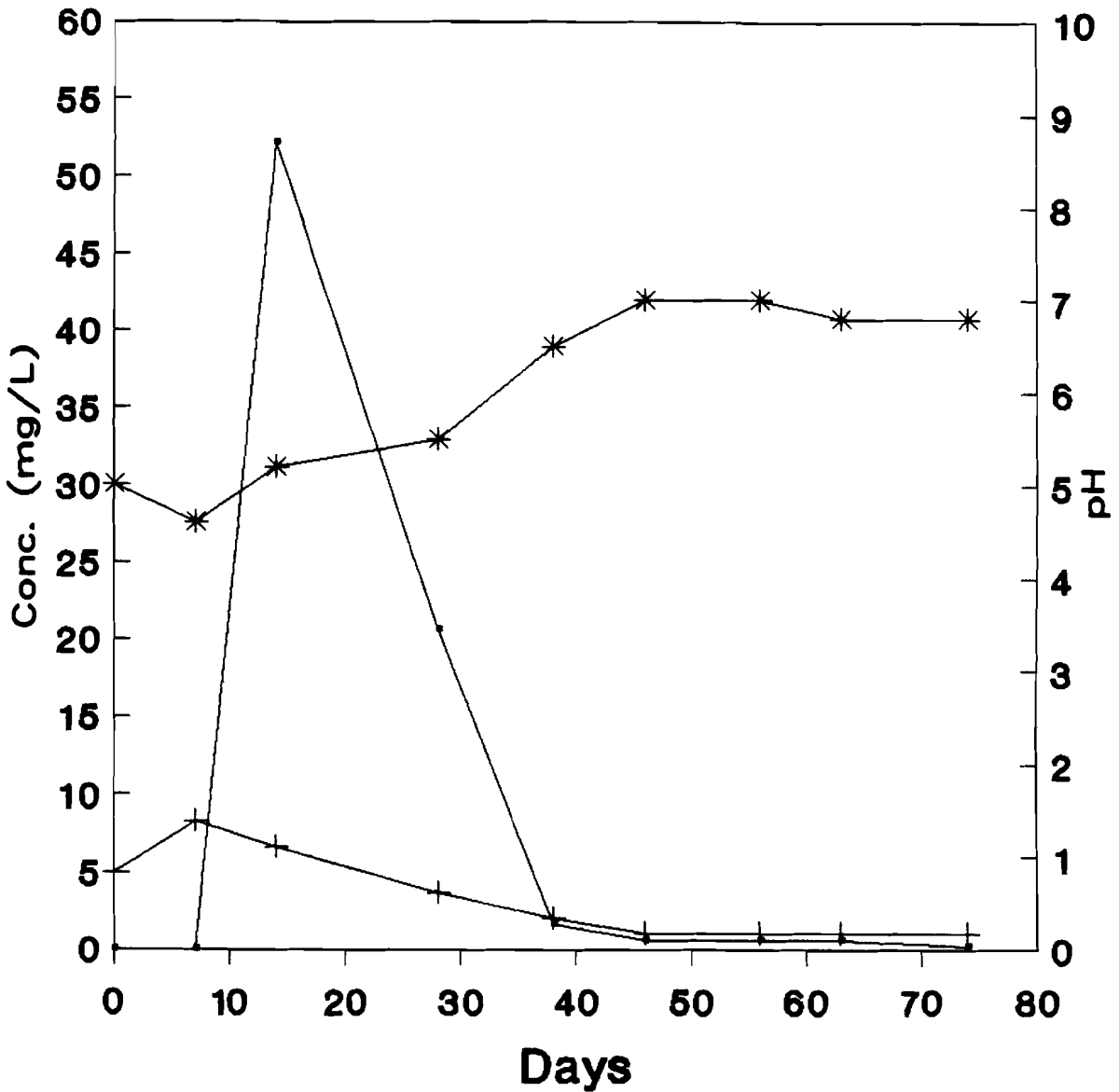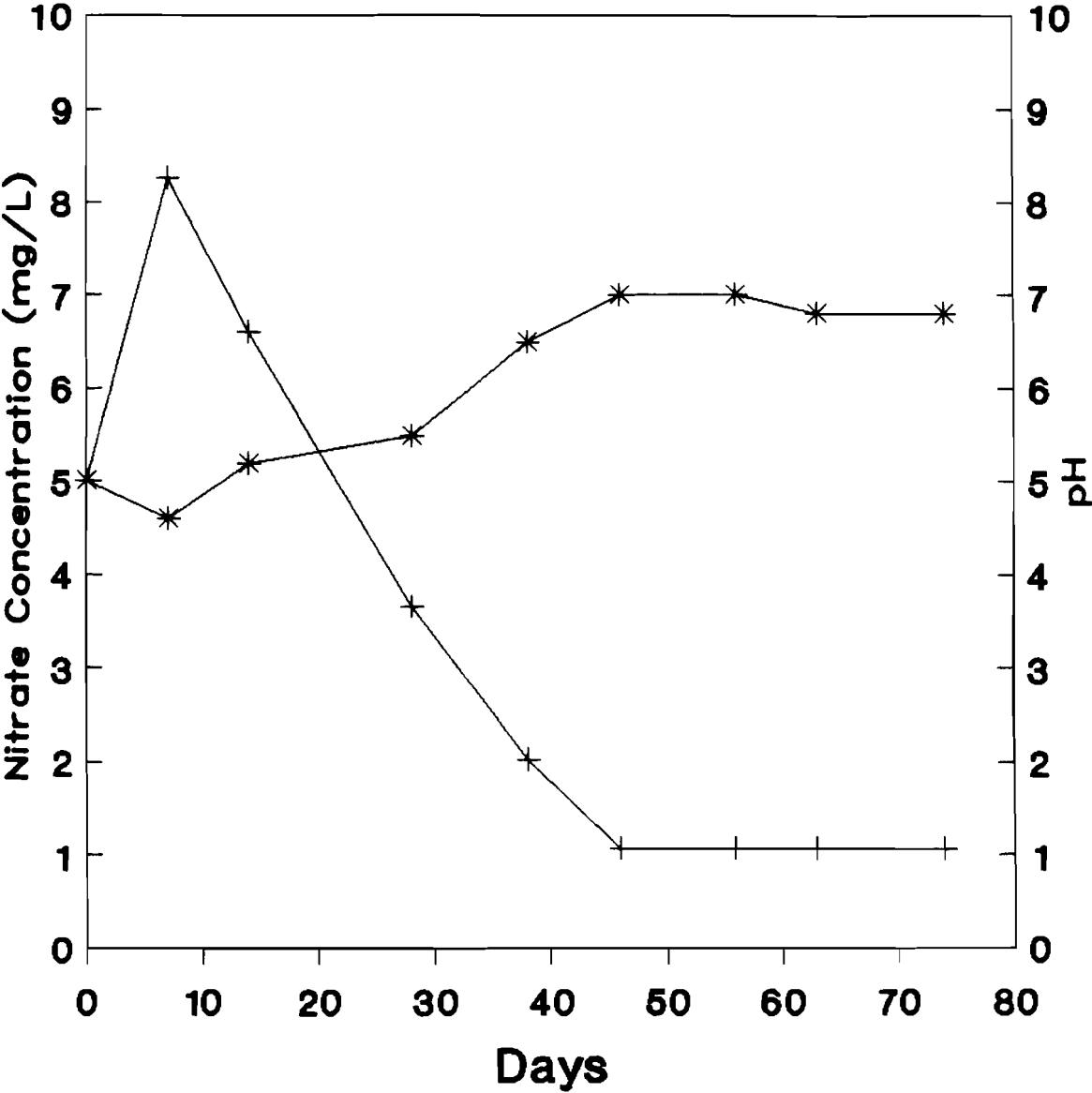## Preliminary Beaker Test No.3
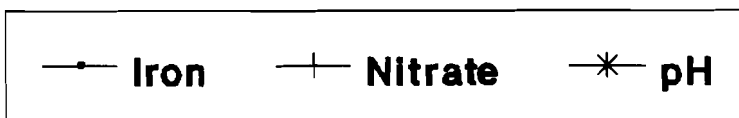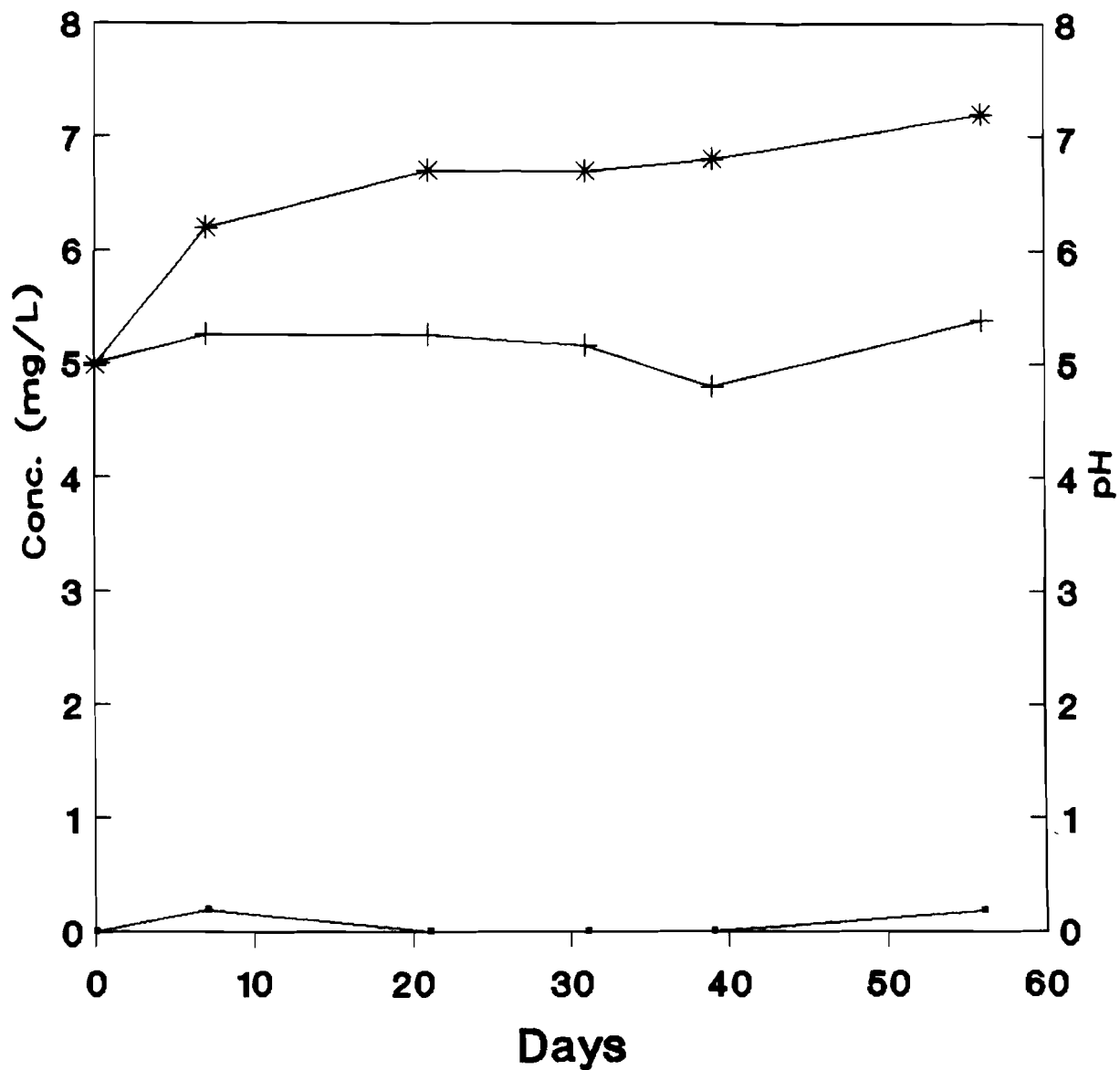
<u>Final</u> <u>Beaker</u> <u>Test</u> <u>No.</u> <u>1</u>:

The test began on 3/26/91 and completed on 5/23/91. It was carried out with pyrite (grain size <0.125 mm) and with 5 mg/L nitrate solution, pH values gradually decreased and became stable at 2.5. The results (Table 6 and Fig. 24) indicated a gradual decrease in apparent nitrate concentration and gradual increase in iron concentration. The HPLC measurements showed no reduction of nitrate in the test (Table. 6 and Fig. 24).

<u>Final</u> <u>Beaker</u> <u>Test</u> <u>No.</u> <u>2</u>:

The test began on 4/2/91 and completed on 5/23/91 with a positive indication of nitrate reduction (Table 7 and Fig. 25). The test was conducted by pyrite (grain size <0.125) and with synthetic ground water solution where nitrate concentration was 5 mg/L. Like test no. 1, this test revealed high absorbance as well as high apparent nitrate concentrations. The test exhibited gradual decrease in iron concentration, pH value initially decreased and later it increased again. The HPLC measurements showed that about 10 percent of nitrate was reduced during the test (Table 7 and Fig. 25). All the experiments revealed high absorbance of nitrate as a result of high apparent nitrate concentration. It was caused by background effects which was confirmed by HPLC measurements. The HPLC method separates nitrate from background before UV analysis. This background usually comes from dissolved organic matter and was not expected in these tests.

Table - 6

Absorbance of nitrate-nitrogen and iron

Final Beaker Test No. 1:

Date	Abs. of NO_3 at 220 nm	Abs. of NO_3 at 275 nm	Abs. of Fe at 248.3 nm
3/29/91	2.305	0.123	0.273
4/2/91	2.767	0.170	0.524
4/5/91	2.809	0.188	0.188
4/9/91	2.954	0.232	0.724
4/12/91	2.762	0.181	0.817
4/16/91	2.666	0.157	0.914
4/19/91	2.532	0.139	0.975
4/23/91	2.362	0.126	1.530
4/26/91	2.208	0.117	1.540
4/30/91	2.050	0.104	1.542
5/3/91	1.962	0.110	1.554
5/6/91	1.768	0.101	1.558
5/9/91	1.764	0.116	1.562
5/12/91	1.642	0.096	1.567
5/15/91	1.792	0.161	1.570
5/19/91	1.685	0.132	1.573
5/23/91	-	-	1.578

Nitrate determination by HPLC method:

Date	Trial No.	NO_3 Sample Peak ht.(cm)	NO_3 Standard Peak ht.(cm)	NO_3 Conc. (mg/L)
5/23/91	1.	12.1	12.15	4.98
	2.	12.15	12.15	5.00

78

Figure-24:   Line diagram of pH, and concentration of nitrate and iron in final beaker test No. 1, 58 days.

pH and Concentration of Nitrate & Iron
Final Beaker Test No.1
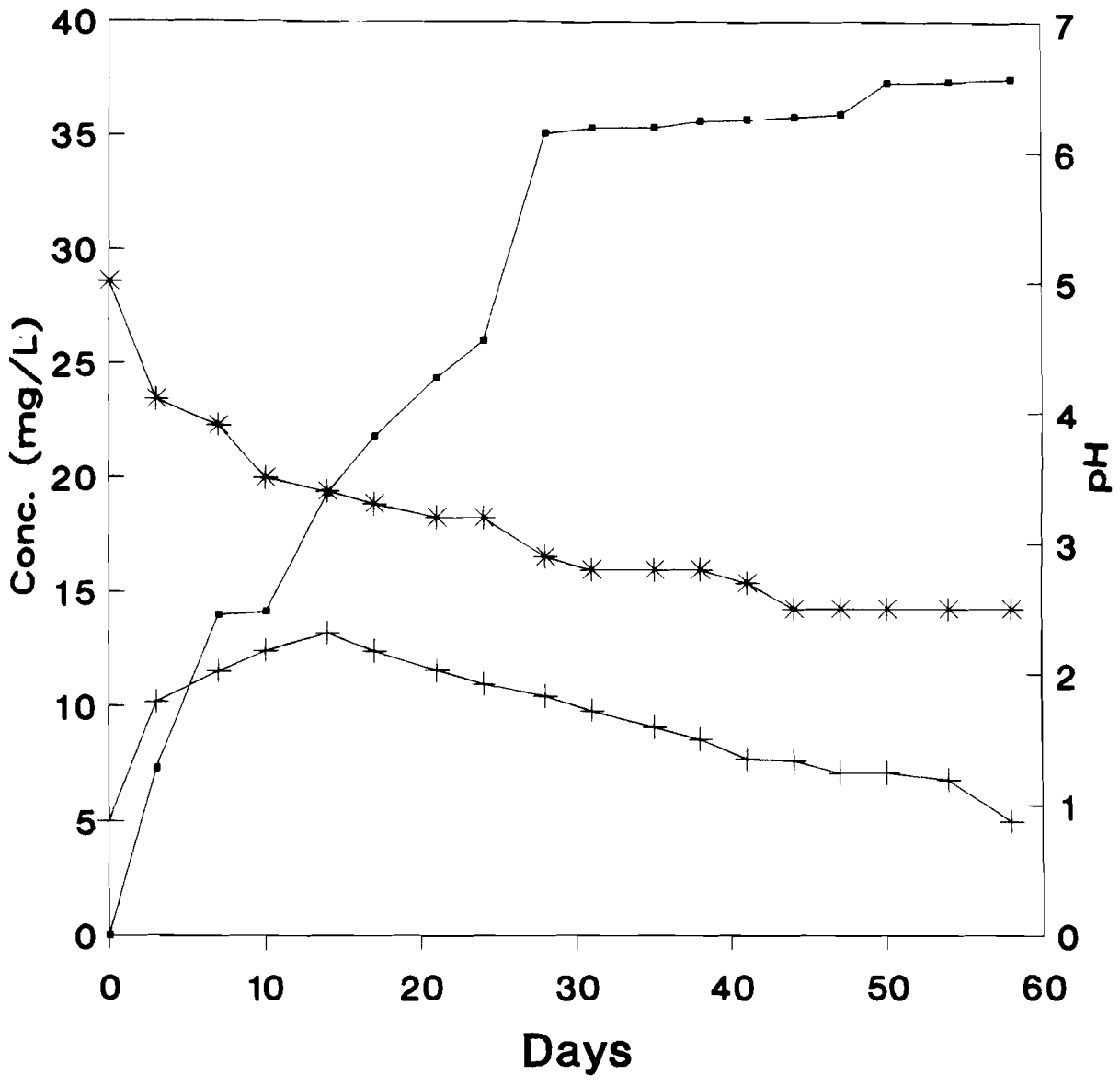
Table - 7

Absorbance of nitrate-nitrogen and iron

Final Beaker Test No. 2:

Date	Abs. of NO_3 at 220 nm	Abs. of NO_3 at 275 nm	Abs. of Fe at 248.3 nm
4/5/91	2.117	0.020	0.003
4/9/91	2.970	0.169	0.660
4/12/91	2.833	0.102	0.042
4/16/91	2.855	0.106	0.014
4/19/91	2.864	0.113	0.004
4/23/91	2.862	0.106	0.006
4/26/91	2.905	0.120	0.006
4/30/91	2.904	0.123	0.003
5/3/91	2.945	0.239	0.004
5/6/91	2.914	0.180	0.017
5/9/91	2.952	0.303	0.021
5/12/91	2.875	0.154	0.024
5/15/91	2.954	0.189	0.027
5/19/91	2.942	0.162	0.031
5/23/91	-	-	0.036

Nitrate determination by HPLC method:

Date	Trial No.	NO_3 Sample Peak ht.(cm)	NO_3 Standard Peak ht.(cm)	NO_3 Conc. (mg/L)
5/23/91	1.	11.00	12.15	4.53
	2.	11.00	12.15	4.53

81

Figure-25:   Line diagram of pH, and concentration of nitrate and iron in final beaker test No. 2, 51 days.

# pH and Concentration of Nitrate & Iron
Final Beaker Test No.2

Measured by HPLC

Legend: Iron, Nitrate, pH
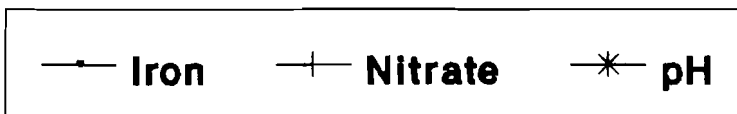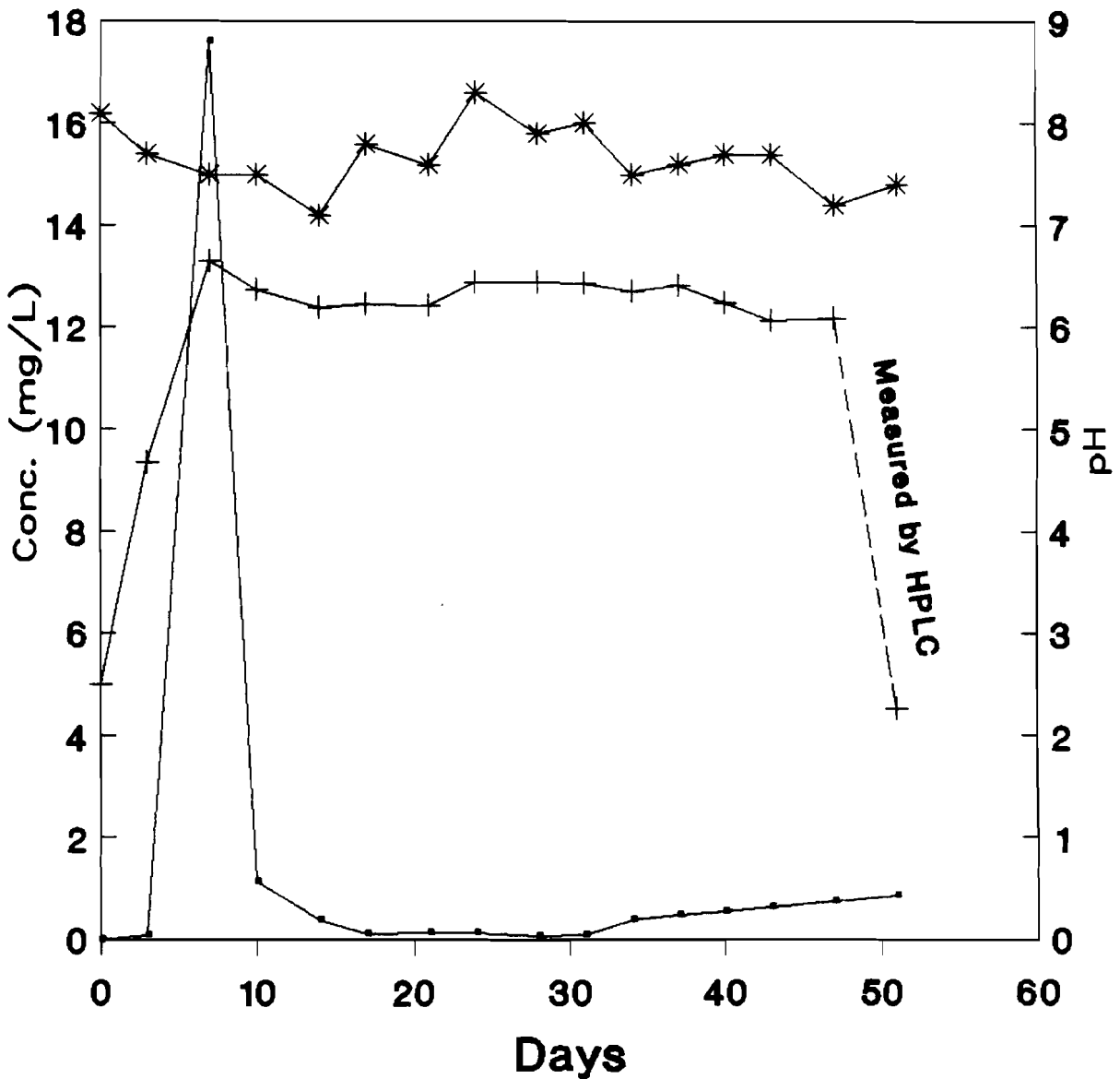
Table - 8

Absorbance of nitrate and iron standards
final beaker tests

Date	Abs. of NO$_3$ Standard		Abs. of Fe Standard at 248.3 nm		
	Abs.220nm	Abs.275nm	10 ppm	5ppm	2ppm
3/29/91	1.132	0.002	0.375	0.211	0.102
4/2/91	1.141	0.002	0.375	0.211	0.102
4/5/91	1.131	-0.007	0.375	0.211	0.102
4/9/91	1.118	-0.001	0.375	0.211	0.102
4/12/91	1.113	0.001	0.375	0.211	0.102
4/16/91	1.153	0.000	0.375	0.211	0.102
4/19/91	1.150	0.000	0.375	0.211	0.102
4/23/91	1.128	0.002	0.436	0.240	0.110
4/26/91	1.126	0.000	0.436	0.240	0.110
4/30/91	1.126	0.000	0.436	0.240	0.110
5/3/91	1.146	0.000	0.436	0.240	0.110
5/6/91	1.146	0.000	0.436	0.240	0.110
5/9/91	1.152	0.001	0.436	0.240	0.110
5/12/91	1.152	0.001	0.436	0.240	0.110
5/15/91	1.140	0.000	0.421	0.235	0.109
5/19/91	1.140	0.000	0.421	0.235	0.109
5/23/91	-	-	0.421	0.235	0.109

DISCUSSION

Nitrate and nitrite are generally reduced by two micro-
bially mediated processes : nitrate reduction and denitrifi-
cation.

Information on inorganic reactions concerning reduction
of nitrate in ground water in Kansas is not available. The
five years data of iron and nitrate concentration in 7
observation wells in Nemaha, Chase and Harvey Counties
clearly indicated some kind of geological factors involved
in the reduction of nitrate in ground water. The variation
of iron concentration indicated possibly iron bearing miner-
als controlling the reactions.

Nitrate reduction by Fe (II) bearing minerals such as
arfvedsonite and augite has been reported by Postma (1990)
who found that both minerals are able to reduce nitrate at
pH range 2 to 7. In Kansas abundant Fe (II) bearing minerals
are pyrite and siderite. In order to examine the reduction
of nitrate by pyrite and siderite minerals both flow test
and beaker tests were conducted. Flow tests 1 and 2 (Table
1, 2 & 3) did not reveal any reduction of nitrate. The
results indicated that no reaction between nitrate and iron
had occurred. It also indicated that the reaction is not a
direct one. On the other hand residence time of nitrate
solution in pyrite column could be an important factor. In
the first flow test, 7 samples (40 ml each) were collected

during three hours whereas in the second test, 3 samples (25 ml each) were collected during 5 hours. In the second test, nitrate solution had more residence time and more surface area (finer fraction) than the first test. Yet the test did not produce any reduction of nitrate.

The preliminary beaker test no. 1 (Fig. 20) also did not show any reduction of nitrate. It is assumed that the surface area was not adequate enough for the reaction between iron and nitrate. The preliminary beaker test no. 2 revealed excellent result of nitrate reduction (Figs. 21 & 22). It is assumed that the surface area and residence time of solution were adequate enough for the reaction to take place; pH values gradually increased and the nitrate concentration gradually decreased and became stable. The iron concentration was initially very high but later with the reduction of nitrate the iron concentration became low. The result clearly indicated that the reaction is not direct, and it took place after a lag period, which indicates that some kind of agent was involved to catalyze the reaction. The reaction is as follows :

$$2Fe^{2+} + 1/2O_2 + 5H_2O \longrightarrow 2Fe(OH)_3 + 4H^+$$

$$5FeS_2 + 4H^+ + 14NO_3^- \longrightarrow 5Fe^{2+} + 10SO_4^{2-} + 7N_2 + 2H_2O$$
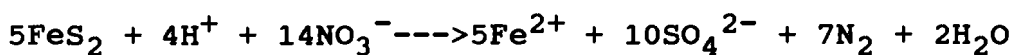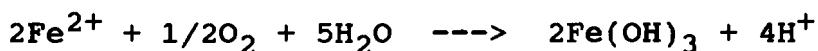
The results of the test indicate that the reaction is possibly catalyzed by either $Fe(OH)_3$ or by bacteria.

The preliminary beaker test no. 3 was carried out with the mineral siderite. The test did not produce any reduction of nitrate (Fig. 23). It is assumed that the mineral was not

pure or the reaction is prevented by the formation of bicarbonate.

The results of final beaker test no. 1 (Table 6 & Fig. 24) show a gradual decrease of apparent nitrate concentration. The pH values gradually decreased and became stable at 2.5. High concentration of nitrate was due to background effects. The HPLC measurement of nitrate revealed that no reduction of nitrate took place. The possible reasons could be that under the condition of this test either no bacteria was developed or stable lower pH had stopped the reaction. The color of the solution remained the same throughout the testing period (dark gray).

The results of final beaker test no. 2 (Table 7, Fig. 25) indicate reduction of nitrate. pH value initially decreased but later increased and always remained above 7.5. Initially, for a few days, the color of the solution turned to greenish gray and later changed to yellowish/reddish brown. The reaction is very slow, and it is possibly catalyzed by either $Fe(OH)_3$ or by bacteria. The reaction is as follows :

$$5FeS_2 + 4H^+ + 14NO_3^- ---> 5Fe^{2+} + 10SO_4^{2-} + 7N_2 + 2H_2O$$

The results obtained from the preliminary beaker test no. 2 and final beaker test no. 2 can be related to the reduction of nitrate in ground water condition in Kansas. Because pyrite occurs in rock of all ages, it can be assumed that the aquifer rock materials also contain pyrite.

Alluvial aquifer, well no. 4 in Harvey county (Fig. 7)

and glacial drift aquifer, well no. 1 in Nemaha county (Fig. 5) show very little reduction of nitrate. These aquifers indicate low rate of nitrate reduction that took place by Fe (II) bearing minerals.

High Plains aquifer, well no. 5 in Harvey County (Fig. 7), Chase and Council Grove Group aquifer, well no. 6 in Chase County (Fig. 8), Pleistocene aquifer, well no.7 in Harvey County (Fig. 8), and well 2 and 3 in Nemaha county (Fig. 6) revealed an excellent reduction of nitrate by Fe (II) bearing minerals. The reduction process in the aquifers very closely corresponds to the results of preliminary beaker test no. 2 and final beaker test no. 2. In the preliminary beaker test no. 2, nitrate reduction took place between 5.5 and 7.0 where as in final beaker test no. 2, nitrate reduction occurred at 7.4. The pH values also closely correspond to the pH values of aquifers (Figs. 3 & 4).

Reduction of nitrate by pyrite must have a great influence on the chemical quality of ground water especially on the concentration of sulfate, nitrate and dissolved iron. Depending on the variation of sulfate, iron and nitrate concentration as well as the nature of reduction of nitrate, the source of Fe (II) bearing minerals could possibly be predicted. Stiff diagrams (Fig. 13 - 19) and NO_2 + NO_3 and iron concentration diagrams (Fig. 5 - 8) clearly indicate that the source of Fe(II) bearing mineral which caused reduction of nitrate in the aquifers is pyrite.

In natural ground water conditions, the reduction of

nitrate by pyrite cannot be fully validated because the tests were carried out using pure minerals. Besides this, several other factors are also involved, such as purity of minerals, grain size and shape, distribution of minerals through out the aquifers, residence time of water in the aquifers, addition of dissolved iron, nitrate and sulfate from precipitation sources and lateral migration of water from adjacent aquifer systems.

However, in order to obtain detailed information regarding reaction between nitrate and pyrite mineral and rate of reduction of nitrate in ground water in Kansas, several experiments could be carried out in the following way :

1. Core samples at different locations of each principal aquifers can be collected. The sample should cover a full thickness of aquifer.

2. The location of the samples should be selected on the basis of available geological (composition of soil and rock, thickness and aquifer boundary conditions), hydrological (confined or unconfined aquifer, down gradient water movement rate), climatological (type and rate of precipitation) and water quality (chemical analysis and depth of sampling).

3. The samples can be ground (consolidated), washed with deionized water to make the sample free from clay and dried in oven for grain-size analysis.

4. The samples can be separated at 0.42 - 0.25 mm, 0.210 - 0.125 mm, 0.105 - 0.0625 mm and <0.0625 mm sizes.

5. Pyrite and other heavy minerals can be separated by treating with bromoform (Sp.gr. 2.8). The heavier fractions can be washed and dried up in oven. The heavy minerals other than pyrite can be separated by other available methods.

6. Synthetic ground water solutions having nitrate concentration of 5.0, 10.0, 15.0, 20.0 and 25.0 mg/L can be prepared by adding deionized water and all other major cations and anions according to the overall ground water quality of aquifers. The pH values should be 8.0, 7.5, 7.0, 6.5 and 6.0 respectively.

7. Four beaker tests (like final beaker tests) for each solution should be conducted with each grain size of pyrite minerals. The circulation of water should be as minimum as possible because ground water movement in an undisturbed aquifer is very slow and it varies from aquifer to aquifer.

8. For 0.42 - 0.25 mm and 0.210 - 0.125 mm grain size, samples should be analyzed at seven days interval where as for 0.105 - 0.0625 mm and < 0.0625 mm grain size, sample should be analyzed at 3 days interval.

9. Nitrate measurements should be performed by HPLC method because it removes background effects.

10. The sample should be analyzed for the presence and type of bacteria.

CONCLUSIONS

The tests' results using pyrite and siderite with nitrate solutions revealed that pyrite (if finely ground) is able to reduce nitrate in water over a period of several weeks. Tests using siderite produced negative results.

The reaction between nitrate and pyrite is complex, and occurs after a lag period. The reaction is possibly catalyzed either by freshly precipitated $Fe(OH)_3$ or by bacteria.

The iron and nitrate relationship within alluvial aquifer in Harvey County, glacial drift aquifer in Nemaha County, High Plains aquifer in Harvey County, Chase and Council Grove Group aquifer in Chase County and Pleistocene aquifer in Nemaha and Chase Counties closely corresponds to the reduction of nitrate obtained by the beaker tests. All these indicate that, other than microbial processes, the reduction of nitrate in ground water in Kansas is also controlled by pyrite. Besides pyrite, siderite and other Fe(II) bearing minerals may also capable for the reduction of nitrate, but this was not verified in these experiments.

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