SAMPLE BIAS
IN A HYDROCHEMICAL INVESTIGATION
OF THE OAKES AQUIFER,
SOUTHEASTERN NORTH DAKOTA

By Robert B. Shaver

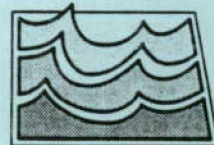# SAMPLE BIAS IN A HYDROCHEMICAL INVESTIGATION
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North Dakota State Water Commission

NORTH DAKOTA STATE WATER COMMISSION

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INTRODUCTION

There are two types of error that affect the authenticity of all environmental measurements (Barcelona, 1983). These are indeterminate and determinate sources of error. Indeterminate or random errors affect the precision or distribution around a central value and are caused by natural variability, human influences during collection, handling, preservation and analysis. Random errors are different for each measurement and vary according to a distribution law that is frequently Gaussian (normal) (Thorton, 1983, p. 97). Determinate errors are constant or systematic and they directly influence the accuracy of the sample mean estimate of the true mean. Determinate errors contribute to inaccurate or biased results and may significantly distort the geochemical picture drawn from a water-chemistry data set (Barcelona, 1983).

Changes in the concentration of chemical species during the collection, transport, and shelf life of ground-water samples prior to laboratory analysis are a source of determinate error or bias. Many of these chemical changes commonly are caused by changes in partial pressure of carbon dioxide (CO_2) gas and water-sample temperature. Wallick (1977) and Schuller and others (1981) documented the affects of CO_2 degassing on ground-water samples. The studies demonstrate significant loss of H^+ (increased pH), Ca^{2+} and HCO_3^- between the time of sample collection and laboratory analysis.

To mitigate changes in the concentration of certain ions caused by CO_2 degassing, Braun and others (1970) and Wallick (1977) recommend filtering (0.45 micron) and acidifying samples to be used for the analysis of Ca^{2+}, Mg^{2+}, and other cations immediately upon collection. In addition, these authors recommend that pH, temperature and specific conductance be measured in the field at the time of sample collection. Braun and others (1970) also recommend that alkalinity be measured in the field at the time of sample collection to calculate bicarbonate concentration.

During May and June, 1989, the North Dakota State Water Commission collected water samples for chemical analysis from 52 observation wells, and the United States Geological Survey collected water samples for chemical analysis from 43 observation wells completed in the Oakes aquifer, southeastern North Dakota (figs. 1 and 2). The purpose of sampling was to determine the spatial distribution of hydrochemical facies in the Oakes aquifer. The author anticipated a decrease in H^+, Ca^{2+}, Mg^{2+}, and HCO_3^- from field to lab (negative sample bias) similar to that of Wallick (1977) and Schuller and others (1981). However, many of the raw, untreated samples showed a significant increase in H^+ and HCO_3^- from field to lab (positive sample bias).

PURPOSE AND SCOPE

The purpose of this report is to describe observed changes in HCO_3^- and pH (sample bias) that occurred during
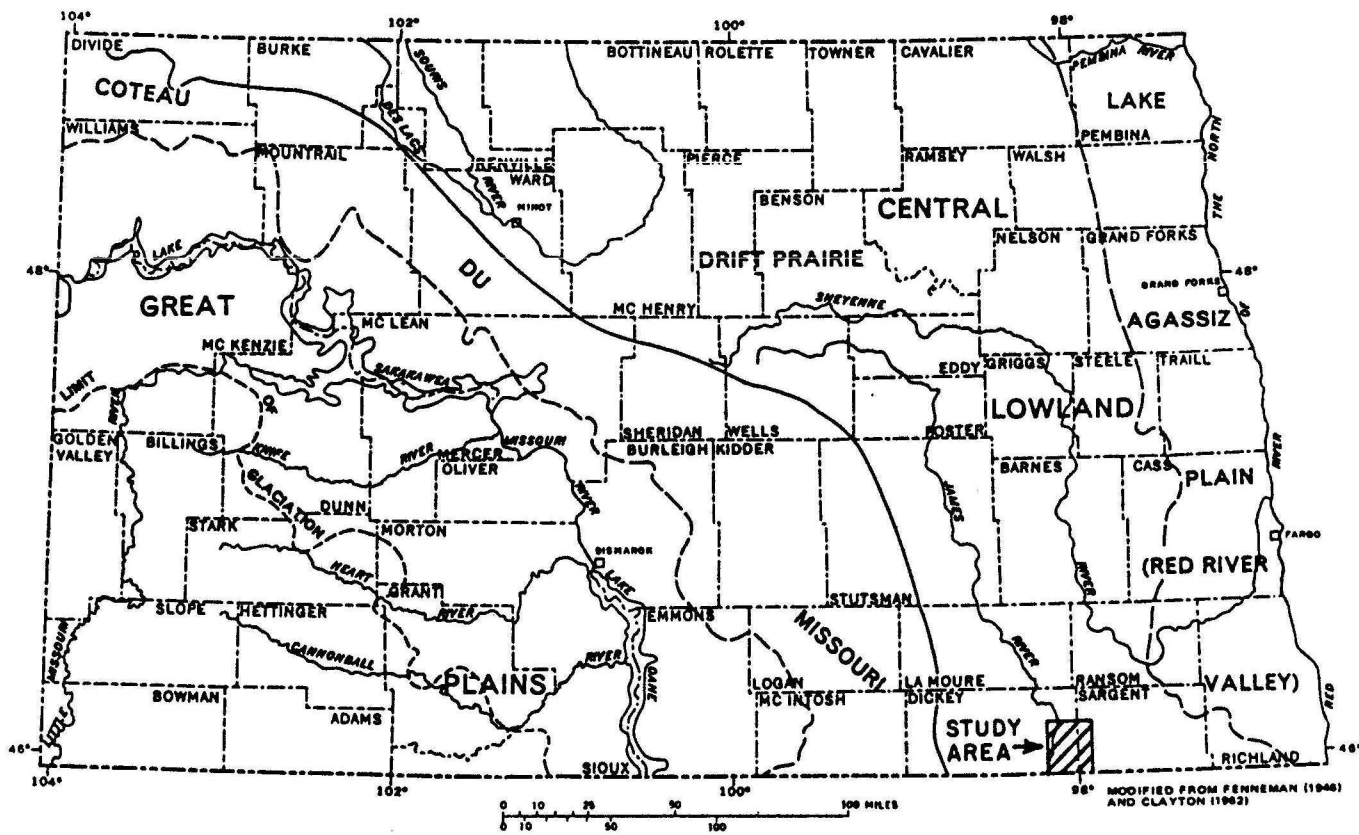
Figure 1. -- Map showing physiographic divisions in North Dakota and location of study area
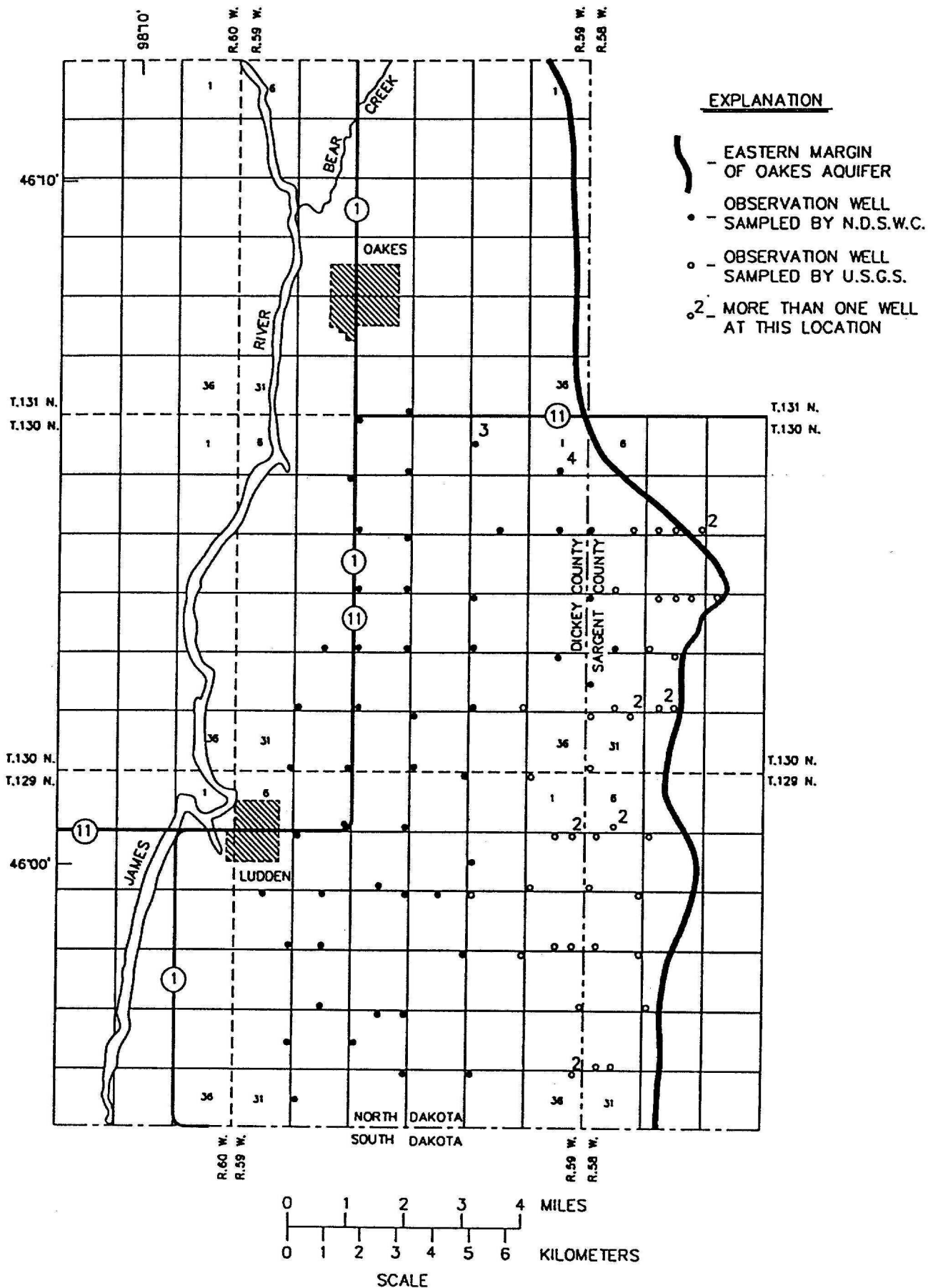
Figure 2. -- Map showing location of Oakes aquifer and observation wells sampled

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the time between field and laboratory analysis. Field HCO_3^- and pH, along with lab HCO_3^- and pH frequency distributions are statistically evaluated to determine the distribution type. Based on distribution type, selected statistical techniques are used to compare the distributions of differences between field and lab HCO_3^- and pH determinations. In addition, the effects of observed HCO_3^- and pH sample bias on ion balance and calcite saturation index are statistically evaluated.

MATERIALS AND METHODS

Prior to sampling, two casing volumes were evacuated from most observation wells using a polyvinyl-chloride (PVC) point-source bailer. Some wells are completed in very-fine grained sediments and were bailed "dry" after evacuating one casing volume. The wells were allowed to recover overnight (10 to 12 hours) prior to sampling. The water level in each well was measured prior to evacuation by bailing and prior to sampling. In most of the wells, the water level had fully recovered prior to sampling.

Two sampling methods were used in this investigation. A gas-squeeze bladder pump connected to a plastic flow-through sampling chamber was used in wells that pumped relatively clean, sediment-free water and had adequate transmitting capacity for continuous pumping (fig. 3). The pump intake was set about one foot above the top of the well screen. Pumping time ranged from 15 to 20 minutes. Temperature, pH,

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TO GAS REGULATOR

pH AND TEMPERATURE PROBE

D.O. PROBE (USGS ONLY)

PLASTIC FLOW-THROUGH CHAMBER

ELECTRICAL CONDUCTIVITY PROBE

INFLOW VALVE

OUTFLOW VALVE

FILTER UNIT (0.45µ)

NEOPRENE HOSE

TO SAMPLING VAN

BYPASS VALVE

2-INCH DIA. PVC WELL CASING

GAS-SQUEEZE BLADDER PUMP

PUMP INTAKE

2-INCH DIA. PVC WELL SCREEN

RAW UNTREATED SAMPLE

FILTERED SAMPLE

FILTERED AND ACIDIFIED SAMPLE

Figure 3. -- Schematic diagram showing sampling apparatus

specific conductance (both U.S. Geological Survey and N. D. State Water Commission) and dissolved oxygen (measured by U.S. Geological Survey only) were measured periodically during the pumping period. The pH usually stabilized to within ± 0.05 pH units after about 10 minutes of pumping. At the end of the pumping period, after pH stabilized, field parameters were measured and recorded. In addition, field alkalinity was measured by sulfuric-acid titration to an end-point pH of 4.5 (Braun and others, 1970). Braun and others (1970) state the determination of the bicarbonate alkalinity of a test sample by 25 laboratories using this method resulted in a mean value of 34.69 mg/L and a standard deviation of 1.17 mg/L. A measurement error of ± 0.10 ml is estimated for the total titrant volume using a 50-ml class A volumetric pipet. Based on the above, an analytical error for field bicarbonate determination is estimated at ± 10 mg/L.

Temperature, pH, specific conductance, and dissolved oxygen were measured with probes installed in sealed ports in the top of the sampling chamber. Temperature and pH were measured by the North Dakota State Water Commission using a Beckman Model 21 digital pH meter with an automatic temperature compensating probe (instrument pH accuracy = ± 0.01 pH). Each morning, the pH meter was calibrated using a two-point standardization technique with pH buffers of 4.0 and 10.0. Temperature and pH were measured by the U.S. Geological Survey using an Extech Model 651 digital pH meter

with an automatic temperature compensating probe (instrument pH accuracy ± 0.01 pH). Each morning, the pH meter was calibrated using a two-point standardization technique with pH buffers of 7.0 and 10.0. Water-sample temperatures were not maintained at the same temperatures of buffer solutions used to calibrate both pH meters each morning. Therefore, analytical error is estimated at ±0.1 pH units.

The North Dakota State Water Commission measured specific conductance using a Hanna Model HI 8633 conductivity meter. The U.S. Geological Survey measured specific conductance using an Extech conductivity meter that was calibrated each morning to a 1,000 micro-siemen standard. Dissolved oxygen was measured by the U.S. Geological Survey using a YSI Model 58 digital meter that also was calibrated each morning.

Over the sampling period, the air temperature during the day reached 31℃ (88°F). As a result, the water temperature measured in the flow-through sampling chamber increased by as much as 5℃ above the in-situ ground-water temperature. To obtain a more accurate temperature of the aquifer interval sampled, the well was bailed after the pump was removed. Water temperature was measured at land surface within about 15 to 30 seconds after the sample was released from the bailer.

Near the end of the pumping period, after pH, temperature, and specific conductance were recorded, samples were bottled using a neoprene discharge hose attached to the

sampling chamber. All bottles were top filled to avoid the occurrence of air pockets. Three samples were collected in plastic bottles for analysis in the laboratory:

1) Raw (500 mL),
2) Filtered (500 mL), and
3) Filtered and acidified (500 mL)

A 2-ml ampule of concentrated nitric acid was added to sample (3) to prevent precipitation of carbonates and metal oxides. Specific conductance, pH, and concentrations of bicarbonate (HCO^-_3) and carbonate (CO_3^{2-}) were measured in the lab using the raw sample. Concentrations of sulfate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), boron (B^{3+}), nitrite (NO_3^-), silica (SiO_2), and total-dissolved solids were measured in the lab using the filtered (0.45 micron) sample. Concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), iron (Fe^{2+}), and manganese (Mn^{2+}) were determined using the filtered and acidified sample.

The bottled samples were not chilled or refrigerated during transport (4-days maximum time) and storage. Aquifer water temperatures generally ranged from about $6^{\circ}C$ to $10^{\circ}C$. Prior to analysis in the North Dakota State Laboratory, samples were stored at room temperature ($20^{\circ}C$ to $22^{\circ}C$) sometimes for periods of up to about two weeks.

Concentrations of the major cations were determined in the lab using a Perkin-Elmer Model 4000 atomic absorption spectrophotometer. Concentrations of HCO_3^-, CO_3^{2-}, and Cl^- were determined using a Fisher Model 741 titralyzer. Concentration of SO_4^{2-} was determined by a gravimetric

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method. The North Dakota State Water Commission laboratory participates in quality-assurance programs with the U.S. Geological Survey.

For observation wells with low transmitting capacity that yielded turbid water, samples were collected using a PVC point-source bailer. Water was transferred from the bailer to a 1.9L plastic container and field determinations of temperature, pH, and specific conductance were made. In addition, field alkalinity was measured by sulfuric-acid titration to an end-point pH of 4.5. After the field determinations were made, three samples, as previously described, were collected in plastic bottles and transported unrefrigerated to the North Dakota State Water Commission laboratory in Bismarck.

RESULTS AND DISCUSSION

Bicarbonate

The frequency distribution of differences between field and lab HCO_3^- pairs is shown by the histogram in figure 4. Results of skewness analysis for the distribution in figure 4 are summarized in table 1.

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SUMMARY STATISTICS	
Minimum	-54
Maximum	66
Sum	-443
Points	92
Mean	-4.82
Median	-1
RMS	19.94
Std Deviation	19.47
Variance	378.55
Std Error	2.03
Skewness	0.04
Kurtosis	1.47

SUMMARY STATISTICS [less one analysis(66mg/L)]	
Minimum	-54
Maximum	40
Sum	-509
Points	91
Mean	-5.59
Median	-1
RMS	18.82
Std Deviation	18.07
Variance	326.42
Std Error	1.89
Skewness	-0.49
Kurtosis	0.33

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NUMBER OF SAMPLES

5

0

-70 -60 -50 -40 -30 -20 -10 0 10 20 30 40 50 60 70 80

FIELD BICARBONATE MINUS LAB BICARBONATE, IN
MILLIGRAMS PER LITER

LAB > FIELD

Figure 4. -- Graph showing frequency distribution of
differences between field bicarbonate and lab
bicarbonate

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TABLE 1. -- Analysis of skewness of distribution of differences between field and lab HCO_3^-

Sample Size	Computed Skewness Coefficient	Tabulated Skewness Coefficient *	Level of Significance
92	0.04	0.40	$p > 0.05$
91**	-0.49	0.40	$p < 0.05$

* from Snedecor and Cochran, 1989 - Table A19i
** less 1 paired sample with a HCO_3^- difference of 66 mg/L

Using 92 differences, the computed skewness coefficient is less than the tabulated skewness coefficient at five percent. Therefore, there is no reason to reject the null hypothesis that the distribution of differences is normal. However, if one paired sample with a difference of 66 mg/L HCO_3^- is removed from the data set, the absolute value of the computed skewness coefficient is larger than the tabulated skewness coefficient at five percent. Therefore, the null hypothesis that the distribution of HCO_3^- differences is normal is rejected and it is concluded that the distribution is not normal.

A probability plot of the differences between field and lab HCO_3^- pairs is illustrated in figure 5. The data plot is non-linear indicating that the distribution of HCO_3^- differences is non-normal.

Results of a chi-squared (X^2) analysis of the frequency distribution shown in figure 5 (92 analyses) are summarized in table 2. The computed X^2 is greater than the tabulated X^2 at one percent and it is therefore concluded that the
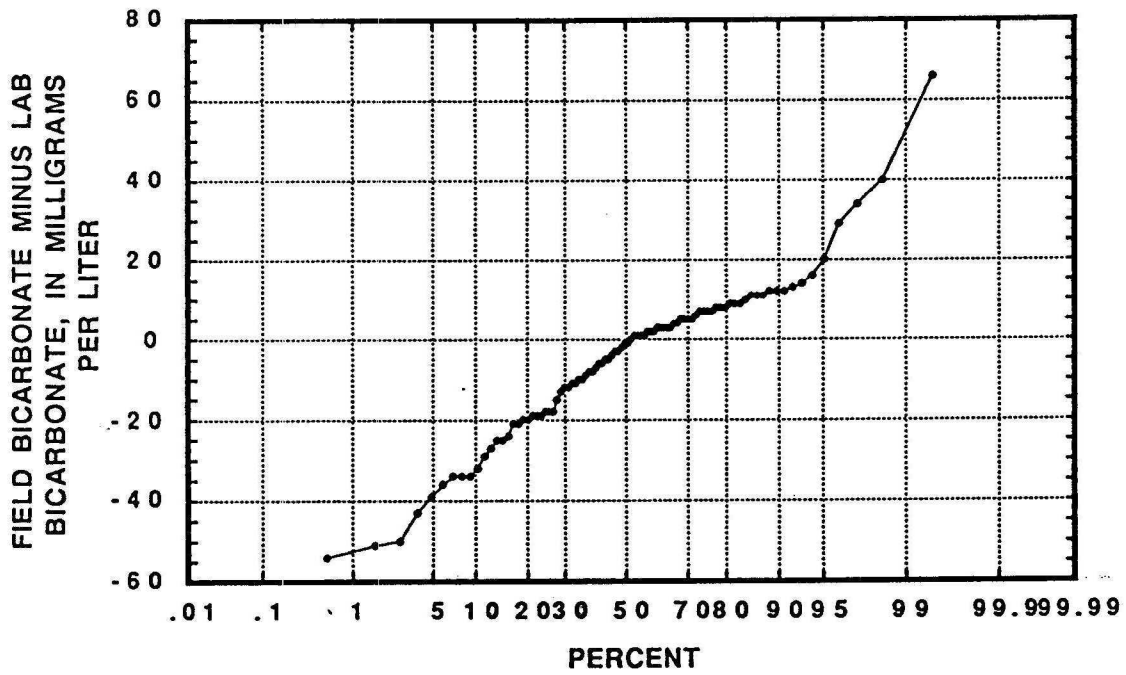
Figure 5. -- Graph showing arithmetic probability plot of differences between field bicarbonate and lab bicarbonate

distribution of field and lab HCO3- differences is not
normal.

TABLE 2. -- Chi-squared analysis of distribution of differences
between field and lab HCO_3^-

Sample Size	X^2 (Computed)	X^2 (Tabulated)[*]	Level of Significance
92	19.58	18.48	$p < 0.01$

[*] from Dixon and Massey, 1969 - Table A-4

Based on the above, the non-parametric, Wilcoxon signed-
rank test is applied to the distribution of field and lab
HCO_3^- differences. The null hypothesis is the mean of the
population of all possible differences is zero, that is,
field HCO_3^- is as likely to be larger than lab HCO_3^- as lab
HCO_3^- is likely to be larger than field HCO_3^-. Results of
the Wilcoxon signed-rank test are summarized in table 3.

TABLE 3. -- Values of the Wilcoxon signed-rank test used to
compare the means of field and lab bicarbonate
distributions

	Number:	S Rank:	Mean Rank:
- Ranks	47	2616.5	55.67
+ Ranks	44	1569.5	35.67

Note: 1 case eliminated for difference = 0.

Z	-2.072	p = .0383
Z corrected for ties	-2.072	p = .0382
# tied groups	20	

X = Field HCO_3^-, in mg/L; Y = lab HCO_3^-, in mg/L

At a four percent level of significance, the null
hypothesis that the population means are the same is rejected

and it is concluded that the two population means differ suggesting sample bias from field to lab. The sum and mean of the negative ranks are both larger than those of the positive ranks indicating a tendency for HCO_3^- to increase from field to lab (positive HCO_3^- sample bias).

Hydrogen-ion concentration (pH)

Probability plots of field and lab pH are shown in figure 6. Field pH data is linear indicating a normal distribution and lab pH data is non linear (concave upward) indicating a non-normal distribution.

Skewness analysis of field and lab pH distributions is summarized in table 4. At a five percent level of significance, there is no reason to reject the null hypothesis that the field pH distribution is normal. At a one percent level of significance, the null hypothesis is rejected and it is concluded that the lab pH distribution is not normal. The change from a normal distribution (field pH) to a non-normal distribution (lab pH) suggests sample bias from field to lab.

TABLE 4. -- Analysis of skewness of field and lab pH distributions

	Sample Size	Computed Skewness Coefficient	Tabulated Skewness Coefficient *	Level of Significance
Field pH	92	-0.20	0.60	$p > 0.05$
Lab pH	92	0.75	0.60	$p < 0.01$

* from Snedecor and Cochran, 1989 - Table A19i

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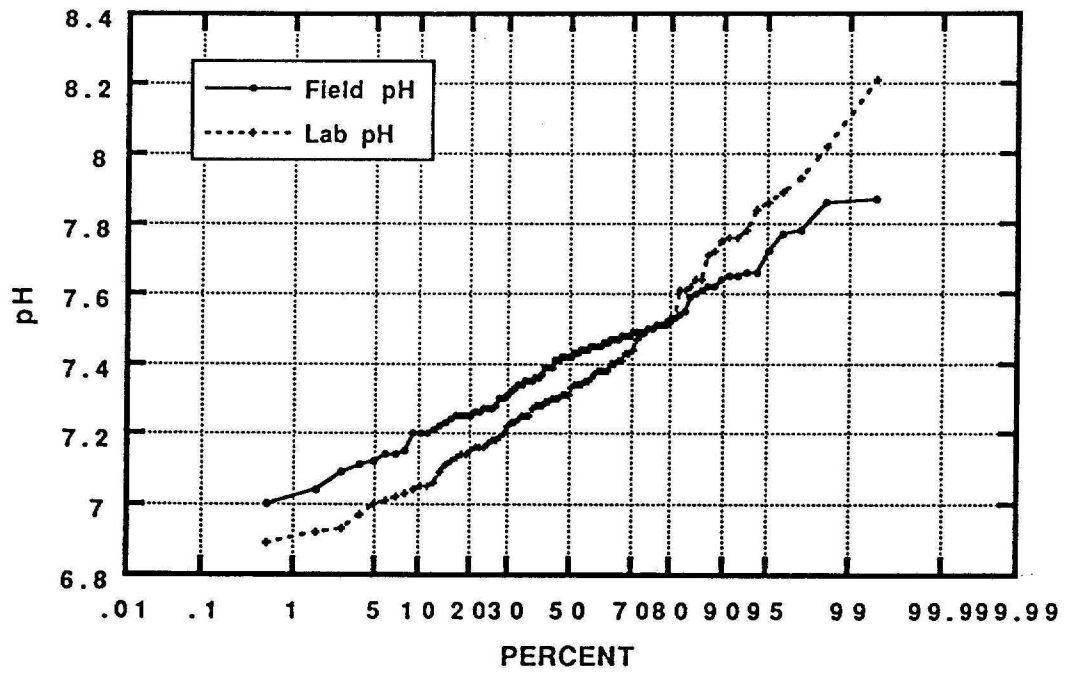
Figure 6. -- Graph showing arithmetic probability plots of field and lab pH

A probability plot of field pH minus lab pH is shown in figure 7. The approximate linear plot indicates the distribution of pH differences is normal.

Skewness analysis of the distribution of pH differences is summarized in table 5. At a five percent level of significance there is no reason to reject the null hypothesis that the distribution of differences between field and lab pH pairs is normal.

TABLE 5. -- Analysis of skewness of distribution of differences between field and lab pH

Sample Size	Computed Skewness Coefficient	Tabulated Skewness Coefficient *	Level of Significance
92	0.16	0.40	p>0.05

* from Snedecor and Cochran, 1989 - Table A19i

Based on the above, the parametric, paired t-test is used to compare the means of the field and pH distributions (table 6). At a five percent level of significance, there is no basis to reject the null hypothesis that the mean of the population of all possible differences is zero. In other words, field pH is likely to be larger than lab pH as lab pH is likely to be larger than field pH.

TABLE 6. -- Values of the paired t-test used to compare the means of field and lab pH distributions

Degrees of Freedom:	Mean X - Y:	Paired t Value:	Probability (2-tail):
91	.05	1.588	.1157

X = Field pH; Y = Lab pH

Figure 7. -- Graph showing arithmetic probability plot of differences between field pH and lab pH

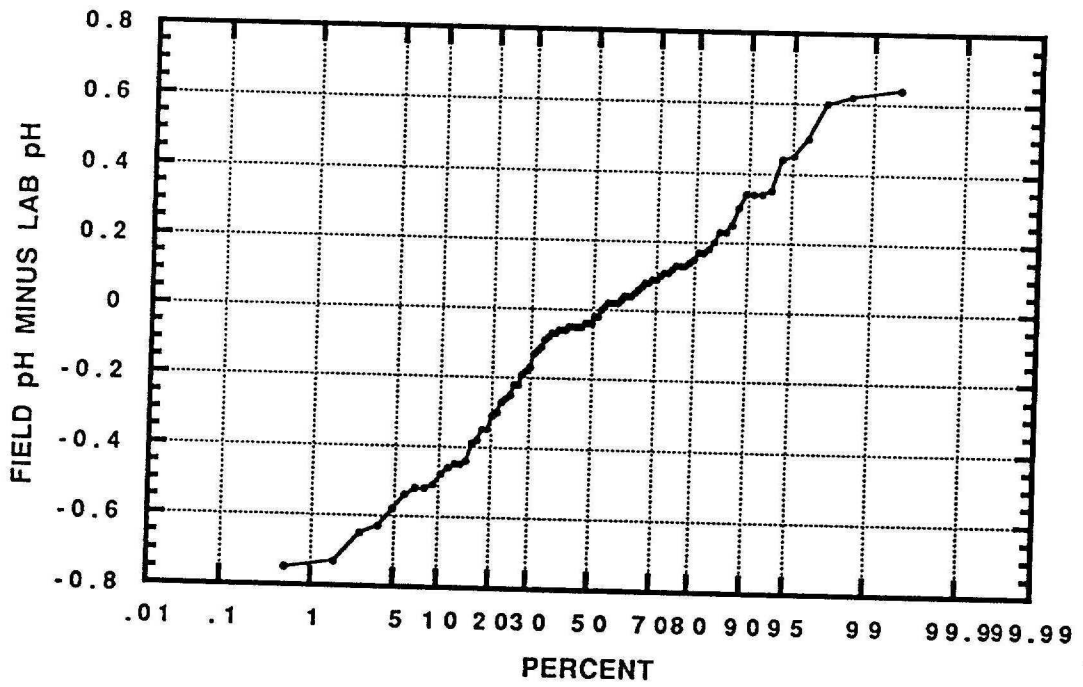An F-test was used to evaluate the differences in variance between field and lab pH distributions (Snedecor and Cochran, 1989). The computed F-statistic is 2.20 and is significant at less than 0.005 (P <0.005). As a result, the null hypothesis that the variances of the two pH distributions are equal is rejected and it is concluded that the variances differ.

Regression analysis indicates that a highly significant correlation (P = 0.0001) exists between the direction of pH change from field to lab and the field pH value (fig. 8). A correlation coefficient of 0.50 indicates 25 percent of the variability in pH change from field to lab is attributed to field pH. Samples characterized by small field pH are somewhat more susceptible to negative pH bias (increase in pH, decrease in H^+) from field to lab. Samples characterized by large field pH are somewhat more susceptible to positive pH bias (decrease in pH, increase in H^+) from field to lab.

Ground water in the Oakes aquifer with dissolved-solids concentrations less than or equal to 400 mg/L is a calcium-magnesium bicarbonate type water associated with local upland recharge areas (Shaver and Schuh, 1990). Dissolved-solids concentrations greater than about 1,000 mg/L generally are sodium-magnesium sulfate type waters associated with local closed topographic depressions that represent net discharge areas. Ground water with dissolved-solids concentrations between 400 and 1,000 mg/L commonly is a mixed ionic type ranging between the above ionic types and is associated with
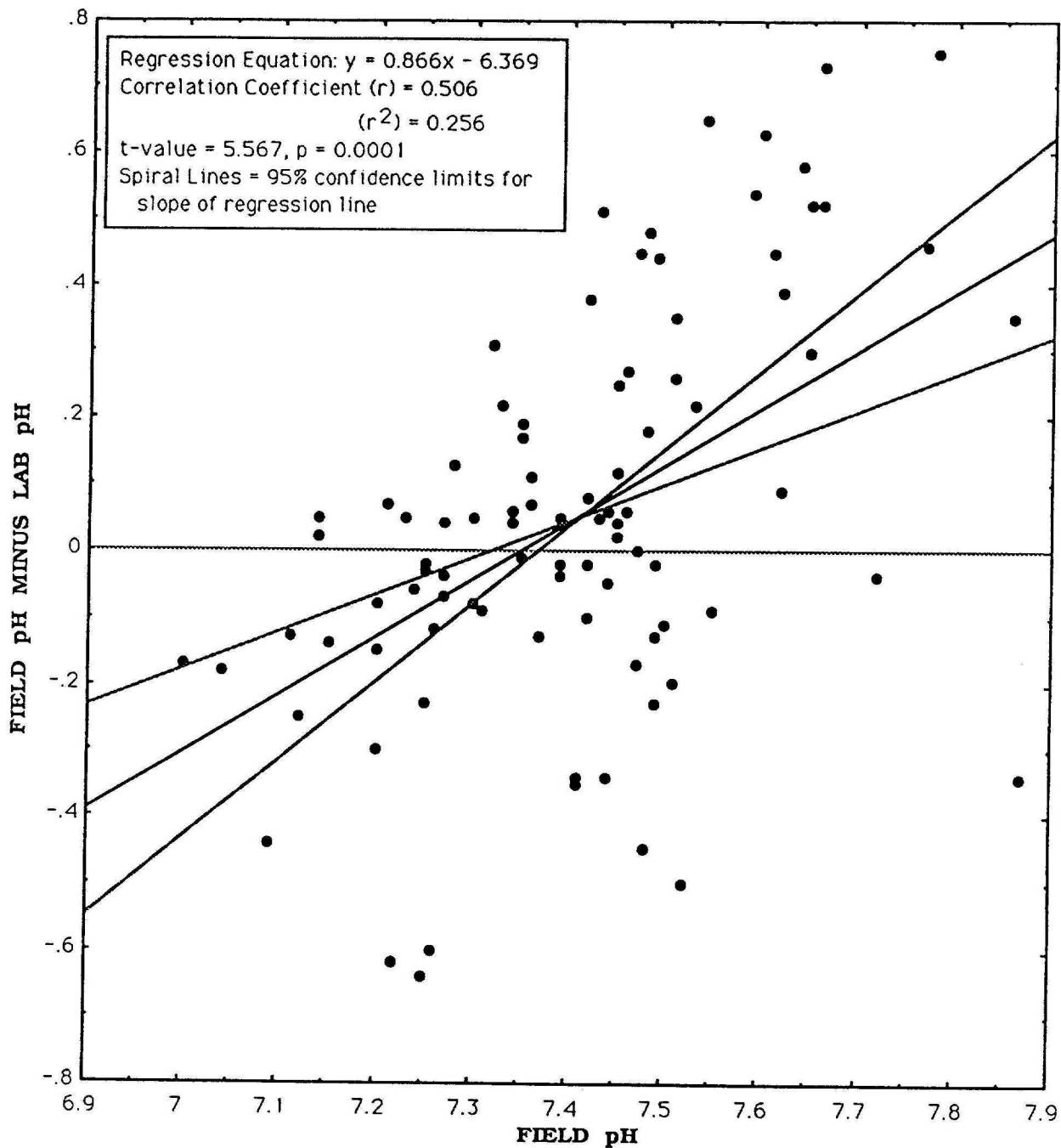
Figure 8. -- Graph showing regression analysis of change in pH from field to lab versus field pH

transitional areas of the aquifer located between upland recharge and lowland discharge areas.

The samples in figure 8 were partitioned into two groups with one group characterized by dissolved-solids concentrations less than or equal to 400 mg/L (fig. 9) and the other group characterized by dissolved-solids concentrations greater than 400 mg/L (fig. 10). The regression analysis in figure 9 indicates a highly significant correlation (P = 0.0001) between change in pH from field to lab versus field pH. Sixty-six percent of the variability in pH change from field to lab is directly attributed to the magnitude of field pH. Samples with dissolved-solids concentrations less than or equal to 400 mg/L are for the most part characterized by a decrease in pH from field to lab (increased H^+, positive bias).

The regression analysis in figure 10 shows a significant correlation (P = 0.02) between change in pH from field to lab and field pH. A correlation coefficient of 0.32 indicates only 10 percent of the variability in pH change from field to lab is attributed to field pH. Samples with dissolved-solids concentrations greater than 400 mg/L are for the most part characterized by an increase in pH from field to lab (decreased H^+, negative bias).

Bicarbonate versus pH

A plot of change in HCO_3^- from field to lab versus change in pH from field to lab is shown in figure 11. The

Figure 9. -- Graph showing regression analysis of change in pH from field to lab versus field pH for samples with dissolved-solids concentrations less than 400 mg/L
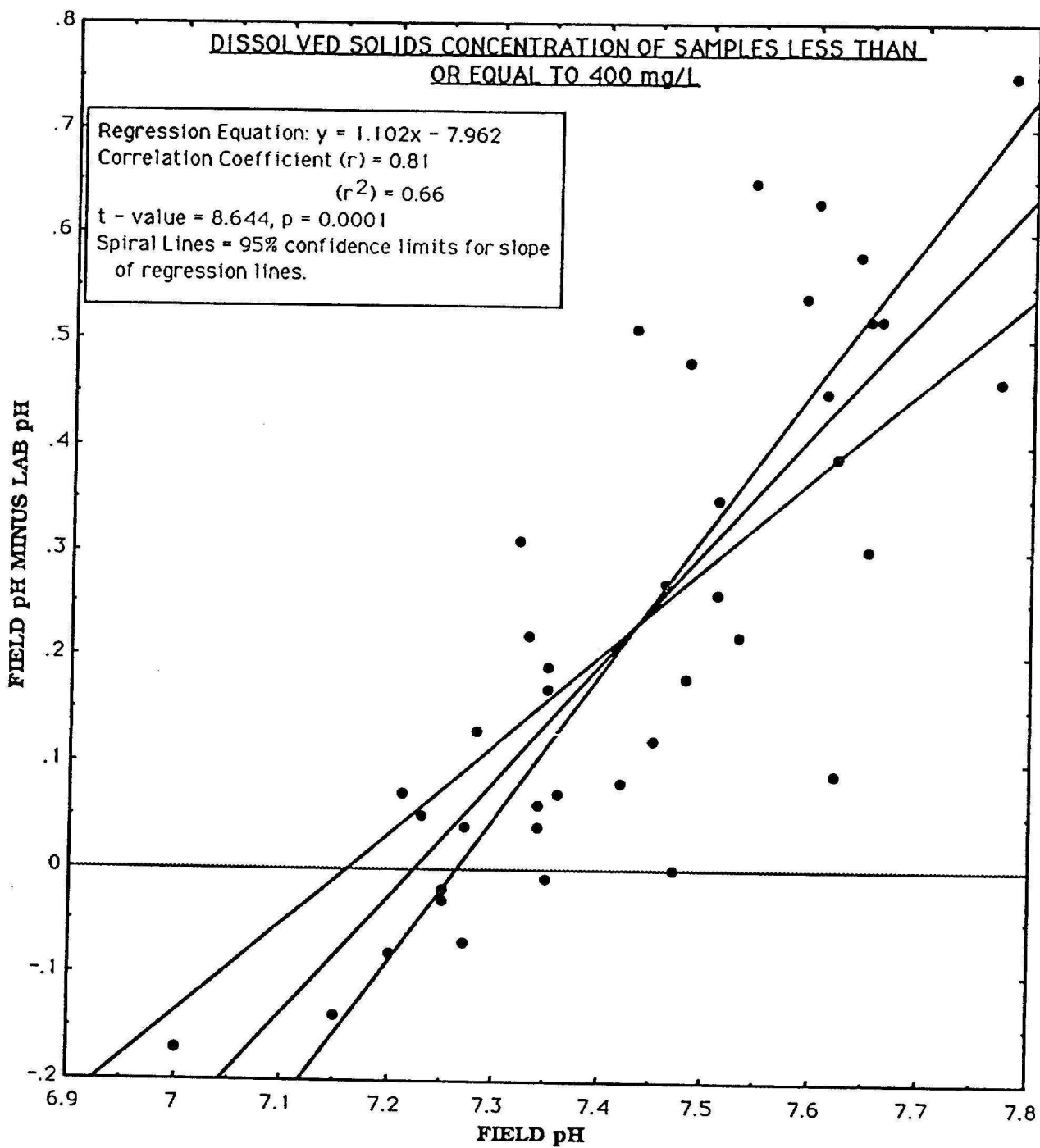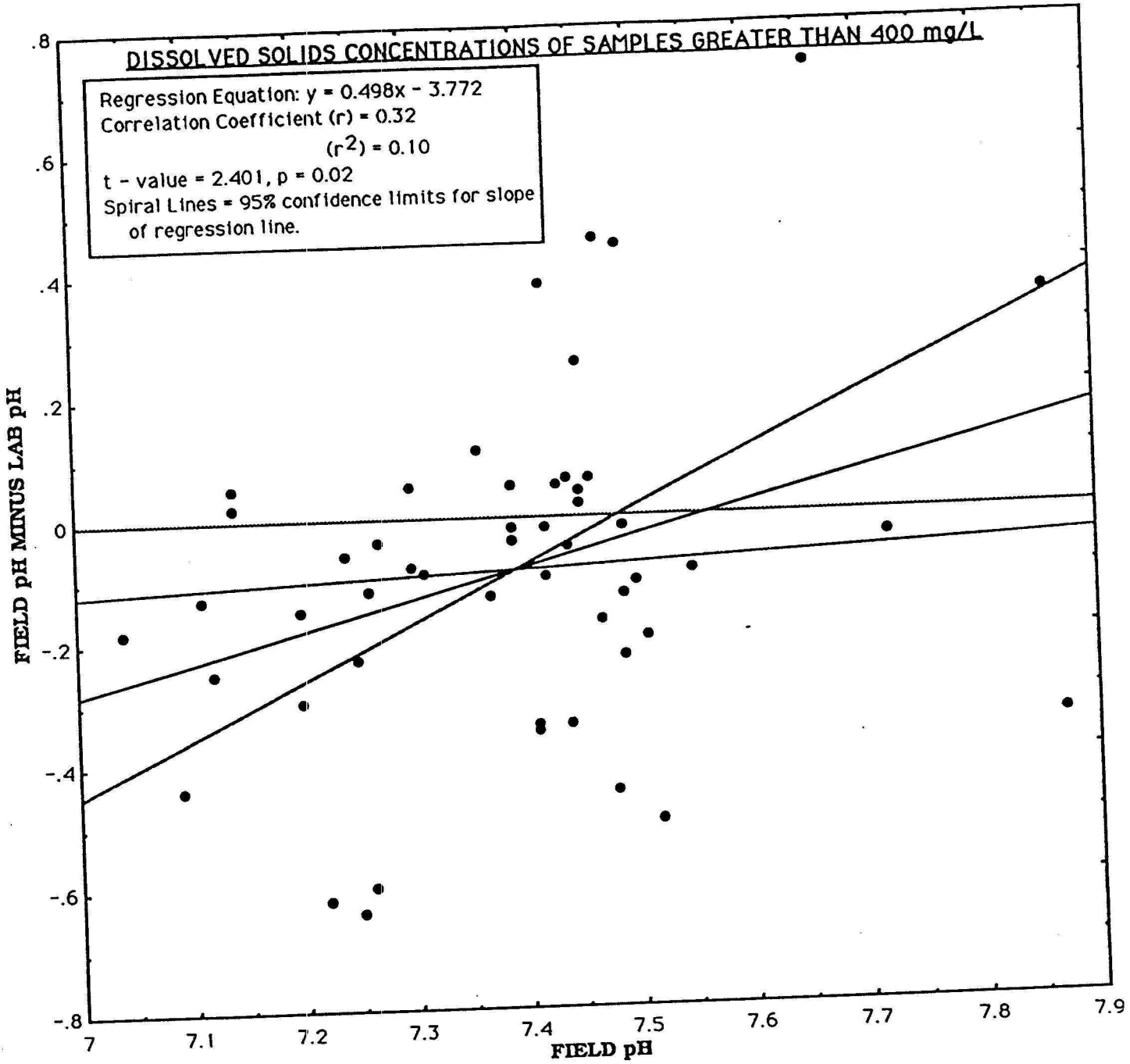
Figure 10. -- Graph showing regression analysis of change in pH from field to lab versus field pH for samples with dissolved-solids concentrations greater than 400 mg/L
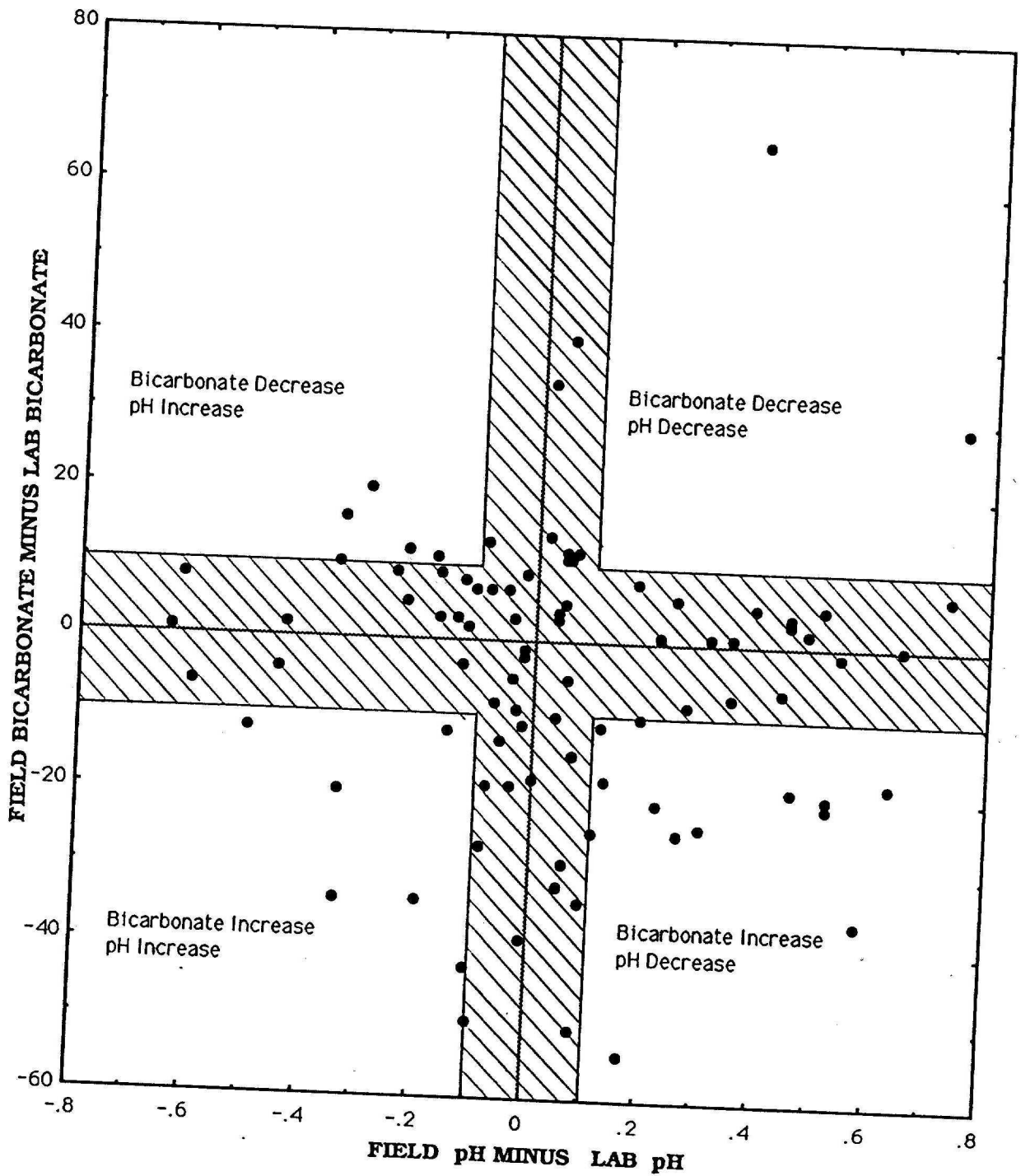
Figure 11. -- Graph showing change in bicarbonate from field to lab versus change in pH from field to lab

parts of the graph outlined by slanted lines represent estimates of analytical error for both field HCO_3^- and pH. Based on the above, 13 samples (14 percent) show a pH decrease coupled with a HCO_3^- increase. This is the dominant change in the pH-HCO_3^- couple from field to lab.

The samples in figure 11 were partitioned according to range in dissolved-solids concentrations. Samples with dissolved-solids concentrations less than 400 mg/L predominantly show a pH decrease and HCO_3^- increase (fig. 12). Samples with dissolved-solids concentrations greater than 400 mg/L predominantly show a pH increase (fig. 13). Although HCO_3^- changes are mixed, the largest changes in HCO_3^- are associated with increased HCO_3^-.

Sample bias hypotheses

Statistical analysis of the Oakes aquifer ground-water samples supports positive HCO_3^- bias (increase in HCO_3^-) from field to lab. The direction of pH bias change from field to lab is a function of initial (field) pH. Negative pH bias (decreased H^+) generally is associated with lower pH ground waters and positive pH bias (increased H^+) generally is associated with higher pH ground waters in the Oakes aquifer. Increased HCO_3^- coupled with a decrease in pH is more pronounced than either an increase in HCO_3^- coupled with an increase in pH or a decrease in HCO_3^- coupled with an increase in pH.
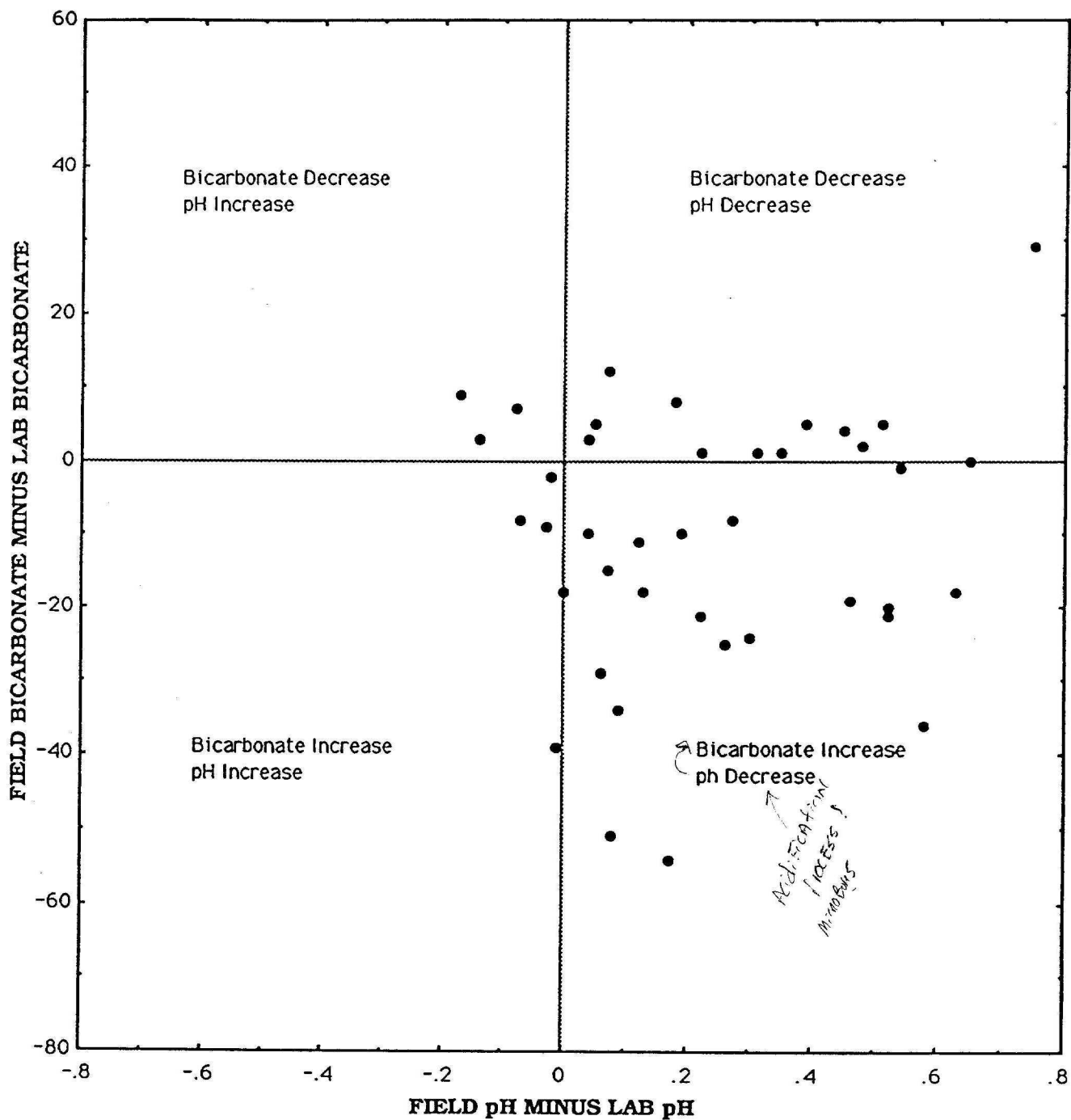
Figure 12. -- Graph showing change in bicarbonate from field
to lab versus change in pH from field to lab for
samples with dissolved-solids concentrations
less than 400 mg/L
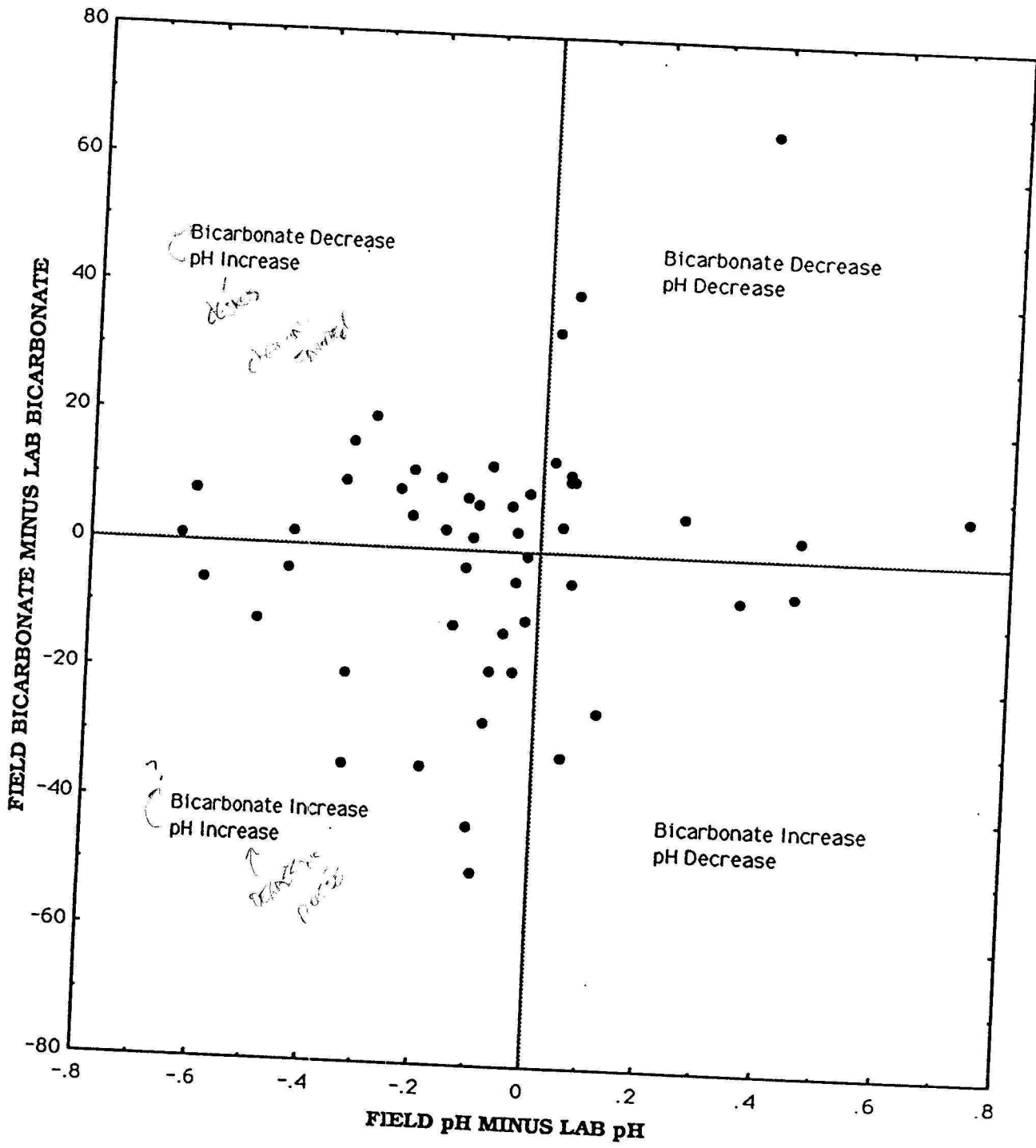
Figure 13. -- Graph showing change in bicarbonate from field to lab versus change in pH from field to lab for samples with dissolved-solids concentrations greater than 400 mg/L

Decreased HCO_3^- and increased pH from field to lab probably are caused by CO_2 degassing. The solubility of CO_2 in water is related directly to the partial pressure of CO_2 (pCO_2). Most ground water contains CO_2 at partial pressures well above the partial pressure of CO_2 in the atmosphere. Plant respiration and microbial oxidation of organic material in the unsaturated zone are major sources of dissolved CO_2. When ground-water samples are exposed to the atmosphere during collection and storage, the ground water becomes supersaturated with respect to CO_2, and CO_2 is degassed until pCO_2 is lowered to the new equilibrium value.

Degassing of CO_2 has a direct affect on pH and HCO_3^- concentration as shown by equation 1.

$$HCO_3^- + H^+ = CO_2 \text{ (aq)} + H_2O \tag{1}$$
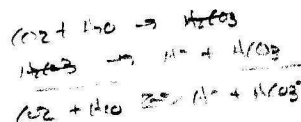
As CO_2 (aq) decreases by loss of CO_2 to the vapor phase, the equilibrium distribution of HCO_3^- and H^+ will be altered to establish a new equilibrium distribution under the new conditions (Gillham and others, 1983). Based on LeChatelier's principle, both H^+ and HCO_3^- will be reduced in concentration. Reduced H^+ concentration causes an increased pH.

Many precipitation and adsorption processes are sensitive to pH. For example, an increase in pH causes a shift in the carbonate equilibrium of the sample. If ground water is at or near saturation with respect to calcite

(common for glacioaqueous aquifers in North Dakota) precipitation of calcite can occur resulting in decreased Ca^{2+} and HCO_3^- concentrations from field to lab.

Temperature changes in the ground-water sample also affect pH. The solubility of CO_2 in water is related inversely to temperature by means of KCO_2 from equation 2 (Wallick, 1977).

$$\log KCO_2 = \log [H_2CO_3] - \log pCO_2 = -13.417 + 2299.6/T + 0.01422T \quad (2)$$

Ground-water temperatures measured at each of the 92 sampling sites ranged from 5.4 to 10.0°C. Samples were not refrigerated during transportation and storage, prior to laboratory analysis and as a result, sample temperatures increased about 15 to 20°C. Reduced solubility of CO_2 caused by increased sample temperature directly affects the H^+ and HCO_3^- concentration as shown by equation 2. This will cause a shift in the carbonate equilibrium of the sample and depending on the saturation state of the sample with respect to calcite, the concentration of Ca^{2+} and HCO_3^- may decrease from field to lab.

To assess the magnitude of carbonate precipitation, the difference between Ca^{2+} plus Mg^{2+} in the treated and raw samples versus the difference between field and lab HCO_3^- was evaluated (fig. 14). If carbonate precipitation in the raw sample is a major reaction, many of the data points should fall on the solid line that is located in the area of the

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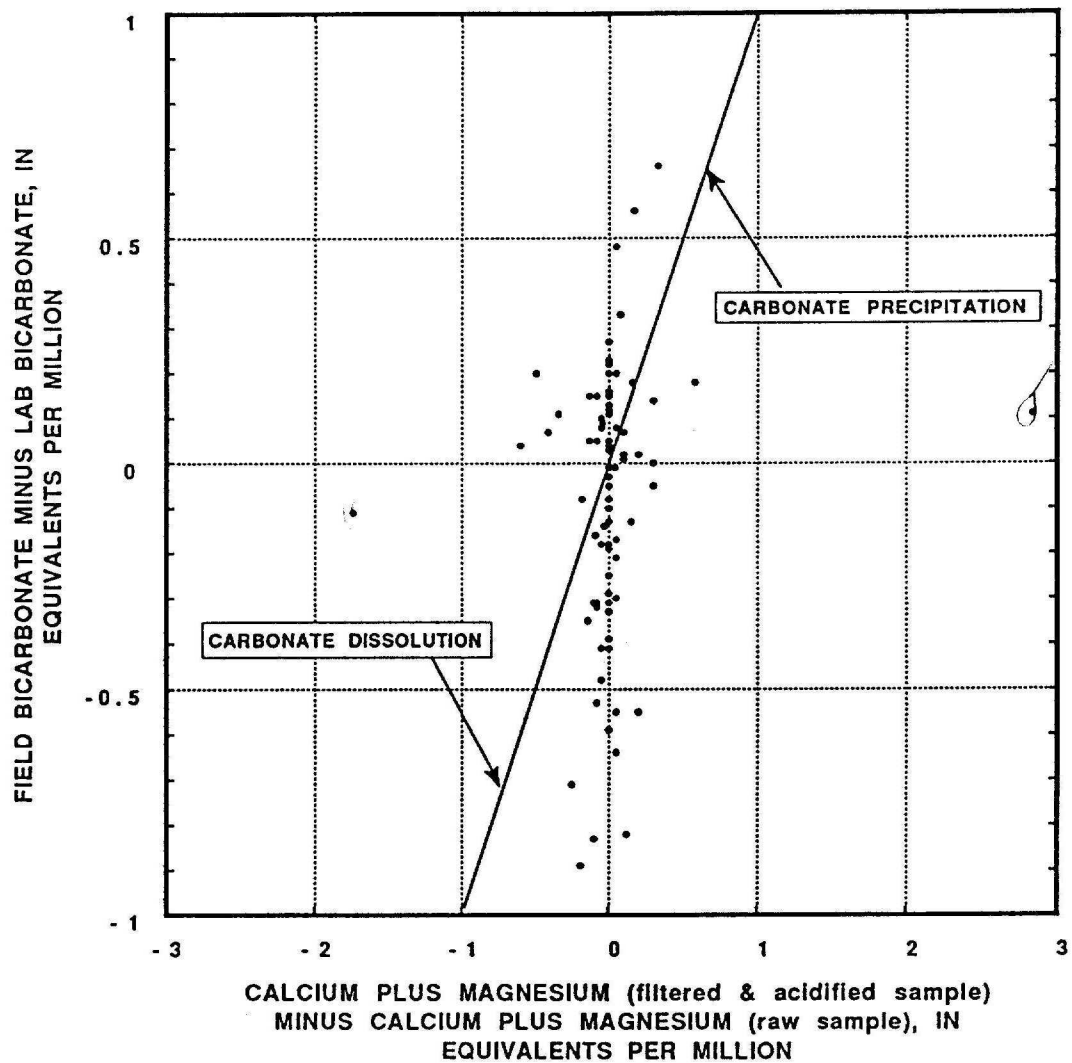
Figure 14. -- Graph showing difference between field and lab
bicarbonate versus difference between calcium
plus magnesium in the treated sample and calcium
plus magnesium in the untreated sample

graph bounded by the positive x and y axes. Carbonate precipitation in the raw samples is minor, as indicated by the small number of points that fall on or close to the solid line.

Carbon-dioxide degassing may increase pH from field to lab without causing significant carbonate precipitation. The lack of apparent carbonate precipitation may be the result of kinetic effects involving, 1) the magnitude of pH changes from field to lab, 2) initial concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^-, 3) activation energy requirements, and 4) availability of nucleating agents in the raw, untreated sample.

Increased pH and HCO_3^- from field to lab may be due to carbonate dissolution in the raw sample. Some of the wells pumped very-fine to fine-grained silty sand. Carbonate minerals (predominantly dolomite and calcite) are ubiquitous in the Oakes aquifer (Shaver and Schuh, 1990). The suspended solids were not removed from the raw sample. If carbonate dissolution in the raw sample is a major reaction, many of the data points should fall on the solid line that is located in the area of the graph bounded by the negative x and y axes (fig. 14). Carbonate dissolution in raw samples is minor as indicated by the lack of points on or close to the solid line.

Increased HCO_3^- coupled with decreased pH, probably is caused by microbial respiration. During respiration, aerobic microbes consume dissolved oxygen (O_2) and introduce CO_2 into

the raw, untreated ground-water sample. CO_2 dissolves in water to form carbonic acid (H_2CO_3). The field pH of the ground-water samples ranged from about 7 to 8. In this pH range, H_2CO_3 dissociates to form H^+ and HCO_3^-. With no carbonate to dissolve in a sediment-free, ground-water sample, the pH must decrease. This process is summarized in equation 3.

$$O_2 \downarrow$$

$$\text{MICROBIAL} \longrightarrow CO_2 + H_2O = H^+ + HCO_3^- \qquad (3)$$
$$\text{RESPIRATION}$$
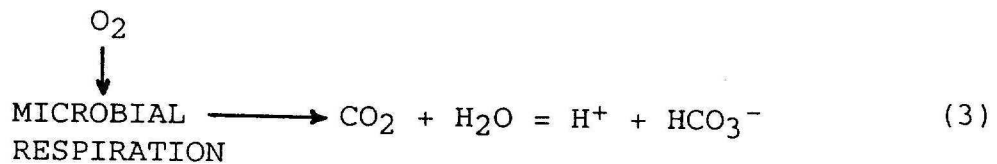
Aerobic microbes are favored over aerobic microbes because ground water in the Oakes aquifer contains dissolved oxygen. Dissolved-oxygen measurements were made on 37 samples collected by the U.S. Geological Survey and concentrations ranged from 0.07 to 4.78 mg/L, with a mean value of 0.75 mg/L. Unfortunately, lab dissolved O_2 measurements were not made on the raw samples. A decrease in dissolved O_2 from field to lab would support microbial respiration.

Oxidation of Fe^{2+} in the raw, untreated sample can also increase H^+ thereby lowering pH. This reaction is shown by equation 4.

$$Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+ + e^- \qquad (4)$$
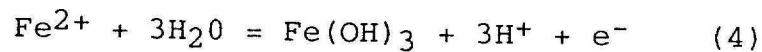
Visual inspection of many of the untreated samples indicated the presence of a reddish-brown precipitate within 12 to 24 hours after collection. Dissolved iron in the Oakes aquifer

probably occurs primarily as Fe^{2+}. Exposure to the atmosphere oxidizes the Fe^{2+} to Fe^{+3} which is unstable and precipitates as $Fe(OH)_3$. Output from WATEQF (Plummer and others, 1976) indicates most ground water samples are at or near saturation with respect to $Fe(OH)_3$.

The strong correlation between field pH and magnitude of pH change for samples with dissolved-solids concentrations less than 400 mg/L (figure 9) may be the result of preferential microbial growth. As a general rule, bacterial growth is enhanced by increased pH from acidic to moderately alkaline conditions (Alexander, 1977, p. 22). The most alkaline samples showed the largest decrease in pH from field to lab. In addition, increased temperature from field to lab probably further enhanced bacterial growth.

Effect of sample bias on ion balance

When cation and anion totals are not equal, the chemical analysis may be incomplete, inaccurate, or may have undergone a chemical change from field to lab. The North Dakota State Laboratory uses equation 5 to estimate ion-balance percent error (e):

$$e = \frac{r_c - r_a}{r_c + r_a} \times 100 \qquad (5)$$

where:

$\quad r_c$ = sum of cations, in meq/L
$\quad r_a$ = sum of anions, in meq/L

Values of e greater than 5 percent suggest a significant enough error to preclude the analysis from certain interpretive applications. In general, the value of e should be less than 2 percent (Matthess, 1982). However, Hem (1970) states that errors exceeding 5 percent are sometimes unavoidable when the total of cations and anions is less than 5 meq/L. For this study, however, there are no analyses with total cations and anions less than 5 meq/L.

Figure 15 is a plot of ion balance (e) computed using lab HCO_3^- versus field HCO_3^- minus lab HCO_3^-. The regression analysis shows a highly significant correlation (P = 0.0001) between ion balance using lab HCO_3^- and the difference between field and lab HCO_3^-. A correlation coefficient of 0.74 indicates 55 percent of the variability in ion balance computed using lab HCO_3^- is attributed to the change in HCO_3^- from field to lab. Excess anions (negative e values) generally correspond to increased HCO_3^- from field to lab and excess cations (positive e values) generally correspond to decreased HCO_3^- from field to lab.

Most of the data points in figure 15 are clustered around the x(0), y(-1) coordinates. The HCO_3^- scatter for this group of data points is within ± 0.16 e.p.m. (10 mg/L) and is considered within the range of analytical accuracy for the method used to measure field alkalinity. These samples are within an ion balance of ± 2 percent.

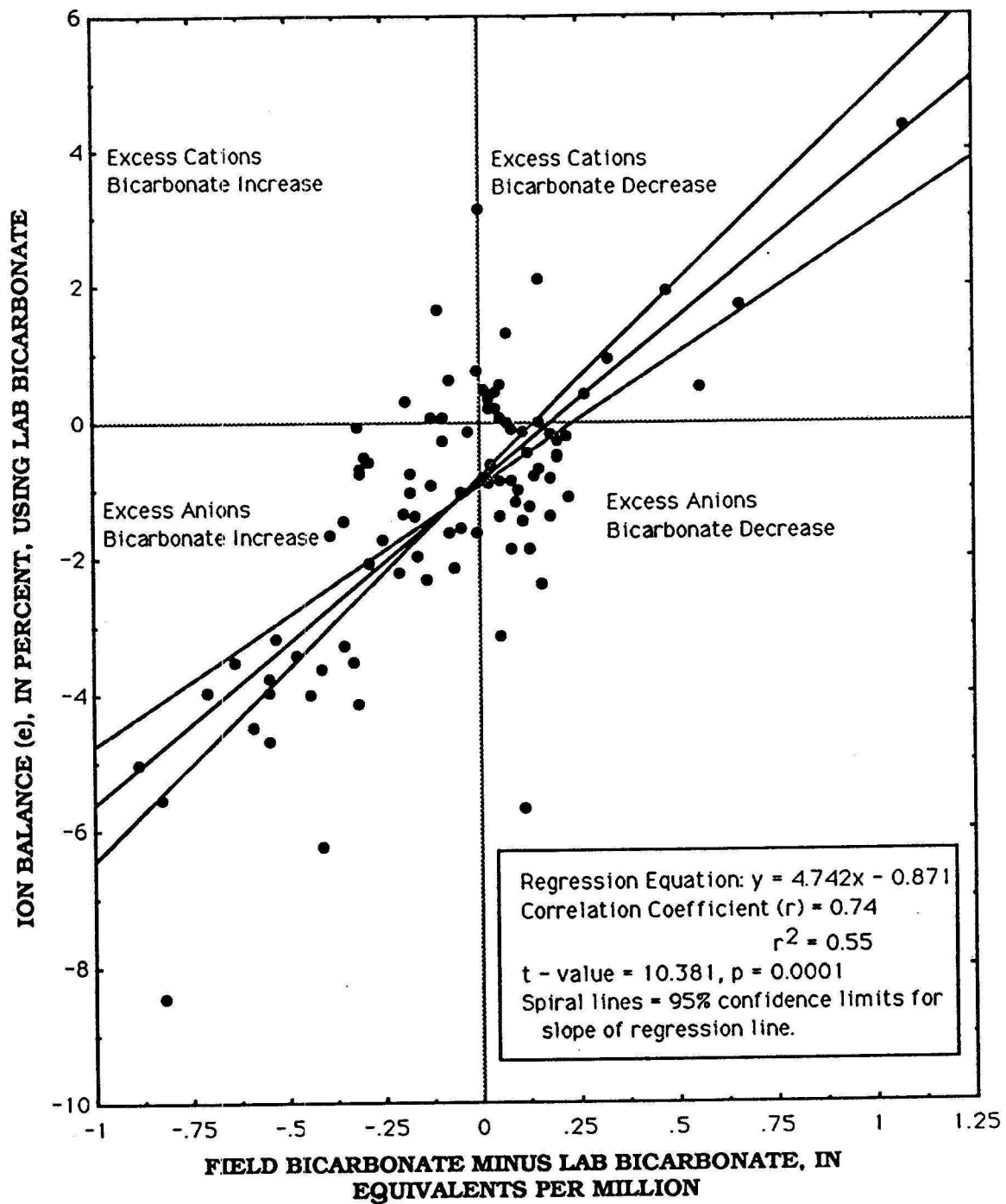A smaller cluster of data points occurs around the

Figure 15. -- Graph showing regression analysis of percent ion balance calculated using lab bicarbonate versus change in bicarbonate from field to lab

x(-0.5), y(-4) coordinates of the graph shown in figure 15. The data points have negative e values greater than 3 percent. These samples could be eliminated for certain interpretive applications because ion balance exceeds 2 percent.

There is a lack of data with positive e values greater than 2.5 percent (fig. 15). This further suggests that the magnitude of carbonate precipitation from field to lab is minor.

Arithmetic probability plots of ion balance computed using field HCO_3^- and computed using lab HCO_3^- are shown in figure 16. Except for the two end points, the plot of ion balance computed using field HCO_3^- is approximately linear indicating a normal distribution. The plot of ion balance computed using lab HCO_3^- is concave downward indicating a non-normal distribution.

Skewness analysis of the distributions of ion balance computed using field HCO_3^- and ion balance computed using lab HCO_3^- are summarized in table 7. At a five percent level of significance, there is no reason to reject the null hypothesis that the ion-balance distribution computed using field HCO_3^- is normal. At a level of significance of less than one percent, the null hypothesis that the ion balance distribution computed using lab HCO_3^- is normal is rejected and it is concluded that the distribution is not normal.
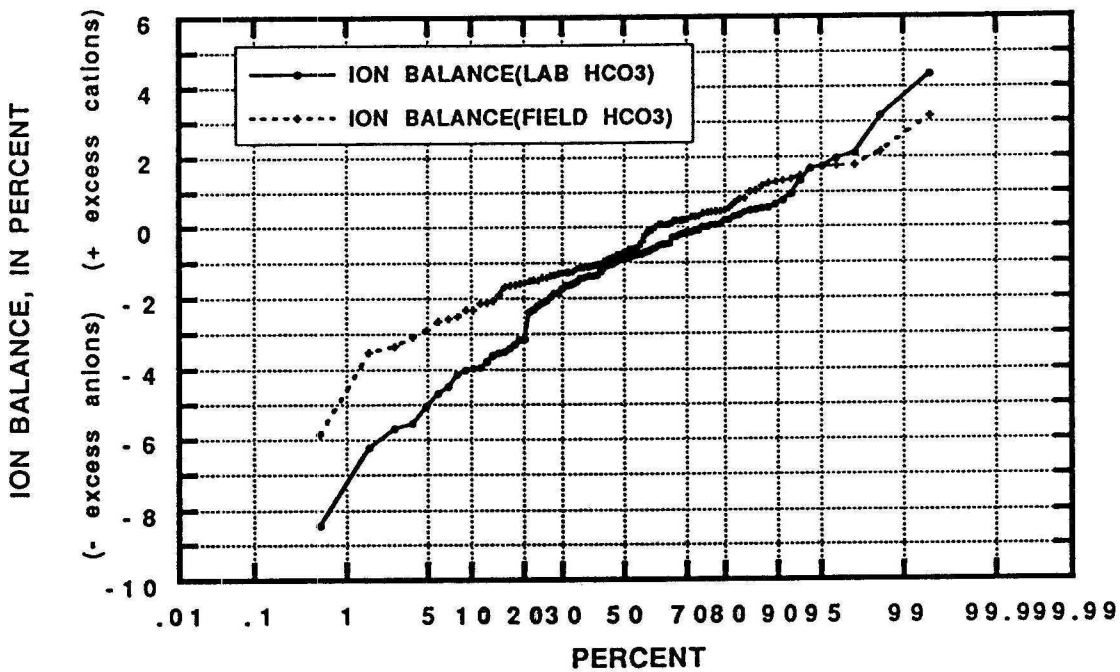
Figure 16. -- Graph showing arithmetic probability plots of ion balance computed using lab and field bicarbonate

TABLE 7. -- Analysis of skewness of ion-balance computed using field HCO_3^- and ion-balance computed using lab HCO_3^-

	Sample Size	Computed Skewness Coefficient	Tabulated Skewness Coefficient	Level of Significance
Ion Balance (Field HCO_3^-)	92	-0.35	0.40	>0.05
Ion Balance (Lab HCO_3^-)	92	-0.63	0.60	<0.01

[*] from Snedecor and Cochran, 1989 - Table A19i

Based on the regression analysis in figure 15 and skewness analysis of the frequency distributions of ion balance it is apparent that change in HCO_3^- from field to lab significantly affects ion balance. When ion balance is computed using HCO_3^- calculated from field alkalinity measurements, five percent of the analyses (5 out of 92) could be discarded because ion balance exceeds three percent. When ion balance is computed using HCO_3^- calculated from lab alkalinity measurements, 23 percent of the analyses (21 out of 92) could be discarded because ion balance exceeds three percent.

Analysis of skewness of the frequency distribution of differences between ion balance computed using field HCO_3^- and ion balance computed using lab HCO_3^- is summarized in table 8. At a five percent level of significance there is no reason to reject the null hypothesis that the distribution of ion balance differences is normal.

TABLE 8. -- Analysis of skewness of the distribution of differences between ion balance computed using field HCO_3^- and ion balance computed using lab HCO_3^-

Sample Size	Computed Skewness Coefficient	Tabulated Skewness Coefficient *	Level of Significance
92	0.37	0.40	p>0.05

* from Snedecor and Cochran, 1989 - Table A19i

Based on the above, the parametric, paired t-test is used to compare the means of both ion balance distributions. A paired t value of 3.09 is computed and is significant at 0.003 percent (table 9). The mean ion balance difference is 0.67 indicating a slight tendency for ion balance computed using lab HCO_3^- to have excess anions. Therefore, the null hypothesis that population means are the same is rejected and it is concluded that the two population means differ suggesting that ion balance computed using lab HCO_3^- is characterized by determinate error (bias).

TABLE 9. -- Values of the paired t-test used to compare the means of ion balance computed using field and lab bicarbonate

Degrees of Freedom:	Mean X - Y:	Paired t Value:	Probability (2-tail):
91	.666	3.09	.0027

X = ion balance, in percent, computed using field HCO_3^-

Y = ion balance, in percent, computed using lab HCO_3^-

Effect of sample bias on equilibrium distribution of calcite

The equilibrium state between ground water and mineral phases of the aquifer matrix can be examined by use of

saturation indices (SI), expressed as: SI mineral = log IAP/Ksp, where IAP is the ion-activity product calculated from analytical data and Ksp is the solubility product, an equilibrium constant for ions in a saturated solution in contact with excess solid phases. A saturation index of 0.0 indicates that IAP and Ksp are equal and that thermo-dynamic equilibrium of the solution exists with the mineral phase in question. A negative or positive index indicate undersaturation and oversaturation, respectively.

Saturation indices with respect to calcite for 91 water samples were computed using WATEQF (Plummer and others, 1976) using field HCO_3^- and pH. The frequency distribution of these saturation indices is illustrated by the histogram in figure 17. The indices range from 0.637 to -0.242 and the mean and standard deviation are 0.161 and 0.218, respectively. Twenty-two ground-water samples are undersaturated with respect to calcite and 69 samples are oversaturated with respect to calcite. These data indicate that throughout much of the Oakes aquifer, ground water is at or near thermo-dynamic equilibrium with calcite (Shaver and Schuh, 1990).

Saturation indices with respect to calcite for the same 91 water samples were also computed by WATEQF using lab HCO_3^- and pH. The frequency distribution of these saturation indices is shown by the histogram in figure 18. The indices range from 1.005 to -0.738 and the mean and standard deviation are 0.140 and 0.436, respectively.
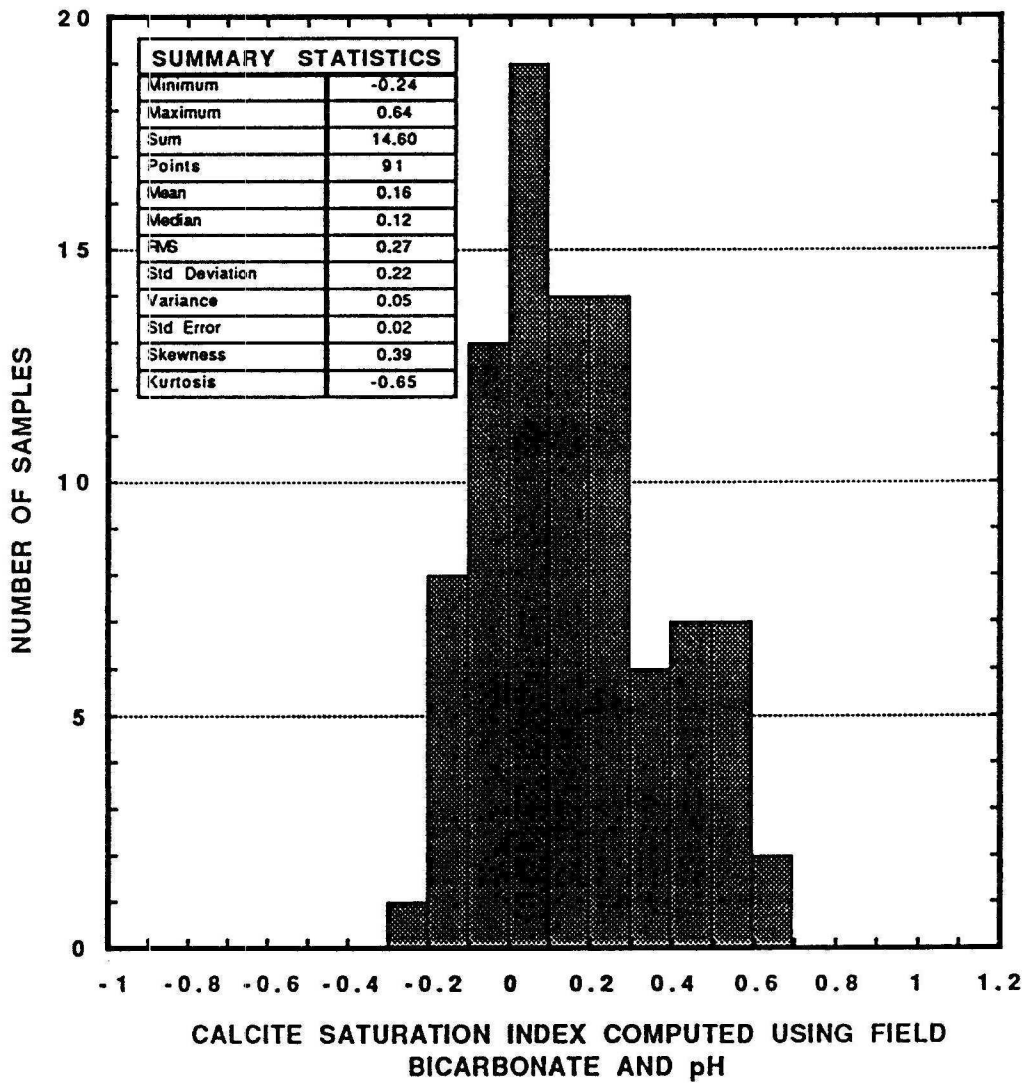
40

Figure 17. -- Graph showing frequency distribution of calcite
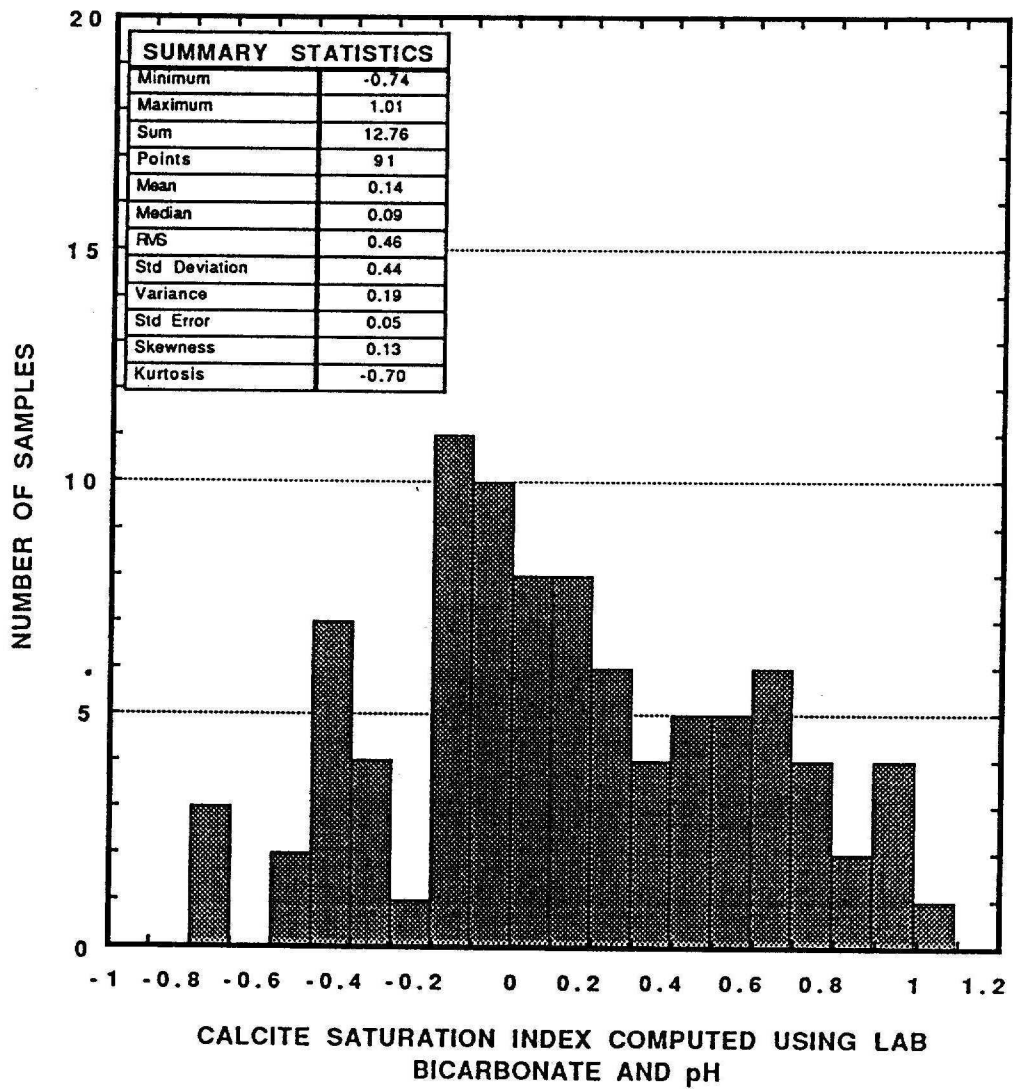saturation index computed using field
bicarbonate and pH

Figure 18. -- Graph showing frequency distribution of calcite saturation index computed using lab bicarbonate and pH

The difference between calcite saturation indices computed using field HCO_3^- and pH and calcite saturation indices computed using lab HCO_3^- and pH is illustrated by the historgram in figure 19. The differences range from 0.630 to -0.788 and the mean and standard deviation are -0.020 and 0.316, respectively.

Analysis of skewness for the frequency distributions in figures 17, 18, and 19 indicate no basis for rejecting the null hypothesis that the distributions are normal at a five percent level of significance (table 10). Based on normality, the parametric paired t-test was used to compare the means of the two saturation index frequency distributions shown on figures 17 and 18.

TABLE 10. -- Analysis of skewness of distributions of calcite saturation indices computed using field and lab HCO_3^- and distribution of differences in calcite saturation indices

	Sample Size	Computed Skewness Coefficient	Tabulated Skewness Coefficient [*]	Level of Significance
SI Calcite (Field HCO_3^-)	91	0.39	0.40	$p > 0.05$
SI Calcite (Lab HCO_3^-)	91	0.13	0.40	$P > 0.05$
SI Calcite (Differences)	91	-0.19	0.40	$P > 0.05$

[*] from Snedecor and Cochran, 1989 - Table A19i

The paired t-test (table 11) indicates that there is no basis to reject the null hypothesis that the means of the two saturation index distributions are equal. Therefore, a calcite saturation index computed using field pH and HCO_3^- is just as likely to be larger than the calcite saturation index
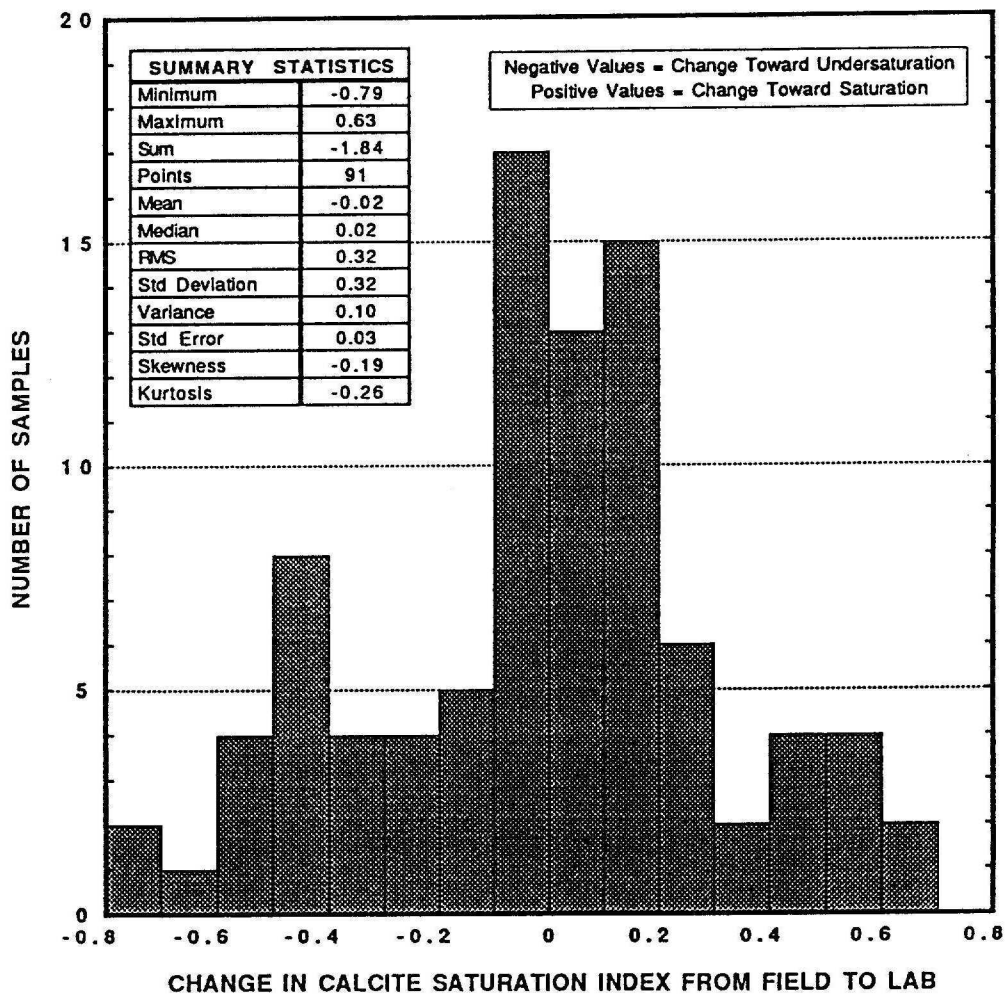
43

Figure 19. -- Graph showing frequency distribution of difference in calcite saturation index computed using field bicarbonate and pH and calcite saturation index computed using lab bicarbonate and pH.

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computed using lab pH and HCO_3^- as the calcite saturation
index computed using lab pH and HCO_3^- is likely to be larger
than the calcite saturation index computed using field pH and
HCO_3^-.

TABLE 11. -- Values of the paired t-test used to compare the
means of calcite saturation index computed using
field pH and bicarbonate and using lab pH and
bicarbonate

Degrees of Freedom:	Mean X - Y:	Paired t Value:	Probability (2-tail):
90	.02	.611	.5427

X = Calcite saturation index computed using field pH and HCO_3^-

Y = Calcite saturation index computed using lab pH and HCO_3^-

The range and variance in figures 17 and 18 differ
considerably. An F-test is used to compare the variances
(Snedecor and Cochran, 1989). The computed F-statistic is
4.04 and is significant at less than 0.005 percent
($P < 0.005$). As a result, the null hypothesis that the
variances of the two saturation index distributions are equal
is rejected, and it is concluded that the variances differ.

The samples in figure 19 were partitioned into two
groups, one with dissolved-solids concentrations less than
400 mg/L (fig. 20) and the other group with dissolved-solids
concentrations greater than 400 mg/L (fig. 21). Analysis of
figures 20 and 21 indicate a predominate change toward
undersaturation from field to lab for samples with dissolved-
solids concentrations less than 400 mg/L and a predominate
change toward oversaturation for samples with dissolved-
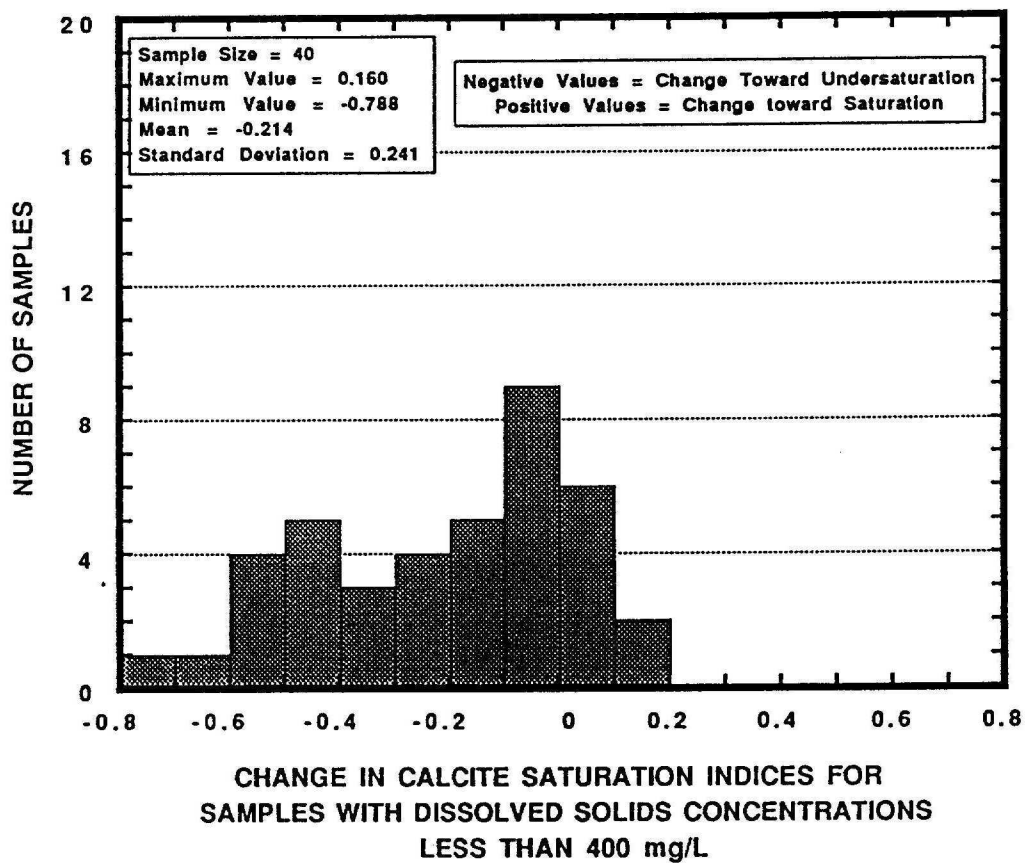
Figure 20. -- Graph showing frequency distribution of change
in calcite saturation index from field to lab
for samples with dissolved-solids concentrations
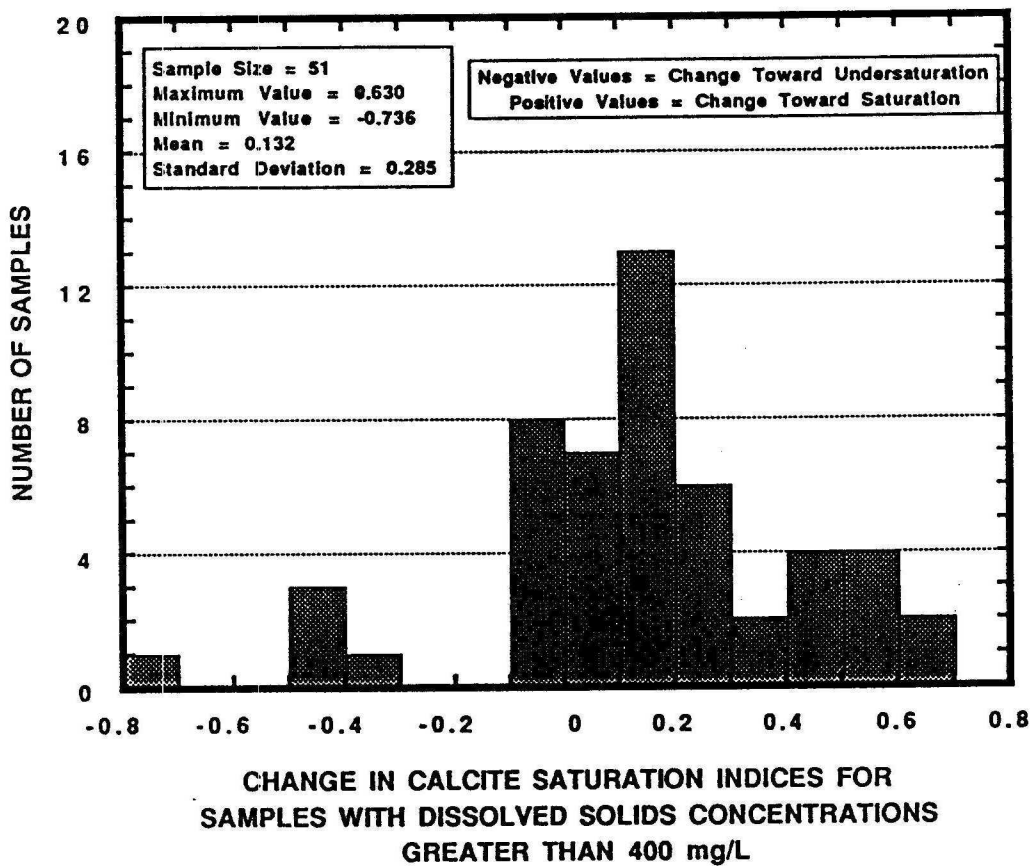less than 400 mg/L

Figure 21. -- Graph showing frequency distribution of change
            in calcite saturation index from field to lab
            for samples with dissolved-solids concentrations
            greater than 400 mg/L

solids concentrations greater than 400 mg/L. Since pH predominantly decreased from field to lab in samples with dissolved-solids concentration less than 400 mg/L (fig. 9) and increased in samples with dissolved-solids concentrations greater than 400 mg/L (fig. 10) , the change in calcite saturation indices appears strongly pH dependent.

Figure 22 is a linear regression analysis of change in calcite saturation index versus field pH minus lab pH. A correlation coefficient (r) of 0.98 indicates 96 percent of the variability in calcite saturation index change from field to lab is attributed to change in pH from field to lab.

The dominance of pH change over HCO_3^- change in relation to change in calcite saturation index is further illustrated by the frequency distribution in figure 23. Figure 23 shows the distribution of differences between calcite saturation indices calculated using field HCO_3^- and pH and calcite saturation indices calculated using lab HCO_3^- and field pH. The difference in calcite saturation indices range from -0.339 to 0.232 and the mean and standard deviation are -0.028 and 0.078, respectively. Comparison of the frequency distributions shown in figures 19 and 23 indicate that changes in calcite saturation index from field to lab are dominated by observed pH bias and not by observed HCO_3^- bias.

SUMMARY AND CONCLUSIONS

Ground-water samples collected in May and June 1989, for the Oakes aquifer hydrochemical study showed positive HCO_3^-
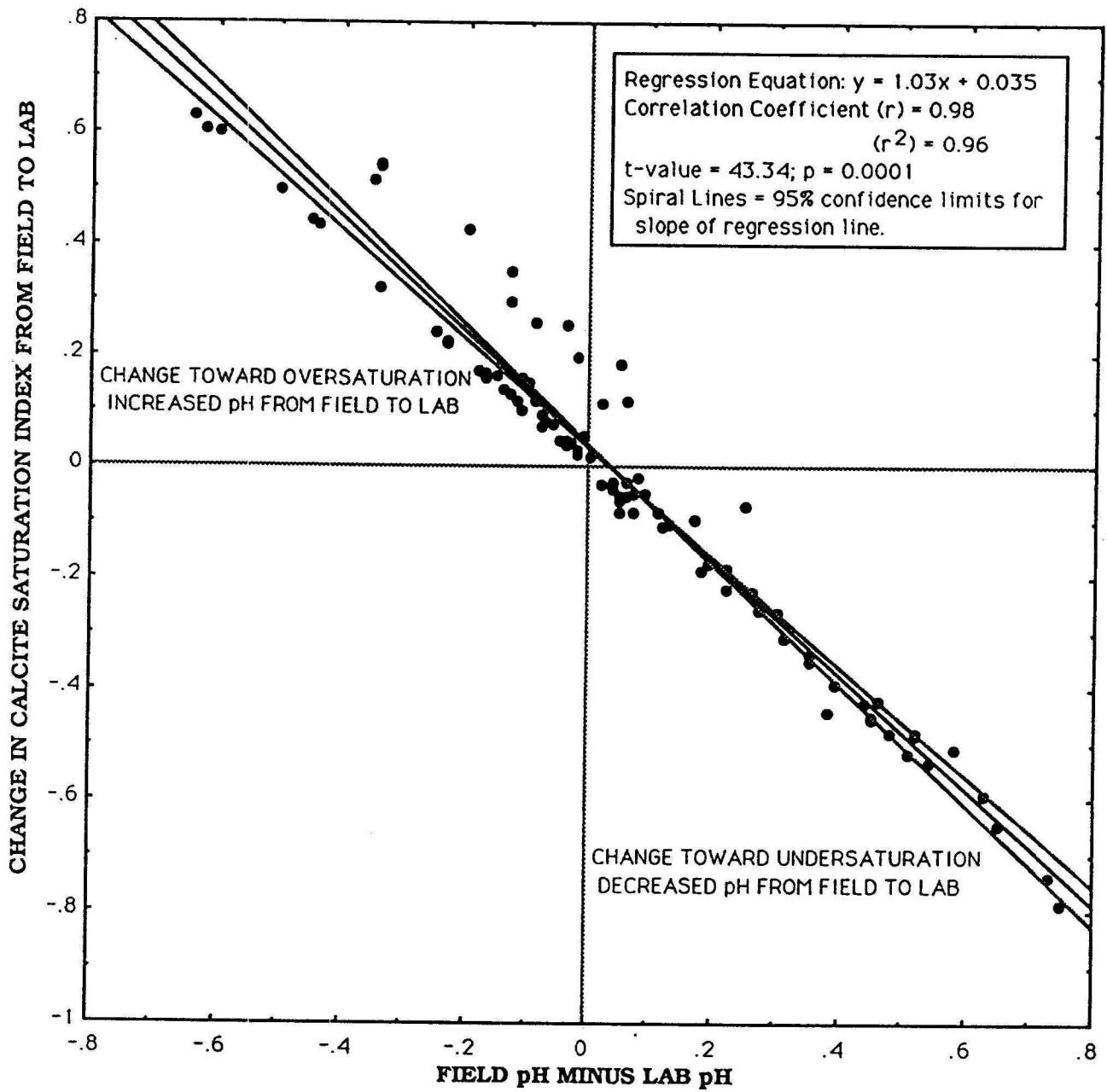
Figure 22. -- Graph showing regression analysis of change in calcite saturation index from field to lab versus change in pH from field to lab
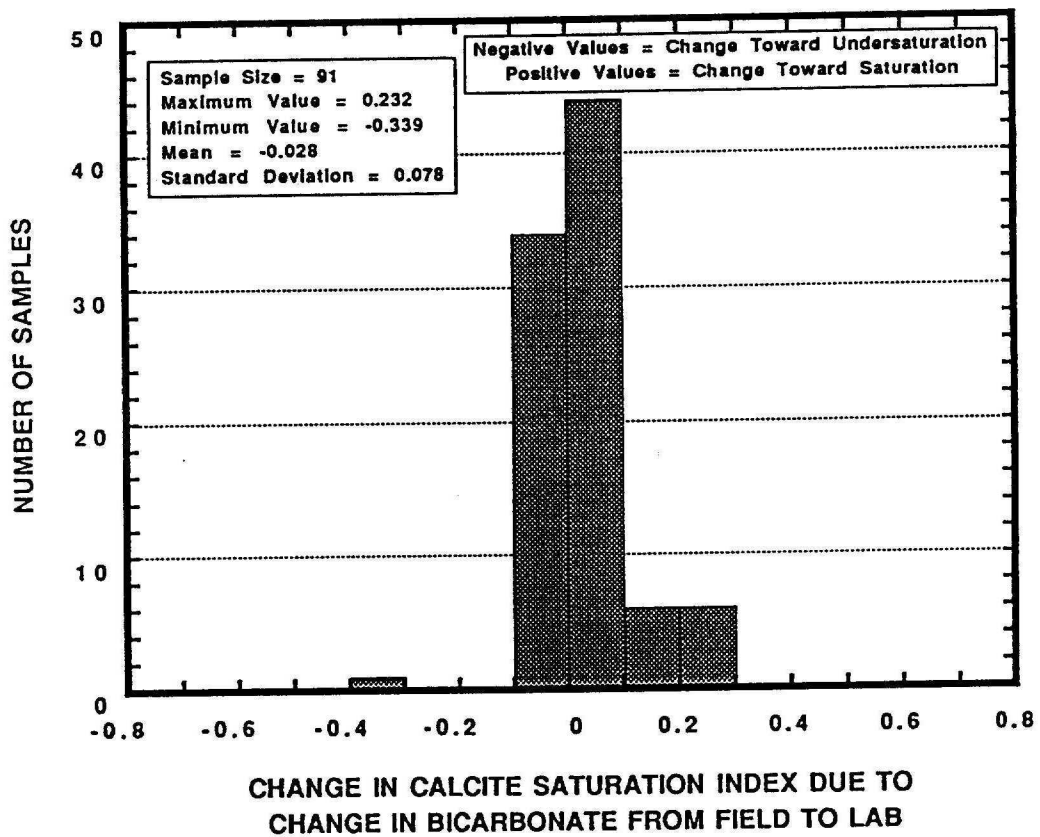
Figure 23. -- Graph showing frequency distribution of difference in calcite saturation index computed using field bicarbonate and pH and calcite saturation index computed using lab bicarbonate and field pH

bias (increased HCO_3^-) from field to lab. The direction of pH bias from field to lab is a function of initial (field) pH. Positive pH bias (decreased pH) generally is associated with lower pH ground water and negative pH bias (increased pH) generally is associated with higher pH ground water. Preferential bacterial growth may cause this observed pH relationship. As a general rule, bacterial growth is enhanced by increased pH from acidic to moderately alkaline conditions. Increased water temperatures of about 15°C to 20°C from field to lab probably further enhanced bacteria growth.

Increased HCO_3^- coupled with a decrease in pH is more pronounced than either an increase in HCO_3^- coupled with an increase in pH or a decrease in HCO_3^- coupled with an increase in pH. Increased HCO_3^- coupled with a decrease in pH from field to lab was not anticipated prior to sampling. Bacterial respiration is a plausible explanation for this sample bias. Aerobic bacteria are favored over anaerobic bacteria because ground water in the Oakes aquifer is characterized by dissolved-oxygen concentrations ranging between 0.07 and 4.78 mg/L, with a mean value of 0.75 mg/L (32 samples).

Increased HCO_3^- coupled with an increase in pH is attributed to carbonate dissolution in the untreated sample from field to lab. The magnitude of carbonate dissolution was minor.

Decreased HCO_3^- coupled with an increase in pH from field to lab is attributed to CO_2 degassing and subsequent carbonate precipitation. The magnitude of carbonate precipitation was minor.

Observed HCO_3^- bias from field to lab significantly distorted ion balance distribution. Excess anions generally correspond to increased HCO_3^- from field to lab and excess cations generally correspond to decreased HCO_3^- from field to lab. When ion balance is computed using HCO_3^- calculated from field alkalinity measurements, five percent of the analyses (5 out of 92) may be discarded because ion balance exceeds three percent. When ion balance is computed using lab HCO_3^- determinations 23 percent of the analyses (21 out of 92) may be discarded because ion balance exceeds three percent.

Observed HCO_3^- and pH bias from field to lab significantly distorted the distribution of calcite saturation indices. Change in calcite saturation index was more sensitive to observed pH bias and less sensitive to observed HCO_3^- bias. Samples with dissolved-solids concentrations less than 400 mg/L that were characterized by a positive pH bias (decreased pH) showed a shift in calcite saturation index toward undersaturation. Samples with dissolved-solids concentrations greater than 400 mg/L that were characterized by a negative pH bias (increased pH) showed a shift in calcite saturation index toward oversaturation.

Based on the results of this study, it is recommended that field measurements of pH and alkalinity (for HCO_3^- determination) be made to reduce sample bias. Reduction of observed pH and HCO_3^- sample bias leads to a more accurate geochemical interpretation of the ground-water flow system.

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