

DETERMINING THE SOURCE OF SALINE SODIC SOILS  
IN NORTH CENTRAL OKLAHOMA

By

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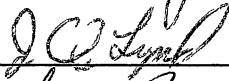
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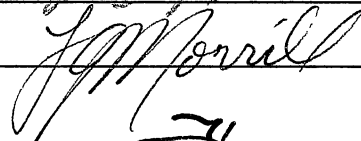
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## INTRODUCTION

This thesis is a manuscript to be submitted for publication in Ground Water Journal.



DETERMINING THE SOURCE OF SALINE SODIC SOILS IN  
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ABSTRACT

Saline sodic soils of north central Oklahoma are a major problem for crop production. Saline sodic soils result in acres of unproductive land in the area. Saline sodic soils are caused by high concentrations of sodium (Na) and chloride (Cl) in the soils.

Saline - sodic soils in the study area are the result of halite crystallization from evaporation of shallow ground water on the surface of the soils. The cause of saturation of ground water with halite is due to dissolution of halite by ground water, which is brought to the surface by evaporation. Evapotranspiration acts as the driving force in bringing the ground water to the surface and increasing sodium and chloride concentrations. The source of ground water saturated with halite was studied to determine whether the ground water and soils were high in salinity by natural phenomena or by oil activity in the study area. The two possible sources of salinity in the study area are; 1. shallow halite beds occurring as lenses in the subsurface due to stratigraphic facies change or 2. disposal of oil brines on the soil surface which will infiltrate through the unsaturated zone and eventually contaminate the ground water.

On extensive monitoring of the ground water for a period of one year, and chemical analysis of ground water with comparison to oil brine chemical data from the study area, the source of salinity was identified. Chloride anions being very conservative constituents of natural waters make an ideal base for assumptions to be made. Chloride anions are not adsorbed by clays or degraded during infiltration of surface water through the soil column, when contaminants in the surface water slowly infiltrates the soil through pore spaces in the soil matrix. As water moves downward under the influence of gravity, it dissolves any soluble salts with which it comes into contact. In this study, deep oil brine spilled on the soil surface could infiltrate to the ground water aquifer through the vadose zone. Deep oil brines can also migrate directly into ground water from subsurface sources such as; broken pipes, leaking oil well casings or storage tanks which lie within the saturated zone. The other possible contamination of ground water with high concentrations of sodium and chloride can occur through inter aquifer exchange in which one water bearing unit "communicates" hydraulically with another. In this study this possibility was ruled out due to the very large distances between the shallow ground water aquifer which is only 2.1 meters from the surface, and the deep oil brine

aquifers which ranged in depths greater than 304.8 meters (Fig.1).

On comparing the chemistry of the ground water being monitored and the oil brines, by trilinear plotting and studying the cation anion ratios of Na/Cl vs Cl and Mg vs Cl, it was determined that the chemistry of the ground water and the deep oil brine were of two different entities. It was also determined that the deep oil brines were not mixing with the ground water in this study area. On studying the fluctuation of chloride concentrations with time, the source of halite dissolution appeared to be highly localized as a point source from relatively shallow depths due to the abrupt changes in chloride concentrations. Within the Permian basin of New Mexico, Texas, Oklahoma and Kansas, natural salt springs and salt seeps discharge more than 2268 tones of sodium chloride per day into major streams and their distributaries (9).

In Grant county, north central Oklahoma, a different form of salinity is evident, it is indicated by the presence of efflorescence on the soil surface. Efflorescence is the visual evidence of high concentrations of sodium chloride occurring in the soils of the study area.

In recent times a controversy has developed to the origin of saline sodic - soils, it has been debated by many scientists that the source of salinity is naturally

occurring from the dissolution of halite beds present in the strata which are brought to the surface by the presence of high water tables. It is also argued that these areas are contaminated by deep oil brines which may have been illegally dumped in the area or are being pumped into the soils from leaking oil well casings and, hence, are the sources of salinity.

The purpose of this study was to determine the cause and source of salinity in the study area. The geochemistry of ground water and the deep oil brines was studied with regard to selected cation anion ratios. From this study it was possible to determine the source of salinity. The presence of natural salinity in north central Oklahoma (Fig.1) made this study especially difficult to determine deep oil brine contamination of ground water. This study also indicates qualitatively the extent of the source area.

## MATERIALS AND METHODS

### Site Investigation

The study area was selected by the very prominent appearance of efflorescence on the soil surface. Once the site was selected, the area was outlined and flagged. Soil samples were obtained from site investigation at various locations and the soils were characterized as follows:

#### Renfrow Series (10)

The soils on site were formed from well weathered shale which was the parent material of Permian red beds.

Slopes are 2 to 5 percent. Soils of the Renfrow series are fine, mixed, thermic Udertic Paleustolls.

Ap - 0 to 9 inches; brown (7.5 YR 4/2) silt loam, dark brown (7.5 YR 3/2) moist; weak fine granular structure; hard, friable; slightly acid; gradual smooth boundary.

B1 - 9 to 12 inches; brown (7.5YR 4/3) silty clay loam, dark brown (7.5YR 3/3) moist; moderate medium blocky structure; hard firm; neutral; clear smooth boundary.

B21t - 12 to 28 inches; reddish brown (2.5YR 4/4) clay, dark reddish brown (2.5YR 3/4) moist; moderate medium and coarse subangular blocky structure; extremely hard, very firm;

continuous clay films on faces of peds; mildly alkaline; gradual smooth boundary.

B22t - 28 to 45 inches; reddish brown (2.5YR 5/4) clay, reddish brown (2.5YR 4/4) moist; moderate coarse subangular blocky structure; extremely hard, very firm; continuous clay films on faces of peds; common fine calcium carbonate concretions and few soft bodies as much as 1/2 inches in diameter, calcareous moderately alkaline; gradual smooth boundary.

Cr - 68 to 78 inches; red (2.5YR 5/6) weathered shale, red (2.5YR 4/6) moist; fine, medium, and coarse light greenish gray (5G 7/1) spots and layers that make up about 30 percent; calcareous, moderately alkaline.

The preliminary investigations indicated a shallow water table. The area was marked and flagged to position the water wells that were to be installed for ground water monitoring and twelve wells were installed in two rows in a east west direction (Figure 2).

#### Installation of Monitoring Wells

Drilling for installation of the monitoring wells depended on hydrologic information, type of formation being

encountered while drilling, depth of drilling, drilling site accessibility, design of monitoring well desired, and availability of drilling equipment (1).

The hydrologic information required for this study was the depth of the unconfined water table aquifer, which was 2.1 m from the surface. This was a shallow aquifer where the red permian beds composed of sandstone and shale made up the aquifer matrix. The study area was located in a wheat field. Accessibility was not a significant problem except during and after periods of heavy rain when the soils were saturated and vehicle passage to the site was hindered.

A truck equipped with a hydraulic probe and a solid stem auger was used to drill the wells. 6.0 cm drill bits were used to obtain the diameter of 4.0 cm. The wells were bored to a depth of 2.2 meters. The well casing was then placed in the bore hole and packed with coarse sand to a height of 30.25 cm., and the polyvinyl chloride well casings were placed in the bore hole and filled back with the original soil material removed during drilling. This procedure was repeated for the all remaining wells.

#### Choosing The Type Of Well Casing

The type of well casing chosen for this study was based mainly on hydrogeologic criteria. In choosing the material of well casing for ground water monitoring, the subsurface

geochemistry and the contaminants present in the study area must be considered. Strength, durability and inertness of well casing should be balanced with cost considerations for the choice of rigid materials. In this study PVC casings were used because no organic chemical constituents were anticipated. PVC casings may cause sorption under conditions where organic contaminants are present in high concentrations.

#### Ground Water Monitoring

Water was sampled from the installed ground water monitoring wells upon installation and at the end of each month thereafter, weather permitting. This schedule permitted monitoring to study fluctuations in ground water quality with changes in water table levels with evapotranspiration.

#### Ground Water Sampling

Precleaned and labeled water sample bottles (teflon) were taken to the field for sampled water containment. Before sampling the wells, water levels in the wells were measured using a chalk marked metal tape. Once the level of water in the well was recorded, the well was purged to remove or isolate stagnant water which would otherwise bias samples collected from the aquifer. This procedure was



repeated for all the wells. After purging, the wells were allowed to recharge for two hours before sampling. The Ground water was sampled from the wells using a peristaltic pump and a sample collection flask.

Between each sampling the sample collection bottle and tubing were rinsed with deionized water to avoid cross contamination between ground water samples. The ground water samples were placed in a teflon bottle and sealed. The water samples were then brought to the laboratory for chemical analyses.

#### Chemical Analysis

Upon arrival, water samples were immediately analyzed for electrical conductivity (EC), pH, Bicarbonate ( $\text{HCO}_3^-$ ) and Carbonate ( $\text{CO}_3^{2-}$ ). Electrical Conductivity was measured using a conductance bridge meter WSI model 31 and pH was measured using a pH meter by placing the water samples in a vial.  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  were titrated using 0.003 Molar  $\text{H}_2\text{SO}_4$  with phenothylene indicator.

The water samples were then filtered with a 100 ml syringe using a 100 micron membrane which was fitted on to the syringe. 100 ml of filtered water samples were adequate for all chemical analysis. The filtered samples were then diluted in appropriate ratios due to very high concentrations of sodium and chloride present in the samples

(see table 1). The water samples were analyzed for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ . The cations were analyzed using a Perkins Elmer 330B Atomic absorption spectrophotometer and anions were determined using a Dionex 2000I Ion chromatograph with a 4270 AG4A integrator.

#### Trilinear Plotting to Interpret Chemical Origin of Ground-Water

The diagram in Figure 4 describes three distinct areas for plotting two triangular areas at the lower left and lower right, respectively, with percentage scales reading in 50 parts; also an intervening diamond-shaped field with scales reading in 100 parts. In the triangular area at the lower left, the percentage reacting values of the three cation-groups ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ) are plotted as a single point according to conventional trilinear coordinates. The three anion groups ( $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) are plotted likewise in the triangular area at the lower right. Thus, two points of the diagram--one in each of the two triangular areas (Fig. 4) indicate the relative concentrations of the several dissolved constituents of a natural water.

The central diamond-shaped area is used to show the overall chemical character of the water by a third single-point plotting, which is at the intersection of rays projected from the plotting of cations and anions as indicated on

Figure 5. The position of this plotting indicates the relative composition of a water in terms of the cation-anion pairs that correspond to the four vertices of the area. This central-area plotting can also be taken directly from the analytical data according to the vectors shown along the outer margins of the area. For such plotting only one cation-variable and one anion-variable need be used--either alkaline earths or alkalis with either weak acids or strong acids; the two percentage reacting values selected from the analytical data are doubled to suit the numerical scales.

As indicated by Revelle, R. , certain distinct types of natural water can be quickly discriminated by their plotting positions in certain subareas of the diamond shaped field as indicated by Fig 4. and the following explanation; area 1, alkaline earths exceed alkalis; area 2, alkalis exceed alkaline earths; area 3, weak acids exceed strong acids; area 4, strong acids exceed weak acids; area 5, secondary alkalinity ("carbonate hardness") exceed 50 percent, i.e., chemical properties of the water are dominated by alkaline earths and weak acids; area 6, secondary salinity ("non-carbonate hardness") exceeds 50 percent; area 7, primary salinity ("non-carbonate alkali") exceeds 50 percent, i.e., chemical properties are dominated by alkalis and strong acids. Ocean water and many brines plot in this area near its right hand vertex. Area 8, primary alkalinity

("carbonate alkali") exceeds 50 percent, here plot the waters which are inordinately soft in proportion to their content of dissolved solids; area 9, no one of the cation-anion pairs exceed 50 percent.

#### Determining Mixing Between Deep Oil Brines and Ground Water

To determine whether the deep oil brines are mixing with the ground water in the study area from any location where oil wells are present or from any point where oil brines may have been spilled and thus mixed with ground water occurring after infiltration through the soils, the ground water chemical ratio is plotted against the deep oil brines. The molar concentrations of  $\text{Na}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Cl}^-$  are plotted.

$\text{Na}/\text{Cl}$  vs  $\text{Cl}$  molar concentrations were first plotted (Fig.5) then  $\text{Mg}^{++}$  vs  $\text{Cl}^-$  molar concentrations were then plotted (Fig.6). From these plots it is determined whether deep oil brines are mixing with the ground water in the study area.

#### Fluctuations of Chloride Levels With Time

The concentrations of chloride levels in the ground water were monitored for fluctuations with time, to study and determine the extent and source of salinity in the ground water. The mean chloride concentrations of all the groundwater wells were compared between each sampling time

i.e. at the beginning and at the end of the month for one year. Fluctuations of chloride concentrations in the groundwater were interpreted with total rainfall shown in Fig.7 and evapotranspiration data.

Scanning Electron Microscopy Study to Determine the Controlling Factor of Efflorescence Occurrence on the Soil Surface

At every sampling trip to the study area, one inch deep soil peds on the surface with efflorescence were collected. Samples were also collected when efflorescence was not prominent on the soil surface. The samples were then taken to the scanning electron microscopy lab (SEM) to be mounted and coated with liquid carbon to study the crystal growth of halite in the soil ped with changes in atmospheric conditions such as rainfall and evapotranspiration.

## RESULTS AND DISCUSSIONS

The polyvinyl chloride well casings functioned as expected for this site due to the absence of volatile organics in the study area. The sampling of groundwater was controlled by the weather especially during the late December through February period as extreme cold temperatures would hinder sampling due to water freezing in the sampling apparatus and, hence, had to be warmed during sampling.

### Comparison of Chemical Analyses Data

From the chemical analyses data and the comparison of this data with the deep oil brine chemical data provided by the United States Geological Survey (Table 2), it appeared that their composition was significantly different, in the concentrations of sodium and chloride levels compared to the surface aquifer ground water composition. However, dilution of oil brines with surface water and or ground water were considered to account for deep oil brines spilled on the soil surface, and transported by infiltration of rain water from the surface or a leaking well casing in the oil well was emitting deep oil brines in the subsurface. For this reason, ratios of cations and anions were studied. As a result, a signature for the ground water and the deep oil brines were established.

As sodium and chloride ions comprise the major chemical constituents in both the ground water and deep oil brines, Na/Cl molar ratios established the signature for the study area. In plotting molar concentrations of Na/Cl vs Cl and Mg vs. Cl, the actual chemical compositions of the ground water and oil brines were plotted.

In the Na/Cl vs. Cl molar plot (Figure 5) the plot indicates that the ground water and the deep oil brines are two different entities. The ground water plotting < 1 mol/L Chloride concentrations and Na/Cl ratio ranging from 0.2 to 2.2 mol/L. The deep oil brines plot at 3.5 to 4.6 mol/L chloride concentrations and Na/Cl ratio being constant at 0.6 mol/L. If mixing between the deep oil brines and ground water were occurring, they both would have plotted in the middle of the chloride range. From past studies by Whittemore, et al., the Na/Cl ratio for deep basin brines for this study was consistent with the Na/Cl ratio obtained in previous studies of < 0.95 mol/L.

In plotting molar concentration of Mg vs. Cl (Figure 7), the plot, again, indicated that there was no mixing between the groundwater and deep oil brines. In this plot the Mg molar concentrations were approximately equal to 0.1 mol/L for both the groundwater and the deep oil brines. In looking at the ratios, there is potential for error in interpreting the cation concentrations for the ground water. Cations can

be absorbed by the clay surfaces, however, the chloride concentrations would always remain consistent, because chloride is a constituent which is not affected by adsorption. Chloride ions are hence strong indicators in demonstrating mixing between the two water bodies.

#### Determining the Source of Salinity

From the above study it is observed that the deep oil brines are not the source of salinity for the formation of saline sodic soils in the study area.

From observing the chloride concentration levels in the study area with time, and the pattern of fluctuations with time, a qualitative interpretation of the extent and origin of the salinity can be inferred.

The fluctuations of chloride concentrations with time is the direct function of rainfall and evapotranspiration in the study area. Chloride concentrations fluctuated between 4500 mg/L and 5250 mg/L during the period of one year study (Fig.7). The highest chloride concentrations occurred between end of August and beginning of September 1987. From the rainfall data Grant county gauged 15.8 cm of total rainfall during the month of September, which was the highest rainfall for the year of study. The high rainfall resulted in greater amounts of dissolution of halite, but the high temperatures during the month of September also



increased evapotranspiration which resulted in the high chloride concentrations.

During the latter part of March 1988 when rainfall gauged at 11 cm, the chloride levels dropped to 4500 mg/L. At this time of the year, the evapotranspiration rates for Grant county, were low, which resulted in a decrease in chloride levels due to dilution by infiltrating water.

From the pattern of chloride fluctuations it can be inferred that halite dissolution is occurring from a shallow depth. It can also be inferred that because the chloride levels change abruptly with varying water table levels, the source for chloride is a point source. The halite beds are not wide spread in the study area but occur sporadically due to facies change in the subsurface.

#### Efflorescence Formation

The thin white salt layer on the soil surface observed in the study area during periods of dry weather is the result of crystallization of halite from the groundwater, which has been brought to the surface by capillary action with evaporation acting as the driving force. The area of study site with the highest water table elevation appeared to be the area where efflorescence occurred more prominently (Fig. 2). The shorter distance from the water table to the soil surface, at the points of highest water elevation, allow

efflorescence to form more rapidly. From the scanning electron microscope study, it was observed that periods of high evapotranspiration and low rainfall were the ideal conditions for efflorescence to form on the soil surface. As shown in Figures 8 and 9, complete formation of cubic halite crystals form during these periods. Soil samples collected when the efflorescence was not prominent on the soil surface showed, halite crystals did not complete crystal growth as shown in Figures 10 and 11. This occurred during periods of low evapotranspiration.

From this study it can be concluded that the origin of saline sodic soils occurred from the dissolution of halite beds in the subsurface. In north central Oklahoma visible efflorescence on the soil surface indicating saline sodic soils is a common sight, however each location is site specific. Hence the occurrence and cause of saline sodic soils in this area must not be generalized.

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Table 1. Dilution of water samples for cations and anions

<b>EC(mmoHs)</b>	<b>Dilution for Ca and Mg Analysis</b>
< 0	1:5
0 to 1.4	1:10
1.5 to 2.8	1:25
2.9 to 3.9	1:50
4 to 9.9	1:100
>10	1:200

\* Diluted with 20% LaCl by volume

<b>EC(mmoHs)</b>	<b>Dilution for Na Analysis</b>
0 to <.5	1:10
.5 to < 1	1:20
1 to < 3	1:50
3 to < 7	1:100
> 7	1:200

\* Diluted with 10% LiCl by volume

<b>EC(mmoHs)</b>	<b>Dilution for K Analysis</b>
all ranges	1:2

\* Diluted with 5 ml of 20% LiCl

<b>EC(mmoHs)</b>	<b>Dilution for Anions</b>
0 < 5	1:5
> 5 < 15	1:10
>15 to 16	1:20

Table 2. Cation and anion concentrations for sampling events and deep oil brines in Grant county

SAMPLE TIME	Cl	SO4	CO3	HCO3	Mg	Na
	-----Meq/l-----					
08/11/87	141.98	56.54	0.10	5.12	43.89	117.33
08/25/87	129.01	56.57	0.38	3.27	46.97	117.92
09/08/87	140.97	54.53	0.00	5.04	46.35	116.41
09/22/87	147.77	53.47	0.23	3.74	43.58	116.80
10/06/87	141.75	51.55	0.28	3.89	42.02	116.70
10/20/87	145.46	51.94	0.23	3.74	40.29	118.33
11/03/87	143.46	52.73	0.26	3.61	43.75	108.87
11/17/87	139.22	53.49	0.13	3.87	43.01	150.65
12/08/87	138.33	50.56	0.15	3.81	44.11	130.00
12/22/87	133.79	54.15	0.06	4.31	44.25	114.93
01/05/88	134.20	49.63	0.14	2.92	41.72	118.99
01/20/88	140.62	51.88	0.00	2.97	43.56	112.58
02/12/88	140.91	52.09	0.00	3.47	48.96	113.97
02/24/88	141.95	52.33	0.00	1.82	45.42	127.67
03/07/88	138.78	51.78	0.00	1.67	50.53	101.96
03/23/88	127.44	47.64	0.00	1.54	47.27	92.11
04/13/88	139.09	52.17	0.00	1.73	37.80	100.54
04/27/88	135.84	51.84	0.00	1.53	42.43	115.38
05/11/88	131.29	54.73	0.00	1.78	49.77	110.18
Oil Field Brine						
Deer Creek 1	3751.44	9.43	0.00	0.70	2139.48	2601.13
Deer Creek 2	3758.00	8.83	0.00	1.02	222.99	2653.33
Grant 1	166.04	53.13	0.00	4.82	52.17	124.41
Grant 2	152.80	55.61	0.00	4.85	43.78	122.15

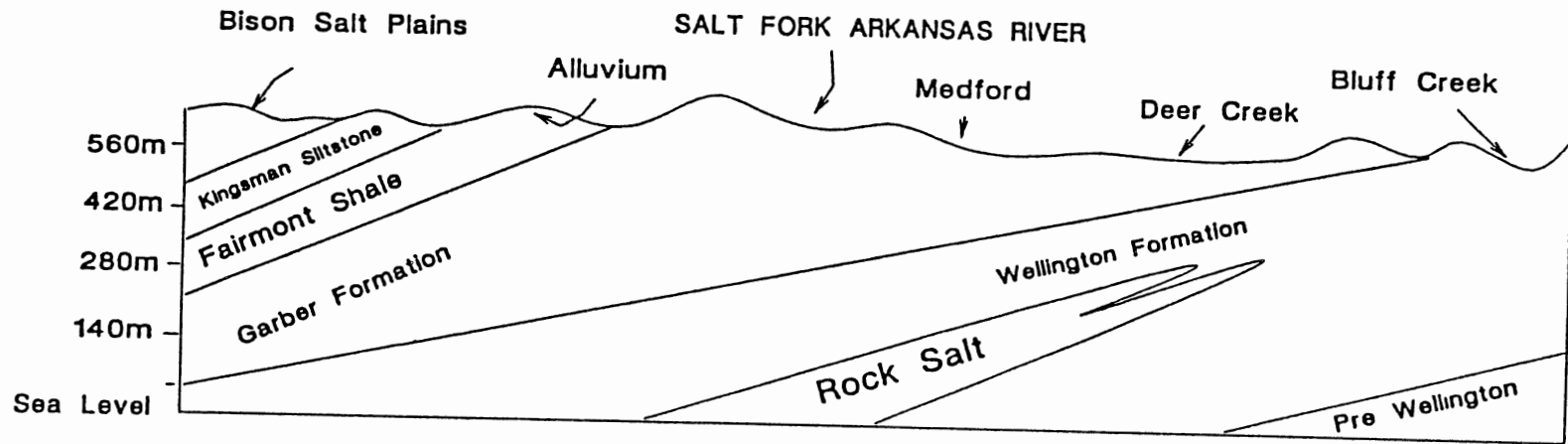


Fig. 1. Geologic cross section of Grant CO.

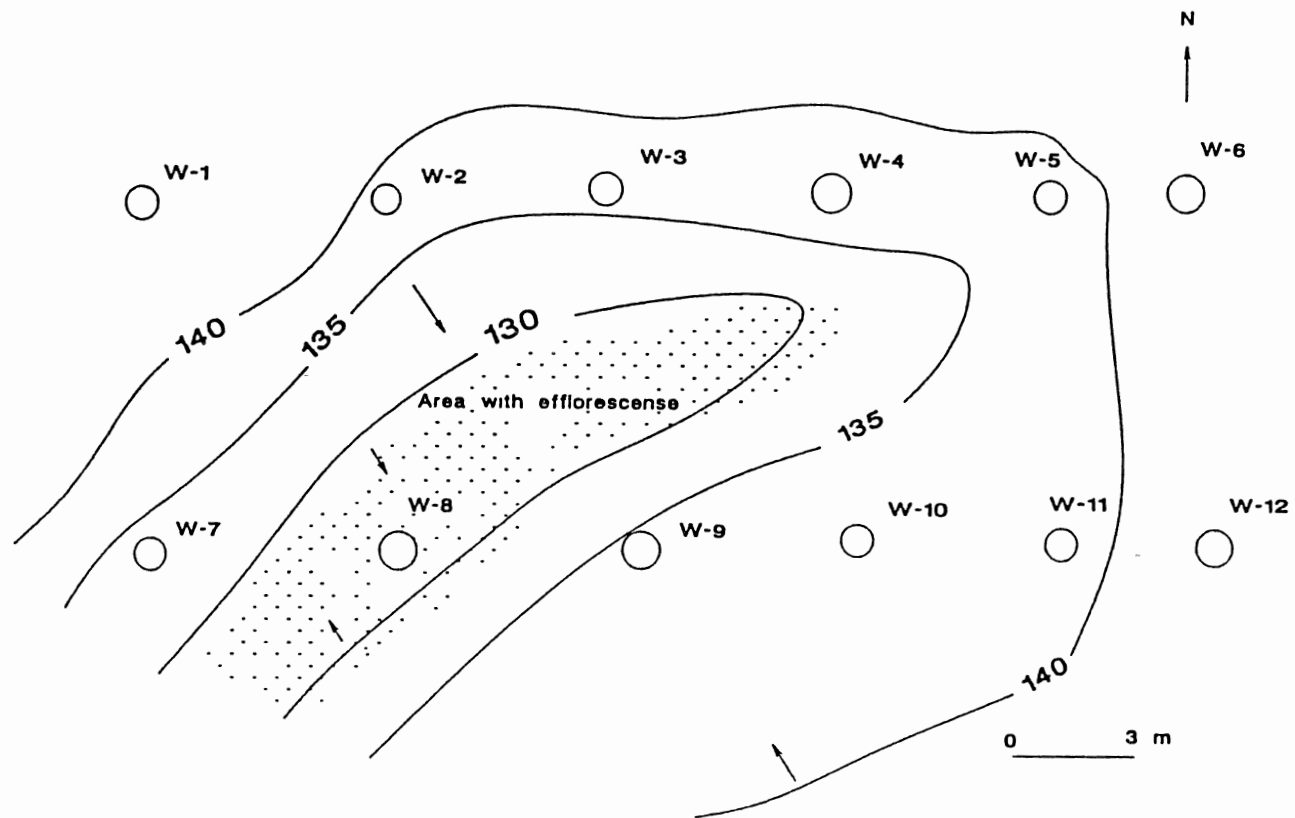


Fig. 2. Potentiometric map of study site



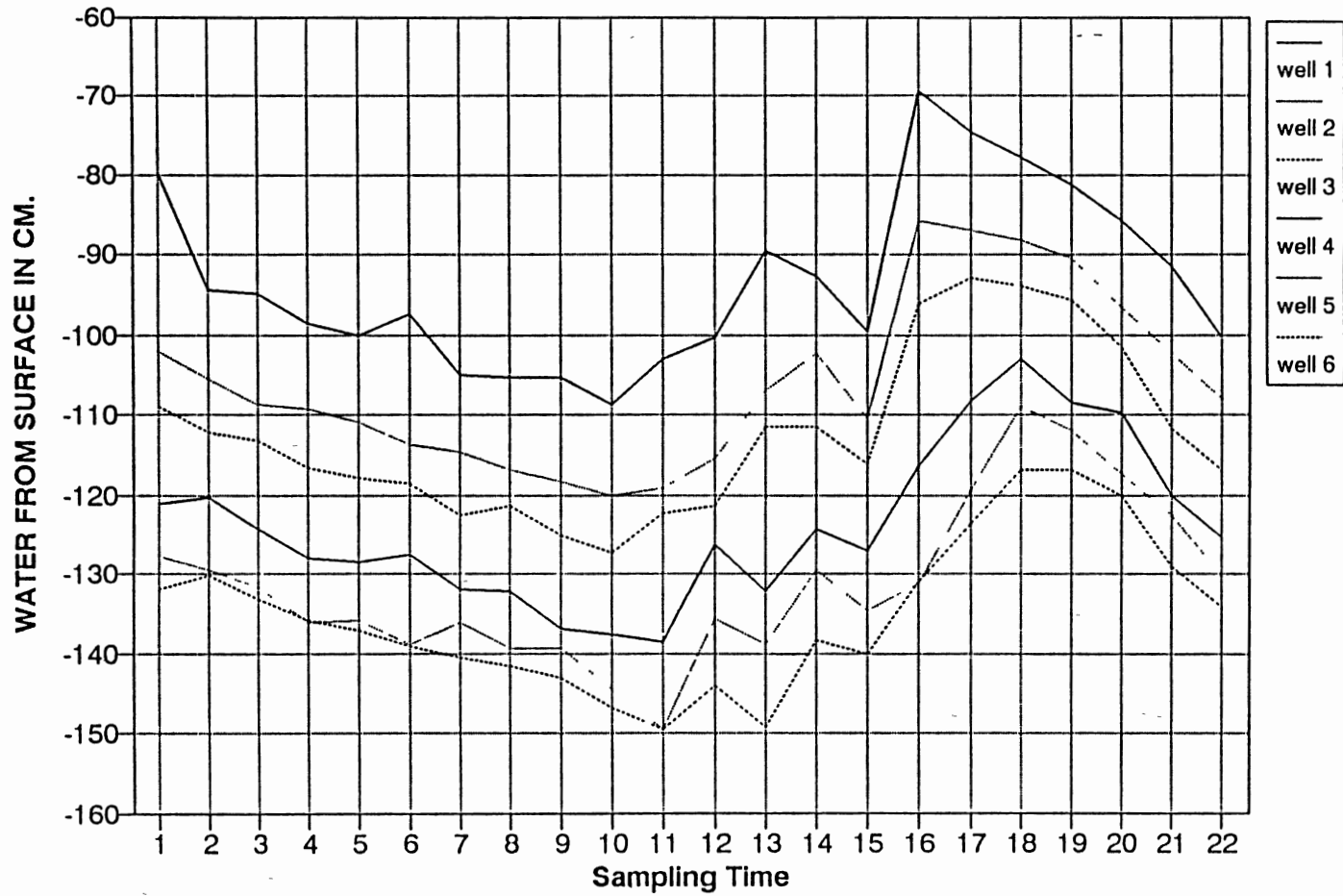
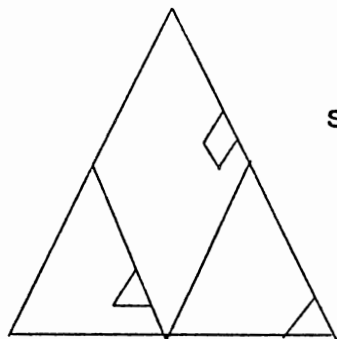


Fig.:3. Water table fluctuations with time for monitor wells 1 to 6 in the study area.



Scheme of plotting extended scales

Subdivision of the diamond-shaped field

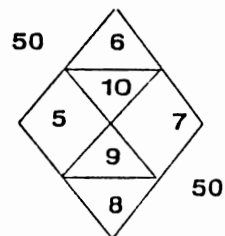
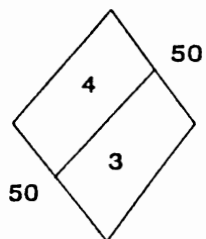
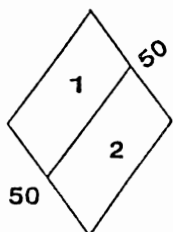


Fig. 4. Trilinear plotting schemes and characterizing subdivisions by area

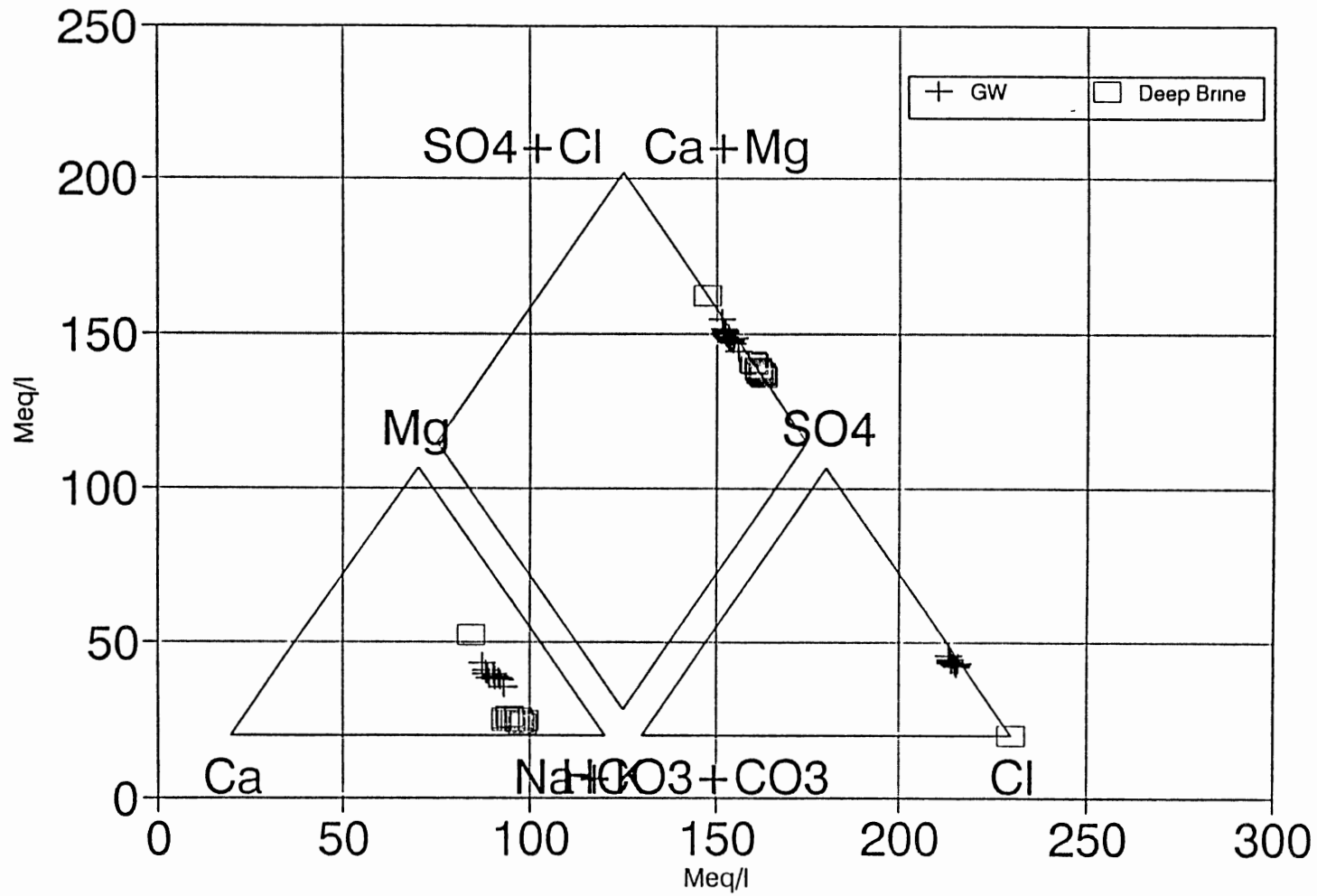


Fig. 5. Trilinear plot differentiating ground-water and deep oil brine.

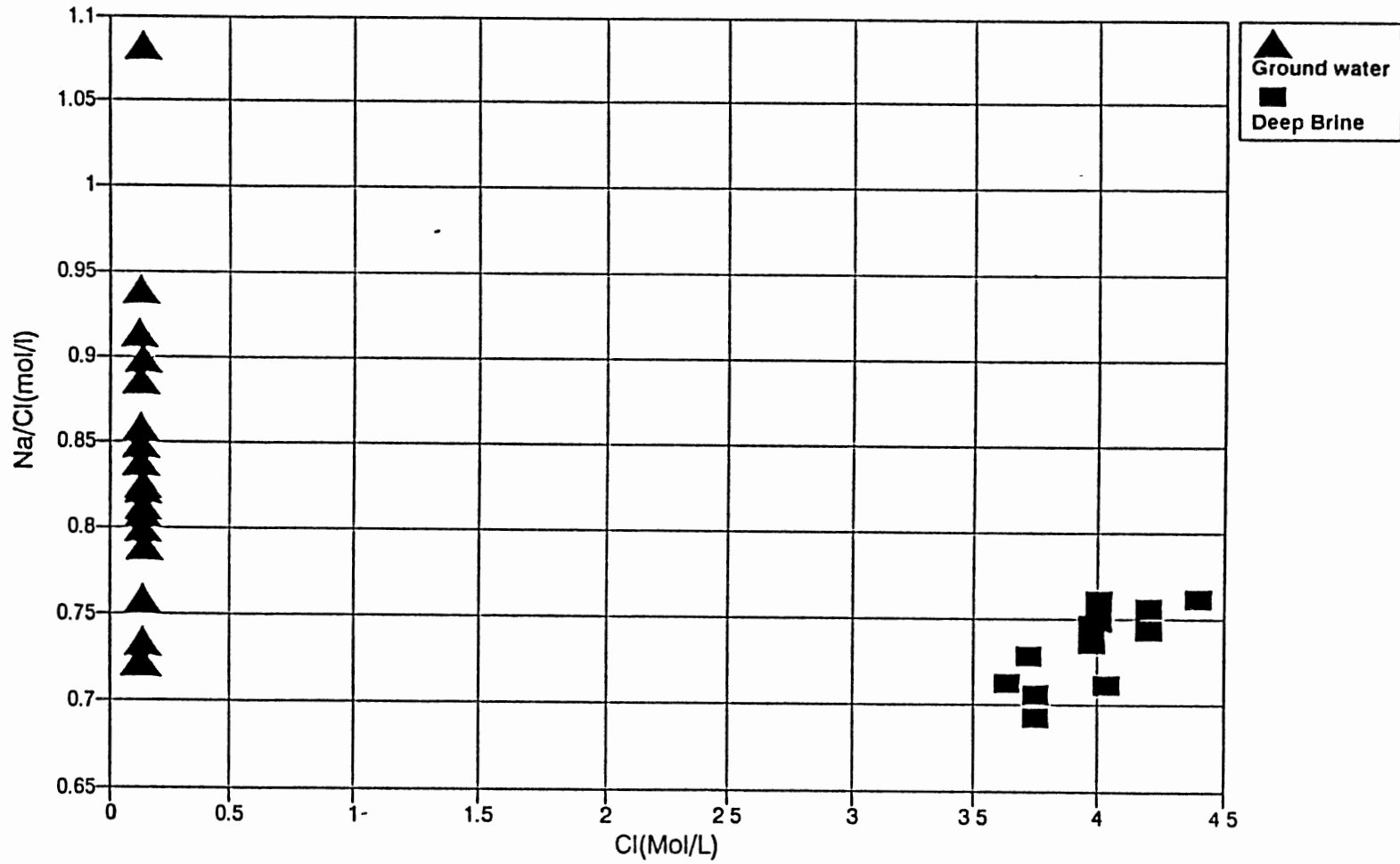


Fig. 6. Na/Cl vs. Cl molar plot of ground-water and deep oil brine.

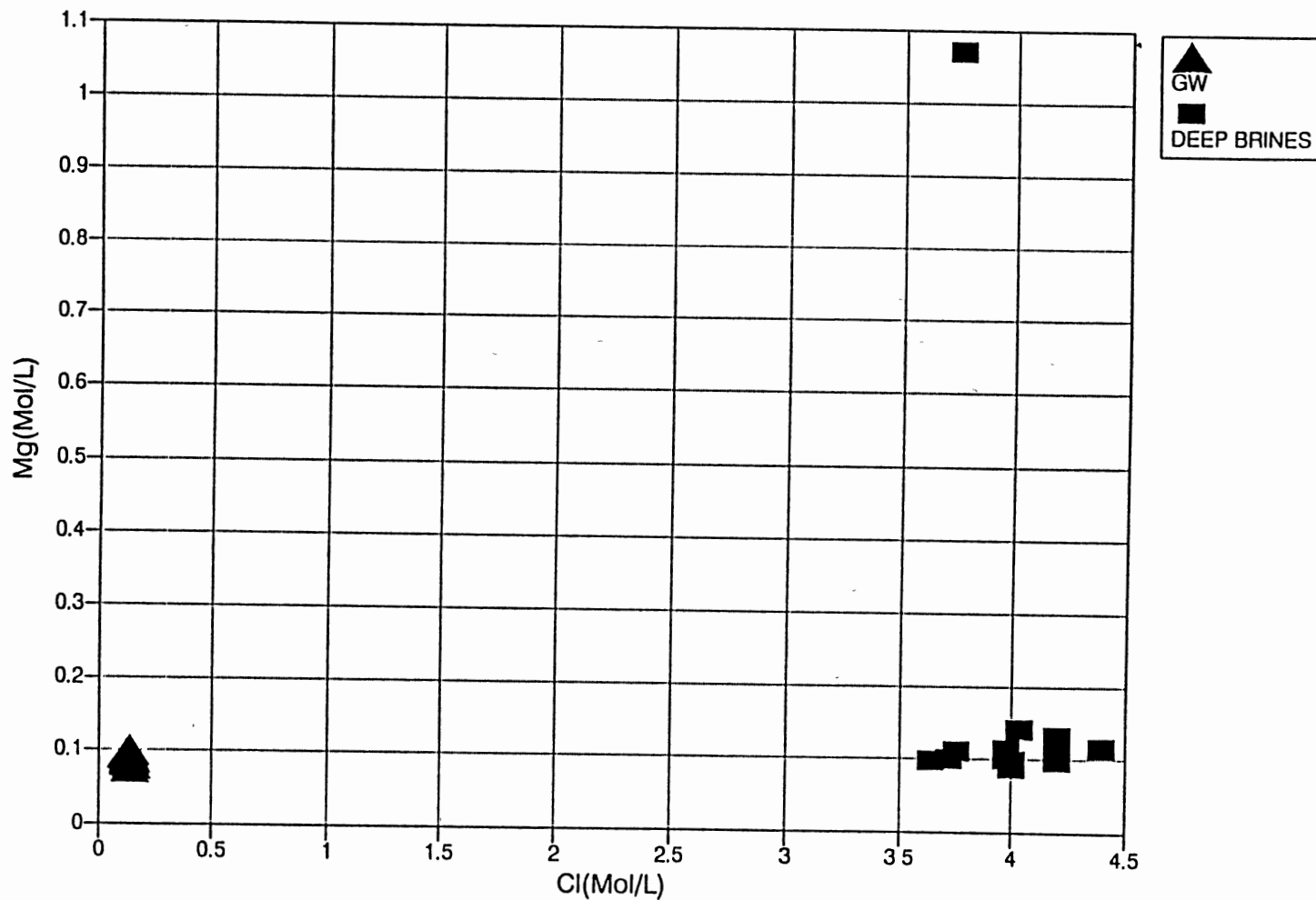


Fig. 7. Mg vs. Cl molar plot of ground-water and deep oil brine.

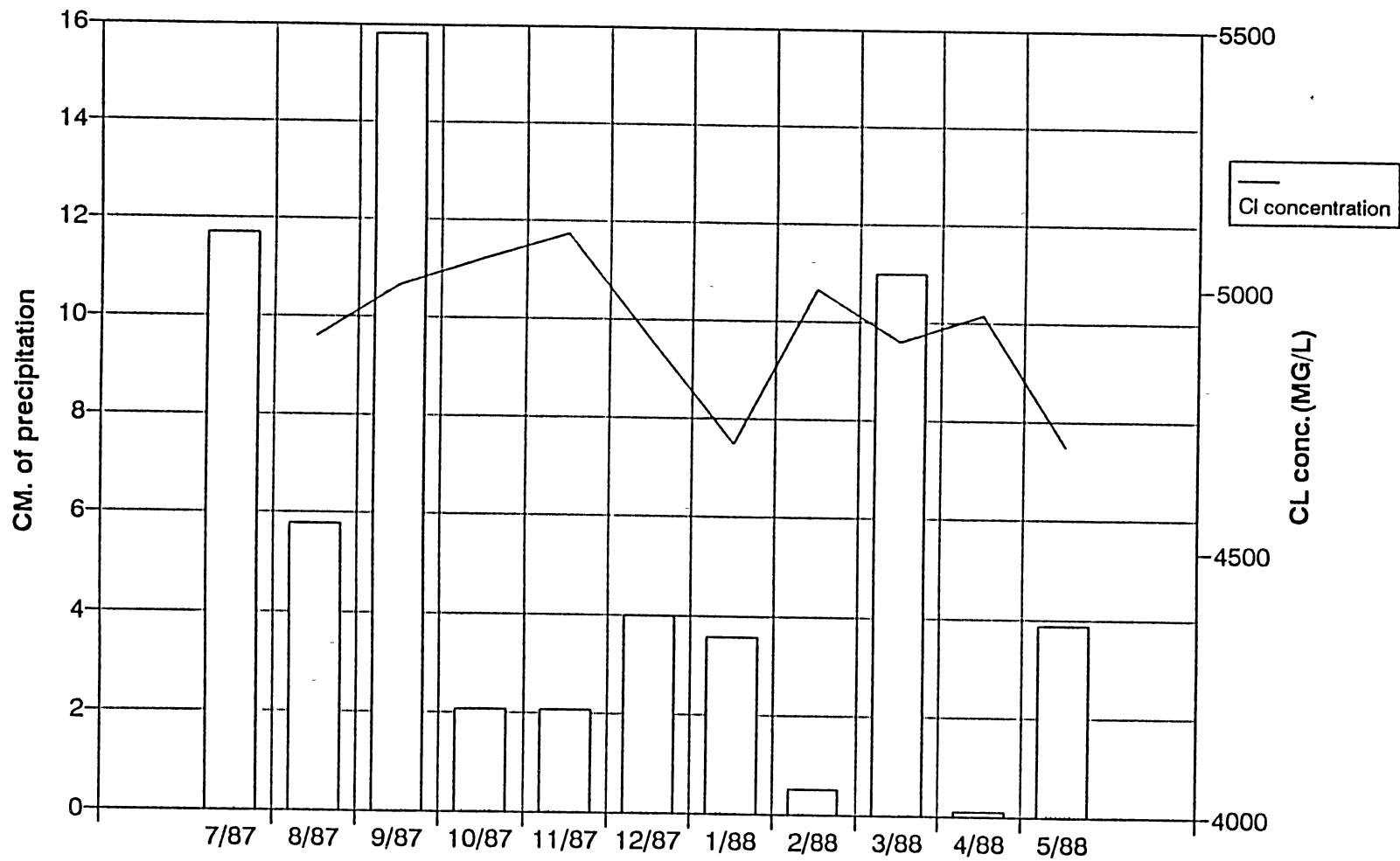


Fig. 8. Chloride concentration fluctuations with time. A direct function of rainfall and evapotranspiration



Fig. 9. Scanning Electron Microscope photo of completely formed Halite crystals in the soil, with magnification of 3000X. Sampled during periods of high evapotranspiration.



Fig. 10. Scanning Electron Microscope photo of completely formed halite crystals in the soil, with magnification of 600X. Sampled during periods high evapotranspiration.





Fig. 11. Scanning Electron Microscope photo of partially formed halite crystals in the soil, with magnification of 2000X. Sampled during periods of low evapotranspiration



Fig. 12. Scanning Electron Microscope photo of partially formed halite crystals in the soil, with magnification of 600X. Sampled during periods of low evapotranspiration

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