# Soil-water geochemistry of Outer Island, Branford, Connecticut: A Conceptual Model

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# Introduction

The purpose of this study has been to develop a conceptual model that describes the factors contributing to the soil water chemistry of a small archipelago island in Long Island Sound. The study attempted to obtain representative samples of island soil, precipitation and soil water for the purpose of understanding their chemical relationships. The source of the soil water chemistry was investigated using a technique known as source-rock deduction which used a simple mass-balance approach and graphical representations such as the Stiff and Piper diagram (Hounslow, 1995). A mass-balance is simply a budget calculation involving the sources from which the dissolved constituents in the soil water are derived (Drever,1982). The possible sources that were investigated in this study are the island precipitation, seawater, and soil mineralogy.

Outer Island is located in Long Island Sound approximately 1 mile off the coast of Branford, Connecticut. It is a small island located on the outer edge of the Thimble Islands archipelago and is approximately 250 meters in length and 90 meters in width. It is oriented lengthwise approximately west to east (Figure 1). There are primarily two structures on the island, a U.S. Fish and Wildlife facility and a residential home which is lived in infrequently in the summer months. Approximately one half of the islands surface is exposed bedrock consisting of a highly foliated granite gneiss composed of primarily quartz, plagioclase, and microcline. Mafics included in the bedrock are principally biotite with minor amounts of hornblende. The soil on the island in primarily restricted to the central portions of the island where attempts have been made to retain it using cement containment walls. These walls are most prevalent on the south and southeast side of the island. This soil is not believed to be indigenous to the island, but was instead brought to the island so as to permit vegetation. The actual source of the soil is not clear, but it is similar to the glacial till found on the nearby inland.

Although the conceptual model presented in this study may be applicable to other small island environments, it should be cautioned that the contributing factors that are involved in the mass-balance approach are quite variable. Therefore, this study should be viewed as specific to this island and perhaps others of the Thimble Island archipelago only. In addition to providing insight into the hydrogeochemistry of the island, this study has also made available information useful in assessing the soil quality in terms of salinity and sodium hazards to the vegetation.

## Investigative Techniques

### Soil Sampling

A reconnaissance of Outer Island was performed on April 28, 1996. Soil depths to bedrock were estimated at 30 locations around the island with the aid of a soil probe and relative moisture was observed. Although moisture increased with depth, the soil did appear to be nearly saturated throughout. Based on the relative soil moisture it was decided that slim tube lysimeters could be used for soil solution extraction.

In addition, a map was produced showing the soil depths that were recorded during the field reconnaissance (Figure 2). The greatest soil depths are reported northwest of the residential home.

The four sites used in this investigation were chosen to provide adequate soil depth and maximum separation from each other. In addition, the sites could not be located on the north end of the island since this area was restricted by the U.S. Fish and Wildlife agency due to bird nesting. The sites were located using a surveyor's compass and an electronic distance measurer (Figure 1). Each site has been assigned an alphabetic designation A though D.

Site A is located 20 m from a 7ft cement containment wall. This wall is discontinuous and leaves the site exposed to south. The surface of the area around the site is covered with lush green grass. There is no natural or artificial canopy over the site leaving it the most exposed site of the four.

Site B is the most secluded of the four and is positioned beneath a thick natural canopy consisting of pine trees. Associated with these trees we find that the surface of the area around the site is covered by a thin blanket of pine needles with very little grass. In general this site is the farthest from the shore front and should experience the most interception from incoming precipitation.

Site C is located approximatly 40 m from the east corner of the cement containment wall. This site is similar to site B although the canopy is not as dense. It is topographically the highest site and is not as exposed as site A. This site is also the second closest to the waters edge during periods of high tide.

Site D is nearest to the shore front especially during periods of high tide. It is relatively exposed although it is positioned near one tree and thus is prone to some interception. The surface is covered by lush green grass.

Soil cores were retrieved from each of the four sites using an Environmental Subsurface Probe. The average depth of the cores was approximately 68 cm with an average compaction of 7.5 cm.

## Soil Analysis

The methods for describing soils presented by ASTM were used to provide a brief profile of each of the soil cores retrieved from each site. Each core was divided into soil zones based on changes in color, texture, and/or grain size (Appendix A).

For the purpose of chemical analysis, each of the cores were separated into two horizons, A near the surface and B at depth. In some cases this required the combining of

**Table 2. Statistical evaluation of the soil chemistry of Outer Island.**

### Soil Evaluation

| TOTAL | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | MnO | CaO | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|
| AA | 68.51 | 12.21 | 3.72 | 0.71 | 0.09 | 0.82 | 2.56 | 1.44 |
| AB | 71.09 | 13.97 | 3.95 | 0.73 | 0.06 | 0.67 | 3.26 | 1.6 |
| BA | 69.7 | 14.05 | 3.57 | 0.62 | 0.07 | 0.72 | 3.35 | 1.64 |
| BB | 67.12 | 14.68 | 4.43 | 0.85 | 0.1 | 0.65 | 3.23 | 1.86 |
| CA | 65.01 | 12.25 | 3.81 | 0.59 | 0.09 | 0.97 | 2.82 | 1.42 |
| CB | 66.12 | 13.4 | 4.33 | 0.77 | 0.07 | 1.03 | 2.69 | 1.44 |
| DA | 69.34 | 11.32 | 3.6 | 0.66 | 0.07 | 0.96 | 2.66 | 1.43 |
| DB | 67.12 | 14.1 | 4.28 | 0.75 | 0.05 | 0.63 | 2.72 | 1.57 |
| SD: | 2.02 | 1.18 | 0.34 | 0.08 | 0.02 | 0.16 | 0.32 | 0.15 |
| Mean: | 68.00 | 13.25 | 3.96 | 0.71 | 0.08 | 0.81 | 2.91 | 1.55 |
| AvgDev: | 1.65875 | 0.990625 | 0.289063 | 0.065 | 0.01375 | 0.13875 | 0.276563 | 0.1175 |

**Near Surface**

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | MnO | CaO | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|
| AA | 68.51 | 12.21 | 3.72 | 0.71 | 0.09 | 0.82 | 2.56 | 1.44 |
| BA | 69.7 | 14.05 | 3.57 | 0.62 | 0.07 | 0.72 | 3.35 | 1.64 |
| CA | 65.01 | 12.25 | 3.81 | 0.59 | 0.09 | 0.97 | 2.82 | 1.42 |
| DA | 69.34 | 11.32 | 3.6 | 0.66 | 0.07 | 0.96 | 2.66 | 1.43 |
| SD: | 2.15 | 1.15 | 0.11 | 0.05 | 0.01 | 0.12 | 0.35 | 0.11 |
| Mean: | 68.14 | 12.46 | 3.68 | 0.65 | 0.08 | 0.87 | 2.85 | 1.48 |

**At Depth**

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | MnO | CaO | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|
| AB | 71.09 | 13.97 | 3.95 | 0.73 | 0.06 | 0.67 | 3.26 | 1.6 |
| BB | 67.12 | 14.68 | 4.43 | 0.85 | 0.1 | 0.65 | 3.23 | 1.86 |
| CB | 66.12 | 13.4 | 4.33 | 0.77 | 0.07 | 1.03 | 2.69 | 1.44 |
| DB | 67.12 | 14.1 | 4.28 | 0.75 | 0.05 | 0.63 | 2.72 | 1.57 |
| SD: | 2.20 | 0.53 | 0.21 | 0.05 | 0.02 | 0.19 | 0.31 | 0.18 |
| Mean: | 67.86 | 14.04 | 4.25 | 0.78 | 0.07 | 0.75 | 2.98 | 1.62 |

Each suction lysimeter was identified with the letter designation of the site and by a number designation 1 through 8. Numbers 1 through 4 represent those suction lysimeters that are at depth while 5 through 8 are those near surface (Table 4).

**Table 4: Suction lysimeter penetration depth measured from surface to bottom of porous cup**

| | | | |
|---|---|---|---|
| A1 | A5 | B2 | B6 |
| 57.2 cm | 30.5 cm | 57.2 cm | 30.5 cm |
| C3 | C7 | D4 | D8 |
| 49.5 cm | 30.5 cm | 57.2 cm | 30.5 cm |

The suction lysimeters were allowed to acclimate for 47 days prior to sample collection. During this time they were purged on a weekly basis and left with various amounts of suction that was applied using a hand pump. It was found that between 50 and 60 cm/Hg resulted in the greatest yield of soil solution. At no time was greater then 60 cm/Hg applied to the suction lysimeters.

Collection of soil solution samples was conducted over 5 days beginning on August 14, 1996. Five days were needed because a minimum of 40 ml was required for chemical analysis from each of the suction lysimeters and the yields were too low at the sites to collect it all in one day. The greatest yields were found at site D which supplied the minimum 40 ml from both its suction lysimeters in only two days while site A required 5 days primarily due to faulty gaskets in both the suction lysimeters at this site. Each sample was collected in a 100 ml plastic bottle and its pH and temperature were checked using pH paper and a thermometer. It was then refrigerated and sent directly to Environmental Research Institute, University of Connecticut. Each time additional samples were collected and brought to the lab, they were combined with the previous samples until the minimum of 40 ml was obtained.

significant amounts that were not tested for in this study. A discoloration of the soil solution was noted at site D consistent with the presence of organic ions. Also, anthropogenic sources my be responsible such as fertilizers.

**Precipitation sampling**

Two rain gauges were setup in separate locations and identified as rain gauge A to the south and B to the north (Figure 1). Since the gauges were usually monitored only on a weekly basis they were modified using plastic wrap to prevent evaporation.

The precipitation amounts recorded from rain gauges A and B are shown in figure 3. Tensiometer readings that were made at sites B and C have been overlain onto the graph reflect the relationship between soil suction and precipitation influx.

Two rain collectors were installed on the island in close proximity to the rain gauges on August 16. A rain sample was collected in a 100 ml plastic bottle from the southern-most collector on August 28. This sample's pH and temperature were checked with pH paper and a thermometer and the sample brought immediately to Environmental Research Institute, University of Connecticut for analysis the same as with the soil solution samples. The northern-most rain collector was contaminated by bird droppings and could not be used. The results of the chemical analysis have been included in table 5. Also shown are the results of the cation-anion balance.

The TDI content of that of Outer Island precipitation is substantially lower than that of seawater. The only distinction between that of Outer Island precipitation and that of seawater apparent in the shape analysis is the Mg:SO4 ratio. Thus it can be inferred that the precipitation on Outer Island has been greatly influenced by seaspray.

When a similar analysis was performed comparing the soil solutions to that of seawater and Outer Island precipitation, it was found that all of the samples retain the characteristic Mg:SO4 ration of that of precipitation. In fact, the C3 and D4 soil solutions are very similar to the Outer Island precipitation per the shape analysis. All other samples show Na+K in excess of Cl which is unlike seawater or precipitation suggesting additional sources of either Na or K or both. Also, A5 and C7 samples show SO4 in excess of Cl suggesting additional sources of SO4 at these suction lysimeters.

## Piper Diagram

Further interpretation of the waters were made with the aid of a Piper diagram (Hounslow, 1995) (Figure 5). With the exception of D4, all of the cations cluster in the diamond portion of the Piper diagram. Samples A, B2, C, and D8 all show greater Na+K values then that of either the rain or the seawater suggesting additional sources. B6 shows a Na+K content similar to that of the rain water, while D4 shows elevated Mg values.

There is a wide range in SO4 values but all are in excess of seawater and A1, B2, and D4 are very close to that of the rain water. The remaining samples all show an additional an source of SO4. All of the water types including the rain water plot as saline.

One hypothesis that was originally presented was that during storm surges large quantities of seawater infiltrated into the soil followed later by precipitation. This would produce a soil solution that was a mixture between that of seawater and precipitation. However, the Piper diagram shows that this can not be the case because none of the soil solution samples occur on a mixing line between that of seawater and rain water.

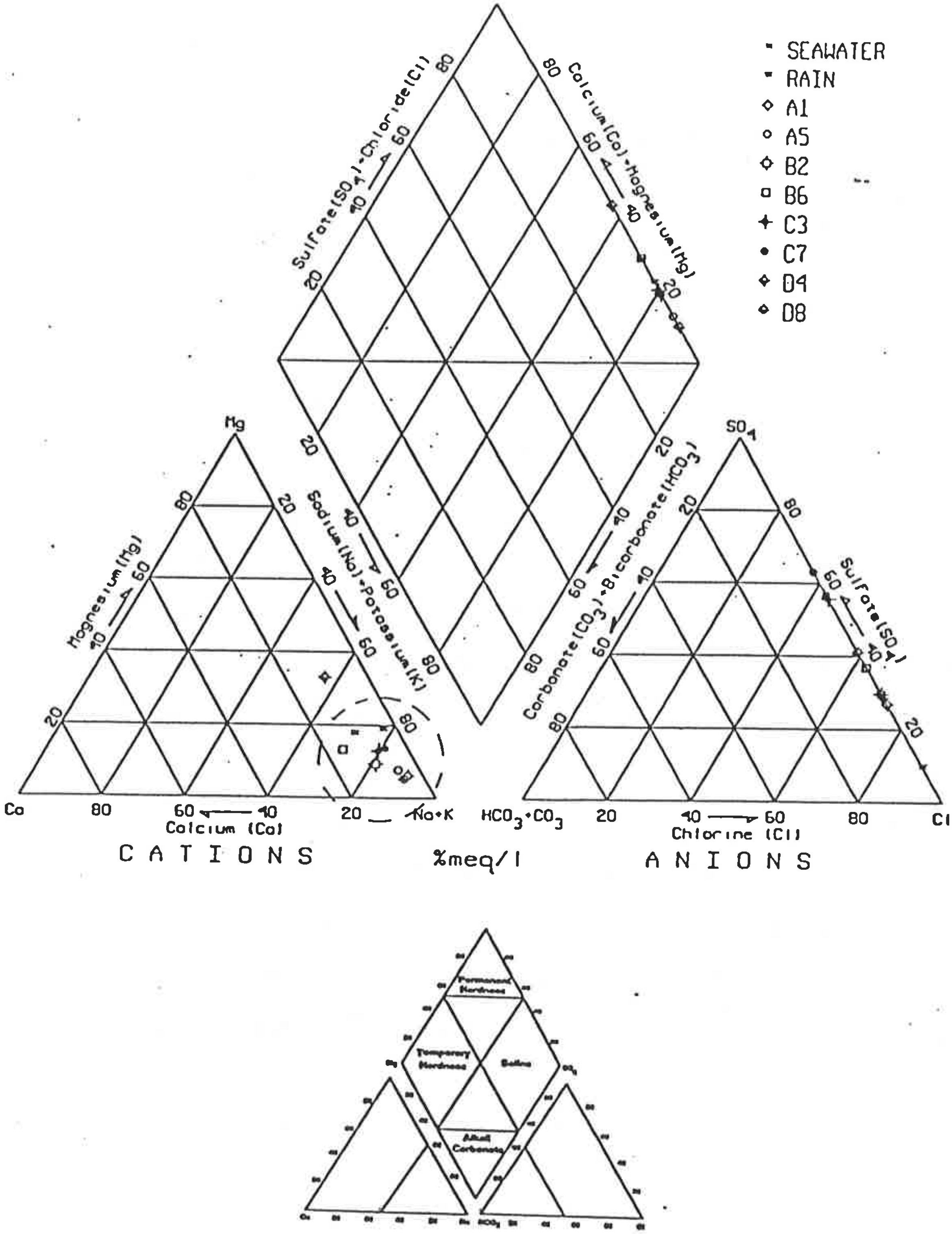


Figure 5. A Piper Diagram plot of the soil solutions, precipitation, and seawater values (Hounslow, 1995). Note the water type diagram shown in the lower half of the figure.

## Table 7. Source-Rock Deduction Summary of Reasoning (Hounslow, 1995).

| Parameter | Value | Conclusion |
|---|---|---|
| $SiO_2$ (mmol/l) | >0.5 | Volcanic glass or hydrothermal waters possible |
| $\frac{HCO_3^-}{SiO_2}$ | >10 | Carbonate weathering |
| | >5 and <10 | Ambiguous |
| | <5 | Silicate weathering |
| $\frac{SiO_2}{Na^+ + K^+ - Cl^-}$ | <1 | Cation exchange |
| | >1 and <2 | Albite weathering |
| | >2 | Ferromagnesian minerals |
| $\frac{Na^+ + K^+ - Cl^-}{Na^+ + K^+ - Cl^- + Ca^{2+}}$ | >0.2 and <0.8 | Plagioclase weathering possible |
| | <0.2 or >0.8 | Plagioclase weathering unlikely |
| $\frac{Na^+}{Na^+ + Cl^-}$ | >0.5 | Sodium source other than halite—albite, ion exchange |
| | = 0 | Halite solution |
| | <0.5 TDS >500 | Reverse softening, seawater |
| | <0.5 TDS <500 >50 | Analysis error |
| | <0.5 TDS <50 | Rainwater |
| | $\frac{HCO_3^-}{SiO_2} > 10$ | Carbonate weathering |
| $\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$ | = 0.5 | Dolomite weathering |
| | <0.5 | Limestone-dolomite weathering |
| | >0.5 | Dolomite dissolution, calcite precipitation, or seawater |
| | $\frac{HCO_3^-}{SiO_2} < 5$ | Silicate weathering |
| | >0.5 | Ferromagnesian minerals |
| | <0.5 | Granitic weathering |
| $\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}}$ | = 0.5 | Gypsum dissolution |
| | <0.5 pH <5.5 | Pyrite oxidation |
| | <0.5 neutral | Calcium removal—ion exchange or calcite precipitation |
| | >0.5 | Calcium source other than gypsum—carbonates or silicates |
| $\frac{Ca^{2+} + Mg^{2+}}{SO_4^{2-}}$ | >0.8 and <1.2 | Dedolomitization |
| TDS | >500 | Carbonate weathering or brine or seawater |
| | <500 | Silicate weathering |
| $\frac{Cl^-}{\text{sum anions}}$ | >0.8 TDS >500 | Seawater, or brine, or evaporites |
| | >0.8 TDS <100 | Rainwater |
| | <0.8 | Rock weathering |
| $\frac{HCO_3^-}{\text{sum anions}}$ | >0.8 | Silicate or carbonate weathering |
| | <0.8 sulfate high | Gypsum dissolution |
| | <0.8 sulfate low | Seawater or brine |
| Langelier index | Positive | Oversaturated with respect to calcite |
| | 0 | Saturated with respect to calcite |
| | Negative | Undersaturated with respect to calcite |
| Conclusion | Aquifer mineralogy | |
| Conclusion | Reactions | |

### *Na:K*

A comparison of the Na:K ratio indicates that in all cases Na>>K except for at D4 were Na>K. This suggest a Na sink at this suction lysimeter. The only common sodium sink occurs when highly saline waters come in contact with calcium-rich clays in a process called natural reverse softening (Hounslow, 1995).

$$\text{Ca-clay} + 2\text{Na}^{+} \longrightarrow \text{Na-clay} + \text{Ca}^{2+}$$

As shown above, this would absorb a much greater amount of Na than it would produce Ca. This may explain why there is no significant Ca increase at D4 despite the Na reverse softening.

### *Ca:Mg*

The Ca:Mg ratios are quite variable in the reported data where samples from site B and sample D8 show Ca≥Mg and the remaining samples show Mg>Ca. It is normally expected that Ca≥Mg unless Ca is removed by precipitation and/or ion exchange (Hounslow, 1995). Calcite precipitation is unlikely because during the soil profiling no reaction was reported when testing with cold dilute HCL at these sites. Evidence for ion exchange is shown at by the Na:Cl ratios at site A and sample C7. The Mg>Ca ratio at samples C3 and D4 may be the result of silicate weathering which is possible at each of these locations per their TDI content.

### *Ca:SO4*

The Ca<<SO4 in all the samples suggest either a source of SO4 and/or a sink for Ca. A source for SO4 may be pyrite oxidation which could help explain the lowered pH values and the Fe content in the soil solution samples. Another possible source for the SO4 are fertilizers.

### *Na:Cl*

exchange is most likely. D4 and C3 are again indicative of seawater consistent with their TDI values.

*Ca/Ca+SO4*

All values are below 0.5 indicative of pyrite oxidation provided that the pH values are less then 5.5. At B6 the pH value is 5.7 suggesting that possible cation ion exchange which has been additionally supported by other parameters presented previously.

**SAR Plot**

A SAR-conductivity plot of the soil solution samples is shown in figure 7. SAR measures the degree to which sodium in the soil solutions replaces the absorbed (Ca + Mg) in the soil clays, thus damaging the soil structure (Hounslow, 1995). Estimated conductivity values that were computed using WATEVAL were used in the plot (Appendix C). Conductivity is used to classify the salinity hazard of the waters.

The plot shows that at all sites, except for site D, a medium salinity hazard exist. Site D has a high salinity hazard. In addition, the sodium hazard can be considered to be low at all samples except for samples A1 and D8.

## Summary and Conclusions

The initial compositions of the soil solutions apear to be that of the precipitation as indicated by the Stiff diagram shape analysis. Exceptions to this are sample D4 and possibly C3 where source rock deductions suggest seawater intrusion. Given the close proximity to the edge of the island this is quite possible. During periods of extreme high tide, the high tide mark was observed within approximately 10m of site D. Unlike sample C3, sample D4 has a TDI content consistent with seawater intrusion. Sample C3's TDI may be lower as a result of only periodically being intruded. This is consistent with its location further from the waters edge. A more detail discussion of these sites will follow.

The elevated silica values reported in the soil solutions of the island may be due to slightly acidic pH values. These may result in the dissolution of significant quantities of clay minerals thereby releasing anomalously high silica and Al into the water.

The mass-balances at many of the sites were probably greatly disturbed by organic ions that were beyond the scope of this study. These could be expected to be common given the shallow soil depth and the abundance of vegetation present on the island.

**Site A**

The soil-water at site A represent waters that originated as precipitation and were subsequently subjected to ion exchange there by increasing in Na content. Associated with this ion exchange, Ca was removed and from the waters.

Elevated chloride levels occur not at the surface, but instead at depth. It is hypothesized that due to the exposure of this site, it is subjected to seaspray during storm events or periods of a strong northwesterly breeze. The seaspray is then flushed down toward the deeper horizon by rain water. Near the surface SO4 increases possibly associated with the addition of fertilizers although pyrite oxidation may also be possible.

**Site B**

As with site A, the waters of this site originate as precipitation. Since the site is more centrally located and is well protected by vegetation and a cement containment wall it is not subjected to as much seaspray activity. Ion exchange may occur in the lower horizon thus supplying Na to the waters at depth. Its Mg and Ca ratio's are that of normal ground water whereby Ca exceeds that of Mg. Near the surface SO4 increases possibly associated with the addition of fertilizers although pyrite oxidation may also be possible.

**Site C**

Site C represents waters of two possible origins. In the upper horizon the soil solution is derived from precipitation. Increased Mg and decreased Cl values probably indicate the formation of magnesium chloride in the near surface. Ion exchange may also be occurring thus supplying additional Na to the waters near the surface (Hounslow, 1995).

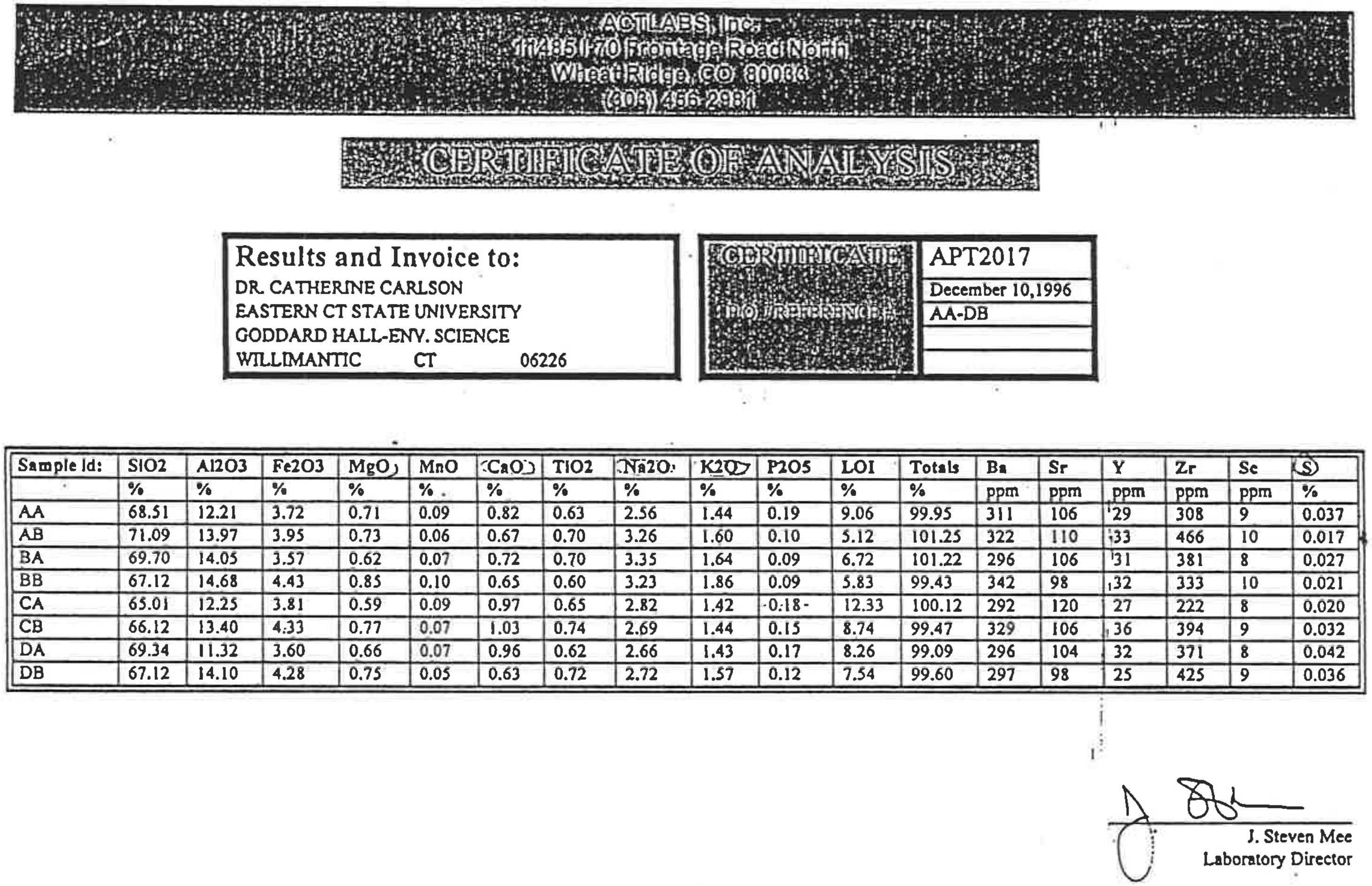
All sites, except for site D, show a medium salinity hazard. Site D has a high salinity hazard. In addition, the sodium hazard can be considered to be low at all samples except for samples A1 and D8.

## Acknowledgments

Financial support for this study was supplied by the Harry O. Haakonsen fellowship. Thanks are extended to the family of Dr. Haakonsen for their generosity. Special thanks to Dr. Catherine Carlson for her patience and guidance in both field work and interpretation. Additional thanks go to Ms. Diane Smith and Ms. Maria Clark for their help in the field and to the folks of the Environmental Research Institute, University of Connecticut.

# REFERENCES

# APPENDIX B



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11485 I-70 Frontage Road North
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(303) 456-2981

## CERTIFICATE OF ANALYSIS

**Results and Invoice to:**
DR. CATHERINE CARLSON
EASTERN CT STATE UNIVERSITY
GODDARD HALL-ENV. SCIENCE
WILLIMANTIC CT 06226

| | |
|---|---|
| CERTIFICATE | APT2017 |
| | December 10,1996 |
| P.O. / REFERENCE | AA-DB |
| | |
| | |

| Sample Id: | SIO2 | Al2O3 | Fe2O3 | MgO | MnO | CaO | TIO2 | Na2O | K2O | P2O5 | LOI | Totals | Ba | Sr | Y | Zr | Sc | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | % | % | % | % | % | % | % | % | % | % | % | ppm | ppm | ppm | ppm | ppm | % |
| AA | 68.51 | 12.21 | 3.72 | 0.71 | 0.09 | 0.82 | 0.63 | 2.56 | 1.44 | 0.19 | 9.06 | 99.95 | 311 | 106 | 29 | 308 | 9 | 0.037 |
| AB | 71.09 | 13.97 | 3.95 | 0.73 | 0.06 | 0.67 | 0.70 | 3.26 | 1.60 | 0.10 | 5.12 | 101.25 | 322 | 110 | 33 | 466 | 10 | 0.017 |
| BA | 69.70 | 14.05 | 3.57 | 0.62 | 0.07 | 0.72 | 0.70 | 3.35 | 1.64 | 0.09 | 6.72 | 101.22 | 296 | 106 | 31 | 381 | 8 | 0.027 |
| BB | 67.12 | 14.68 | 4.43 | 0.85 | 0.10 | 0.65 | 0.60 | 3.23 | 1.86 | 0.09 | 5.83 | 99.43 | 342 | 98 | 32 | 333 | 10 | 0.021 |
| CA | 65.01 | 12.25 | 3.81 | 0.59 | 0.09 | 0.97 | 0.65 | 2.82 | 1.42 | ~~0.18~~ | 12.33 | 100.12 | 292 | 120 | 27 | 222 | 8 | 0.020 |
| CB | 66.12 | 13.40 | 4.33 | 0.77 | 0.07 | 1.03 | 0.74 | 2.69 | 1.44 | 0.15 | 8.74 | 99.47 | 329 | 106 | 36 | 394 | 9 | 0.032 |
| DA | 69.34 | 11.32 | 3.60 | 0.66 | 0.07 | 0.96 | 0.62 | 2.66 | 1.43 | 0.17 | 8.26 | 99.09 | 296 | 104 | 32 | 371 | 8 | 0.042 |
| DB | 67.12 | 14.10 | 4.28 | 0.75 | 0.05 | 0.63 | 0.72 | 2.72 | 1.57 | 0.12 | 7.54 | 99.60 | 297 | 98 | 25 | 425 | 9 | 0.036 |

J. Steven Mee
Laboratory Director

```
                         Sample A1
TempC =      21.4                        pH     =       5.0
TDS   =       0.0                        COND   =       0.0
HARD  =       0.0                        DENS   =       0.0
x-cor =       0.0                        y-cor  =       0.0
Units =  mg/L                            rock   =       0.0

              mg/L      mmole/L    meq/L     % meq/L
Na+          120.6      5.2455     5.2455    82.7
K +            7.9      0.2020     0.2020     3.2
Ca++           4.5      0.1123     0.2246     3.5
Mg++           4.5      0.1851     0.3702     5.8
Cl-          176.9      4.9897     4.9897    73.2
SO4--         87.8      0.9140     1.8280    26.8
HCO3-          0.0      0.0000     0.0000     0.0
CO3--          0.0      0.0000     0.0000     0.0
SiO2          51.1      0.8504     0.0000     0.0
Li+            0.0      0.0000     0.0000     0.0
Sr++           0.0      0.0000     0.0000     0.0
Ba++           0.0      0.0000     0.0000     0.0
Fe++           8.4      0.1508     0.3016     4.8
NO3-           0.0      0.0000     0.0000     0.0
F-             0.0      0.0000     0.0000     0.0
Br-            0.0      0.0000     0.0000     0.0
B              0.0      0.0000     0.0000     0.0

    LANGELIER INDEX =        0.00       SAR                  =        9.6
    Conductivity    =         0 umho    Est. Cond.           =      634 umho

                 Analytical checks and comparisons

Sum cations    =       6.3439           Sum anions     =     6.8177
                                        BALANCE        =     -3.60 %
                 TDS entered      =      0      mg/L
TDS calc       =     462 mg/L           TDS(180) calc =       462 mg/L
Entered TDS - TDS(calc) diff=   0.0 %   Entered TDS - TDS(180) diff=    0.0 %

                      Conductivity =  0  umho
TDS(entered)/Cond ratio     =  0.00     Usual range     = 0.55 to 0.75
TDS(calc)/Cond              =  0.00     Usual range     = 0.55 to 0.75
Conductivity/Sum-cations    =  0        Usual range     = 90 - 110

                 Entered and calculated density
Meas. Density =     0.0000              Calc. Density =       1.0004

                 Entered and calculated hardness
Meas. hardness=     0.0 mg/L CaCO3      Calc. hardness=       29.8 mg/L CaCO3

                         Element ratios
Na/(Na+Cl)       =     51.2 %           Usually > 50%

Ca/(Ca + SO4) =     10.9 %              Usually > 50%
K/(Na + K)       =      3.7 %           Usually < 20%

Mg/(Mg+Ca)       =     62.2 %           Usually < 40%

                   Carbonate/bicarbonate at pH =  5.004
Meas HCO3        =     0.0     mg/L      Meas CO3        =     0.0   mg/L
Calc HCO3        =     0.0     mg/L      Calc CO3        =     0.0   mg/L
```

```
                          Sample A1
                              SOURCE ROCK ESTIMATE

SiO2  (mmol/L)   =        0.85     Volcanic glass or hydrothermal water possible
HCO3/SiO2        =                 HCO3 not analysed
SiO2/(Na+K-Cl)   =        1.86     albite
(Na+K-Cl)/(Na+K-Cl+Ca)= 0.80       Plagioclase weathering unlikely
Na/(Na + Cl)     =        0.51     Albite or ion exchange
Mg/(Mg+Ca)       =        0.62     Ferromagnesian minerals
Ca/(Ca + SO4)    =        0.11     Pyrite oxidation
(Ca + Mg)/SO4    =        0.3      Dedolomitization unlikely
TDS calculated   =      462 mg/L   Silicate weathering possible
Cl/sum anions    =        0.73     Sea water, brine or evaporites possible
HCO3/sum anions  =        0.00     Sea water, brine, or evaporites
Langelier Index  =

                          Mass Balance Calculation
Carbonate option
          Mineral                 Dissolves               Precipitates
          HALITE                     4.990
          CALCITE                                            -0.859
          DOLOMITE                   0.185
          GYPSUM                     0.914
          ION EXCH                   0.128
          CO2 GAS                    0.489

Silicate-option
          Mineral                 Dissolves               Precipitates
          HALITE                     4.990
          ALBITE(K)                  0.256
          ANORTHIT(K)                                        -0.987
          DIOPSIDE                   0.185
          GYPSUM                     0.914
          CO2 GAS                    0.977

    Analysed silica =   51   Silica from albite and diopside =   38 -   53

                   TEMPERATURE ESTIMATES IN DEGREES C

                   Good for temperatures 20 - 350 C
Mg-Li                        -->    0
Na-Li                        -->    0
Na-K-Ca (Mg corrected)       -->   21

                   Good for low temperatures 30 - 70 C
Chalcedony                   -->   73

                   Good for temperatures > 70 C
Quartz-no steam loss         -->  103
Quartz-maximum steam loss -->  104

                   Do not use for oil-field waters
                   May not be useful below 150 C
Na-K (Fournier)              -->  183
Na-K (Truesdell)             -->  161
Na-K-Ca (t < 100 C)          -->  133
Na-K-Ca (t > 100 C)          -->  166
```

```
                           Sample B2
TempC =      21.5                          pH     =       4.8
TDS   =       0.0                          COND   =       0.0
HARD  =       0.0                          DENS   =       0.0
x-cor =       0.0                          y-cor  =       0.0
Units =  mg/L                              rock   =       0.0

                mg/L      mmole/L     meq/L     % meq/L
Na+            114.9      4.9998      4.9998    76.7
K +             11.7      0.2992      0.2992     4.6
Ca++            12.0      0.2994      0.5988     9.2
Mg++             7.4      0.3044      0.6088     9.3
Cl-            166.3      4.6907      4.6907    70.3
SO4--           95.2      0.9910      1.9821    29.7
HCO3-            0.0      0.0000      0.0000     0.0
CO3--            0.0      0.0000      0.0000     0.0
SiO2            43.7      0.7272      0.0000     0.0
Li+              0.0      0.0000      0.0000     0.0
Sr++             0.0      0.0000      0.0000     0.0
Ba++             0.0      0.0000      0.0000     0.0
Fe++             0.3      0.0054      0.0109     0.2
NO3-             0.0      0.0000      0.0000     0.0
F-               0.0      0.0000      0.0000     0.0
Br-              0.0      0.0000      0.0000     0.0
B                0.0      0.0000      0.0000     0.0

    LANGELIER INDEX =        0.00       SAR              =         6.4
    Conductivity    =         0 umho    Est. Cond.       =       652 umho

                  Analytical checks and comparisons

Sum cations    =      6.5174            Sum anions     =    6.6728
                                        BALANCE        =   -1.18 %
                  TDS entered    =      0        mg/L
TDS calc       =      452 mg/L          TDS(180) calc =        452 mg/L
Entered TDS - TDS(calc) diff=   0.0 %   Entered TDS - TDS(180) diff=   0.0 %

                     Conductivity =  0  umho
TDS(entered)/Cond ratio    =  0.00      Usual range    = 0.55 to 0.75
TDS(calc)/Cond             =  0.00      Usual range    = 0.55 to 0.75
Conductivity/Sum-cations   =   0        Usual range    = 90 - 110

                  Entered and calculated density
Meas. Density =      0.0000             Calc. Density =       1.0004

                  Entered and calculated hardness
Meas. hardness=      0.0 mg/L CaCO3     Calc. hardness=      60.4 mg/L CaCO3

                         Element ratios
Na/(Na+Cl)      =      51.6 %           Usually > 50%

Ca/(Ca + SO4)   =      23.2 %           Usually > 50%
K/(Na + K)      =       5.6 %           Usually < 20%

Mg/(Mg+Ca)      =      50.4 %           Usually < 40%

                   Carbonate/bicarbonate at pH =  4.83
Meas HCO3       =      0.0     mg/L     Meas CO3       =      0.0  mg/L
Calc HCO3       =      0.0     mg/L     Calc CO3       =      0.0  mg/L
```

```
                        Sample B2
                             SOURCE ROCK ESTIMATE

SiO2  (mmol/L)    =       0.73    Volcanic glass or hydrothermal water possible
HCO3/SiO2         =               HCO3 not analysed
SiO2/(Na+K-Cl)    =       1.20    albite
(Na+K-Cl)/(Na+K-Cl+Ca)= 0.67     Plagioclase weathering possible
Na/(Na + Cl)      =       0.52    Albite or ion exchange
Mg/(Mg+Ca)        =       0.50    Ferromagnesian minerals
Ca/(Ca + SO4)     =       0.23    Pyrite oxidation
(Ca + Mg)/SO4     =       0.6     Dedolomitization unlikely
TDS calculated    =     452 mg/L  Silicate weathering possible
Cl/sum anions     =       0.70    Sea water, brine or evaporites possible
HCO3/sum anions   =       0.00    Sea water, brine, or evaporites
Langelier Index   =

                       Mass Balance Calculation
Carbonate option
          Mineral               Dissolves             Precipitates
          HALITE                  4.691
          CALCITE                                       -0.841
          DOLOMITE                0.304
          GYPSUM                  0.991
          ION EXCH                0.155
          CO2 GAS                 0.233

Silicate option
          Mineral               Dissolves             Precipitates
          HALITE                  4.691
          ALBITE(K)               0.309
          ANORTHIT(K)                                   -0.996
          DIOPSIDE                0.304
          GYPSUM                  0.991
          CO2 GAS                 0.465

    Analysed silica =   44   Silica from albite and diopside =   55 -   74

                  TEMPERATURE ESTIMATES IN DEGREES C

                  Good for temperatures 20 - 350 C
Mg-Li                       -->    0
Na-Li                       -->    0
Na-K-Ca (Mg corrected)      -->   31

                  Good for low temperatures 30 - 70 C
Chalcedony                  -->   65

                  Good for temperatures > 70 C
Quartz-no steam loss        -->   96
Quartz-maximum steam loss -->     97

                  Do not use for oil-field waters
                  May not be useful below 150 C
Na-K (Fournier)             -->  219
Na-K (Truesdell)            -->  206
Na-K-Ca (t < 100 C)         -->  121
Na-K-Ca (t > 100 C)         -->  179
```

```
                              Sample C3
TempC =      21.3                                   pH     =        4.6
TDS   =       0.0                                   COND   =        0.0
HARD  =       0.0                                   DENS   =        0.0
x-cor =       0.0                                   y-cor  =        0.0
Units =  mg/L                                       rock   =        0.0

                 mg/L      mmole/L     meq/L     % meq/L
Na+              52.4      2.2792     2.2792      71.1
K +              10.0      0.2545     0.2545       7.9
Ca++              4.6      0.1148     0.2295       7.2
Mg++              5.0      0.2057     0.4113      12.8
Cl-             115.9      3.2691     3.2691      53.3
SO4--           137.5      1.4314     2.8628      46.7
HCO3-             0.0      0.0000     0.0000       0.0
CO3--             0.0      0.0000     0.0000       0.0
SiO2             49.7      0.8271     0.0000       0.0
Li+               0.0      0.0000     0.0000       0.0
Sr++              0.0      0.0000     0.0000       0.0
Ba++              0.0      0.0000     0.0000       0.0
Fe++              0.9      0.0160     0.0319       1.0
NO3-              0.0      0.0000     0.0000       0.0
F-                0.0      0.0000     0.0000       0.0
Br-               0.0      0.0000     0.0000       0.0
B                 0.0      0.0000     0.0000       0.0

    LANGELIER INDEX =        0.00      SAR               =        4.0
    Conductivity    =         0 umho   Est. Cond.        =      321 umho

                   Analytical checks and comparisons

 Sum cations    =      3.2064               Sum anions     =    6.1319
                                            BALANCE        =  -31.33 %
                    TDS entered    =        0       mg/L
 TDS calc       =       376 mg/L            TDS(180) calc =      376 mg/L
 Entered TDS - TDS(calc) diff=   0.0 %     Entered TDS - TDS(180) diff=   0.0 %

                         Conductivity =  0  umho
 TDS(entered)/Cond ratio   =  0.00          Usual range   = 0.55 to 0.75
 TDS(calc)/Cond            =  0.00          Usual range   = 0.55 to 0.75
 Conductivity/Sum-cations  =   0            Usual range   = 90 - 110

                    Entered and calculated density
 Meas. Density =      0.0000                Calc. Density =      1.0003

                    Entered and calculated hardness
 Meas. hardness=      0.0 mg/L CaCO3        Calc. hardness=     32.1 mg/L CaCO3

                              Element ratios
 Na/(Na+Cl)      =      41.1 %              Usually > 50%

 Ca/(Ca + SO4) =        7.4 %               Usually > 50%
 K/(Na + K)      =      10.0 %              Usually < 20%

 Mg/(Mg+Ca)      =     64.2 %               Usually < 40%

                         Carbonate/bicarbonate at pH =  4.5775
 Meas HCO3      =        0.0      mg/L      Meas CO3        =      0.0   mg/L
 Calc HCO3      =        0.0      mg/L      Calc CO3        =      0.0   mg/L
```

```
                          Sample C3
                              SOURCE ROCK ESTIMATE

SiO2  (mmol/L)  =        0.83     Volcanic glass or hydrothermal water possible
HCO3/SiO2       =                 HCO3 not analysed
SiO2/(Na+K-Cl)  =                 Cl > (Na+K)
(Na+K-Cl)/(Na+K-Cl+Ca)=           Cl > (Na+K)

Na/(Na + Cl)    =        0.41     Mg/(Mg+Ca)        =       0.64
                                  Ferromagnesian minerals
Ca/(Ca + SO4)   =        0.07     Pyrite oxidation
(Ca + Mg)/SO4   =        0.2      Dedolomitization unlikely
TDS calculated  =      376 mg/L   Silicate weathering possible.
Cl/sum anions   =        0.53     Sea water, brine or evaporites possible
HCO3/sum anions =        0.00     Sea water, brine, or evaporites
Langelier Index =

                           Mass Balance Calculation

Carbonate option
           Mineral                Dissolves               Precipitates
           HALITE                   3.269
           CALCITE                                          -2.017
           DOLOMITE                 0.206
           GYPSUM                   1.431
           ION EXCH                                         -0.495
           CO2 GAS                  1.606

Silicate option
           Mineral                Dissolves               Precipitates
           HALITE                   3.269
           ALBITE(K)                                        -0.990
           ANORTHIT(K)                                      -1.522
           DIOPSIDE                 0.206
           GYPSUM                   1.431
           CO2 GAS                  3.212

    Analysed silica =   50   Silica from albite and diopside =  -35 -  -94

                    TEMPERATURE ESTIMATES IN DEGREES C

                    Good for temperatures 20 - 350 C
Mg-Li                          -->    0
Na-Li                          -->    0
Na-K-Ca (Mg corrected)         -->   24

                    Good for low temperatures 30 - 70 C
Chalcedony                     -->   72

                    Good for temperatures > 70 C
Quartz-no steam loss           -->  102
Quartz-maximum steam loss -->  102

                    Do not use for oil-field waters
                    May not be useful below 150 C
Na-K (Fournier)                -->  279
Na-K (Truesdell)               -->  288
Na-K-Ca (t < 100 C)            -->  130
Na-K-Ca (t > 100 C)            -->  209
```

```
                         Sample D4
TempC =      21.6                          pH     =        5.4
TDS   =       0.0                          COND   =        0.0
HARD  =       0.0                          DENS   =        0.0
x-cor =       0.0                          y-cor  =        0.0
Units =  mg/L                              rock   =        0.0

              mg/L      mmole/L     meq/L     % meq/L
Na+          102.6      4.4626     4.4626     46.7
K +           36.6      0.9360     0.9360      9.8
Ca++          19.9      0.4965     0.9930     10.4
Mg++          38.3      1.5769     3.1538     33.0
Cl-         1550.8     43.7424    43.7424     71.3
SO4--        844.0      8.7862    17.5724     28.7
HCO3-          0.0      0.0000     0.0000      0.0
CO3--          0.0      0.0000     0.0000      0.0
SiO2          33.2      0.5525     0.0000      0.0
Li+            0.0      0.0000     0.0000      0.0
Sr++           0.0      0.0000     0.0000      0.0
Ba++           0.0      0.0000     0.0000      0.0
Fe++           0.5      0.0083     0.0167      0.2
NO3-           0.0      0.0000     0.0000      0.0
F-             0.0      0.0000     0.0000      0.0
Br-            0.0      0.0000     0.0000      0.0
B              0.0      0.0000     0.0000      0.0

   LANGELIER INDEX =        0.00     SAR              =        3.1
   Conductivity    =         0 umho  Est. Cond.       =      956 umho

                 Analytical checks and comparisons

 Sum cations   =       9.5622               Sum anions     =   61.3148
                                            BALANCE        =  -73.02 %
                   TDS entered    =          0        mg/L
 TDS calc       =     2626 mg/L             TDS(180) calc =      2626 mg/L
 Entered TDS - TDS(calc) diff=   0.0 %   Entered TDS - TDS(180) diff=   0.0 %

                         Conductivity =  0  umho
 TDS(entered)/Cond ratio    =  0.00     Usual range    = 0.55 to 0.75
 TDS(calc)/Cond             =  0.00     Usual range    = 0.55 to 0.75
 Conductivity/Sum-cations   =   0       Usual range    = 90 - 110

                  Entered and calculated density
 Meas. Density =     0.0000            Calc. Density =       1 0017

                  Entered and calculated hardness
 Meas. hardness=     0 0 mg/L CaCO3    Calc. hardness=    207.5 mg/L CaCO3

                           Element ratios
 Na/(Na+Cl)     =        9.3 %         Usually > 50%

 Ca/(Ca + SO4) =         5.3 %         Usually > 50%
 K/(Na + K)     =       17.3 %         Usually < 20%

 Mg/(Mg+Ca)     =       76.1 %         Usually < 40%

                      Carbonate/bicarbonate at pH =  5.41
 Meas HCO3      =        0.0    mg/L     Meas CO3       =      0.0   mg/L
 Calc HCO3      =        0.0    mg/L     Calc CO3       =      0.0   mg/L
```

```
                         Sample D4
                             SOURCE ROCK ESTIMATE

SiO2  (mmol/L)  =        0.55    Volcanic glass or hydrothermal water possible
HCO3/SiO2       =                HCO3 not analysed
SiO2/(Na+K-Cl)  =                Cl > (Na+K)
(Na+K-Cl)/(Na+K-Cl+Ca)=          Cl > (Na+K)

Na/(Na + Cl)    =        0.09    Reverse softening, sea water
Mg/(Mg+Ca)      =        0.76    Ferromagnesian minerals
Ca/(Ca + SO4)   =        0.05    Pyrite oxidation
(Ca + Mg)/SO4   =        0.2     Dedolomitization unlikely
TDS calculated  =     2626 mg/L  Carbonate weathering, brine,
                                    evaporites or sea water
Cl/sum anions   =        0.71    Sea water, brine or evaporites possible
HCO3/sum anions =        0.00    Sea water, brine, or evaporites
Langelier Index =

                         Mass Balance Calculation

 Carbonate option                                      Precipitates
          Mineral                  Dissolves
          HALITE                    43.742
          CALCITE                                        -29.506
          DOLOMITE                   1.577
          GYPSUM                     8.786
          ION EXCH                                       -19.640
          CO2 GAS                   26.353

 Silicate option                                       Precipitates
          Mineral                  Dissolves
          HALITE                    43.742
          ALBITE(K)                                      -39.280
          ANORTHIT(K)                                     -9.867
          DIOPSIDE                   1.577
          GYPSUM                     8.786
          CO2 GAS                   52.705

     Analysed silica =   33   Silica from albite and diopside = %-2171 - %-4531

                   TEMPERATURE ESTIMATES IN DEGREES C

                   Good for temperatures 20 - 350 C
                            -->    0
 Mg-Li                      -->    0
 Na-Li                      -->  250
 Na-K-Ca (Mg corrected)

                   Good for low temperatures 30 - 70 C
                            -->   53
 Chalcedony

                   Good for temperatures > 70 C
 Quartz-no steam loss       -->   84
 Quartz-maximum steam loss -->    87

                   Do not use for oil-field waters
                   May not be useful below 150 C
                            -->  357
 Na-K (Fournier)            -->  406
 Na-K (Truesdell)           -->  155
 Na-K-Ca (t < 100 C)        -->  250
 Na-K-Ca (t > 100 C)
```

```
                         Sample rain
  =       21.4
  =        0.0                                pH     =        5.2
  =        0.0                                COND   =        0.0
r =        0.0                                DENS   =        0.0
s =   mg/L                                    y-cor  =        0.0
                                              rock   =        0.0

          mg/L      mmole/L     meq/L      % meq/L
          10.2      0.4457      0.4457      69.2
           0.5      0.0126      0.0126       2.0
           1.4      0.0342      0.0684      10.6
           1.3      0.0553      0.1106      17.2
          18.6      0.5246      0.5246      71.0
          10.3      0.1072      0.2144      29.0
           0.0      0.0000      0.0000       0.0
           0.0      0.0000      0.0000       0.0
           0.0      0.0000      0.0000       0.0
           0.0      0.0000      0.0000       0.0
           0.0      0.0000      0.0000       0.0
           0.0      0.0000      0.0000       0.0
           0.2      0.0036      0.0072       1.1
           0.0      0.0000      0.0000       0.0
           0.0      0.0000      0.0000       0.0
           0.0      0.0000      0.0000       0.0
           0.0      0.0000      0.0000       0.0

LANGELIER INDEX =        0.00       SAR                =        1.5
Conductivity    =         0 umho    Est. Cond.         =        64 umho

                  Analytical checks and comparisons

cations   =       0.6445
                                    Sum anions    =    0.7391
                                    BALANCE       =   -6.83 %
                TDS entered   =      0       mg/L
calc        =      43 mg/L          TDS(180) calc =        43 mg/L
red TDS - TDS(calc) diff=   0.0 %   Entered TDS - TDS(180) diff=   0.0 %

                    Conductivity =  0  umho
entered)/Cond ratio    =  0.00      Usual range    = 0.55 to 0.75
calc)/Cond             =  0.00      Usual range    = 0.55 to 0.75
luctivity/Sum-cations  =   0        Usual range    = 90 - 110

                Entered and calculated density
  Density =       0.0000            Calc. Density =       1.0000

                Entered and calculated hardness
  hardness=       0.0 mg/L CaCO3    Calc. hardness=       9.0 mg/L CaCO3

                         Element ratios
Na+Cl)     =      45.9 %                  Usually > 50%

Ca + SO4) =      24.2 %                   Usually > 50%
a + K)     =       2.7 %                  Usually < 20%

Mg+Ca)     =      61.8 %                  Usually < 40%

                  Carbonate/bicarbonate at pH =  5.16667
 HCO3      =       0.0     mg/L       Meas CO3      =     0.0  mg/L
 HCO3      =       0.0     mg/L       Calc CO3      =     0.0  mg/L
```

```
                              Sample rain
                                   SOURCE ROCK ESTIMATE
  SiO2  (mmol/L)  =
  HCO3/SiO2       =                 SiO2 not analysed
                                    SiO2 not analysed
  SiO2/(Na+K-Cl)  =                 HCO3 not analysed
  (Na+K-Cl)/(Na+K-Cl+Ca)=           SiO2 not analysed
                                    Cl > (Na+K)
  Na/(Na + Cl)        =     0.46    Rain water possible
  Mg/(Mg+Ca)          =     0.62    Ferromagnesian minerals
  Ca/(Ca + SO4)       =     0.24    Pyrite oxidation
  (Ca + Mg)/SO4       =     0.8     Dedolomitization likely
  TDS calculated      =    43 mg/L  Silicate weathering possible
  Cl/sum anions       =     0.71    Sea water, brine or evaporites possible
  HCO3/sum anions     =     0.00    Rain water
  Langelier Index     =

                              Mass Balance Calculation
  Carbonate option
           Mineral               Dissolves            Precipitates
           HALITE                   0.525
           CALCITE                                      -0.168
           DOLOMITE                 0.055
           GYPSUM                   0.107
           ION EXCH                                     -0.039
           CO2 GAS                  0.057

  Silicate option
           Mineral               Dissolves            Precipitates
           HALITE                   0.525
           ALBITE(K)                                    -0.079
           ANORTHIT(K)                                  -0.128
           DIOPSIDE                 0.055
           GYPSUM                   0.107
           CO2 GAS                  0.114

    Analysed silica =     0   Silica from albite and diopside =    2 -   -3

                     TEMPERATURE ESTIMATES IN DEGREES C

                     Good for temperatures 20 - 350 C
  Mg-Li                         -->    0
  Na-Li                         -->    0
  Na-K-Ca (Mg corrected)        -->   39

                     Good for low temperatures 30 - 70 C
  Chalcedony                    -->    0

                     Good for temperatures > 70 C
  Quartz-no steam loss          -->    0
  Quartz-maximum steam loss -->        0

                     Do not use for oil-field waters
                     May not be useful below 150 C
  Na-K (Fournier)               -->  161
  Na-K (Truesdell)              -->  134
  Na-K-Ca (t < 100 C)           -->   39
  Na-K-Ca (t > 100 C)           -->  123
```