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# Self-Sealing Evaporation Ponds for Desalination Facilities in Texas

Prepared for
**Texas Water Development Board**

**Bureau of Economic Geology**
**Scott W. Tinker, Director**
John A. and Katherine G. Jackson School of Geosciences
The University of Texas at Austin
Austin, Texas 78713-8924

**Cover photo**: aerial view of River Oaks Ranch evaporation ponds and facility (Hays County). Courtesy of Google Earth.

# Self-Sealing Evaporation Ponds for Desalination Facilities in Texas

Prepared for
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under
Contract No. 2005-483-027

**Jean-Philippe Nicot, Beth Gross[1], Steven Walden[2], and Russ Baier[2]**

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**Bureau of Economic Geology**
**Scott W. Tinker Director**
John A. and Katherine G. Jackson School of Geosciences
The University of Texas at Austin
Austin, Texas 78713-8924

[1]Geosyntec, Austin, TX
[2]Steve Walden Consulting, Austin, TX

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# Glossary and Abbreviations

| | |
|---|---|
| ADEQ | Arizona Department of Environmental Quality |
| ARS | Arizona Revised Statutes |
| ASTM | American Society for Testing and Materials |
| | |
| BADCT | Best Available Demonstrated Control Technology |
| | |
| CWA | Clean Water Act |
| | |
| DC | Design capacity |
| DO | Dissolved oxygen |
| DW | Drinking water |
| | |
| ED | Electrodialysis |
| EDR | Electrodialysis reversal |
| EP | Evaporation pond |
| EPA | Environmental Protection Agency |
| | |
| GCL | Geosynthetic clay liner |
| GW | Groundwater |
| | |
| HDPE | High-density polyethylene |
| | |
| IND | Industrial |
| IRR | Irrigation |
| iWUD | TCEQ water utility database search engine |
| | |
| LA | Land application |
| LLNL | Lawrence Livermore National Laboratory |
| | |
| MCL | Maximum contaminant level |
| MF | Microfiltration |
| MGD | Million gallons per day |
| mil | 1/1000th of 1 inch |
| | |
| NCDC | National Climatic Data Center |
| NF | Nanofiltration |
| NMAC | New Mexico Administrative Code |
| NMED | New Mexico Environment Department |
| NPDES | National Pollutant Discharge Elimination System |
| NRCS | Natural Resources Conservation Service (in New Mexico) |
| | |
| OAC | Oklahoma Administrative Code |
| ODEQ | Oklahoma Department of Environmental Quality |

| | |
|---|---|
| ppm | part per million |
| PVC | Polyvinyl chloride |
| PWS | Public water system |
| | |
| RO | Reverse osmosis |
| | |
| SI | Saturation index |
| SSEP | Self-sealing evaporation pond |
| SW | Surface water |
| SWATS | Surface Water and Treatment System |
| | |
| TAC | Texas administrative code |
| TCEQ | Texas Commission on Environmental Quality |
| TCLP | Toxicity Characteristic Leaching Procedure |
| TDS | Total dissolved solids |
| TLAP | Texas Land Application Permit |
| TNRCC | Texas Natural Resources Conservation Commission; name changed to TCEQ |
| TNRIS | Texas Natural Resources Information System |
| TPDES | Texas Pollutant Discharge Elimination System |
| TWDB | Texas Water Development Board |
| | |
| UF | Ultrafiltration |
| USGS | United States Geological Survey |
| | |
| WWTP | Wastewater treatment plant |

# Acknowledgments

The authors would like to thank all individuals and organizations that helped make this work successful. Patrick V. Brady, senior researcher and project manager at Sandia National Laboratories, revived the concept of self-sealing evaporation ponds for desalination facilities. James Krumhansl, senior researcher also at Sandia, did X-ray analyses of the saline lake and evaporation pond sediments at no charge. Andrew Tachovsky at BEG collected the saline lake samples and did the cation chemical analyses. Thanks to David Yohe, Henry Ochella (River Oaks plant), and Toby Alvarado and Joe Paxton (Horizon MUD) from ECO Resources, Inc., for allowing us to visit and sample their facilities. Thanks also to Kenny Hutchins and Rodney Taylor (City of Abilene) and Rufus Beam (City of Brady) for their help in sampling water at various locations of their facility. Thanks to Sanjeev Kalaswad at the Texas Water Development Board (TWDB) and Travis Swanson (BEG) for their help in the sampling.

We would also like to thank the Texas Commission on Environmental Quality (TCEQ) staff, in particular, Kelly Holligan, Michael Chadwick, and Kathy H. Brown, for their input on the regulatory aspects. We also benefited from discussions with Jorge Arroyo, Team Leader at TWDB, and Hari Krishna, Contract Manager, also at TWDB. We are grateful as well to Lana Dieterich for the thorough editing of this report.

# Executive Summary

The State of Texas has taken a renewed interest in desalination of brackish water. Because the Texas population is expected to grow tremendously in coming decades, many municipalities and other water-supplying entities will need to supplement their current fresh-water sources. Desalination of brackish water is high on the list of water-source alternatives for supplying some or all of the increased water needs in many communities. However, disposal of desalination concentrates may pose legal, technical, and economic barriers, especially for smaller communities with water supplies of less than one million gallons per day (MGD). In this report, we examine evaporation ponds and the possibility of incorporating a low-permeability layer (precipitant) into the pond-liner system as a liner component or possibly as the liner itself. One aspect of this analysis was to investigate the regulatory requirements and barriers of using self-sealing ponds, if this strategy proves to be a technically viable alternative to standard pond liners. Another part of the work consisted of understanding the favorable chemical conditions, natural or induced, for the precipitation of such a compound(s). The third and last facet of this work was to investigate the savings or extra costs of this approach.

The following observations characterize the regulatory issues relating to self-sealing pond liners. (1) No significant regulatory barriers currently exist that would prevent the permitting of self-sealing evaporation pond-liner technologies at desalination facilities in Texas. (2) No Federal authorizations are required, but a Texas Land Application Permit (TLAP) must be obtained from the Texas Commission on Environmental Quality (TCEQ) Water Quality Division. (3) TCEQ has considerable latitude for approving alternative permit requirements for industrial permits. Rules for municipal wastewater treatment are used as guides for the evaluation of industrial evaporation ponds but do not impose strict regulatory requirements. Currently approved pond liners include a 3-foot-thick layer of in situ clay or compacted clay (with a maximum hydraulic conductivity of $10^{-7}$ cm/s) or a geomembrane liner (polyvinyl chloride [PVC], high-density polyethylene [HDPE], butyl rubber, polypropylene, etc) of 30 mils (0.76 mm) or more with leak-detection monitoring. An alternative liner technology may be approved by TCEQ if it can be demonstrated to achieve and maintain *equivalent containment capabilities* to the pre-approved liners and that the resulting liner material(s) will not deteriorate because of reactivity with salinity or other compounds in the effluent stream or other ambient conditions. Supporting demonstration information may include previous research, pilot projects, and monitoring data from existing operational facilities currently utilizing the proposed technology. Regulatory processing for the permitting of an evaporation pond could be simplified if the self-sealing technology were recognized by the TCEQ as an accepted type of liner, equivalent to compacted clay or geomembrane liners. No statutory change or rulemaking would be required to revise the permit instructions to add self-sealing pond liners to the list of acceptable methods, although compelling scientific and engineering evidence would be necessary to justify such a modification.

The technical part of this study started with the assessment of previous laboratory experiments and natural analogs, such as saline lakes. The assessment suggests that precipitation of a specific clay mineral called *sepiolite*, which is composed of mostly magnesium oxide and silica, could have many advantages. It has the flow properties of clay minerals but is not expandable when exposed to water or to a change in salinity or aqueous ionic makeup. Despite the absence of sepiolite in the few samples collected from Texas evaporation ponds, geochemical numerical simulations performed using U.S. Geological Survey (USGS) code PHREEQC suggests that sepiolite does precipitate in evaporation ponds but in small quantities. Calcite and gypsum are the two minerals that precipitate in significant amounts. After 5 years of operation, an average precipitate thickness is approximately 0.15 inch, containing about 15% sepiolite, with large geographic variability. Addition of low-cost sepiolite precursors to the concentrate stream has been shown to increase the amount of sepiolite precipitated (with a pH maintained at 8.5), to an average of 0.38 inch after 5 years of operation, with a sepiolite fraction of approximately 60%. Water-chemical composition inputs to the numerical simulations were derived from databases containing information on thousands of brackish groundwater samples at the Texas Water Development Board (TWDB) and surface-water samples from TCEQ. They were categorized into 20 groups corresponding to aquifers or group of aquifers, except for one group comprised entirely of all surface-water samples. Although the range and variety of water composition are large, results are essentially qualitatively similar for all groups: without precursors, mostly calcite, gypsum, and some minor minerals precipitate, whereas with addition of precursors, a significant amount of sepiolite can precipitate. This study did not perform laboratory experiments on the precipitates and, therefore, does not present independent hydraulic conductivity analyses. However, other investigators have measured hydraulic conductivity of a variety of precipitants in laboratory experiments. They have observed that measured conductivity values of the precipitant are still too high and above the threshold value of $10^{-7}$ cm/s. Overall, while developing self-sealing ponds is not technically challenging, doing so at a lower cost than that of present simple technology may be difficult.

The regulation section of this study showed that the practical way to make use of self-sealing properties is to exercise an option to demonstrate that the alternative liner will achieve equivalent containment. Even in the case of pre-approved liners, self-sealing deposition could be advantageous in settings where an additional defense-in-depth layer is needed, such as areas with an underlying unconfined aquifer sensitive to contamination.

Substantial savings can be achieved if waivers are granted. Savings can be as high as 90% if the pond consists of little more than an excavation into the ground. Large savings may also be achieved if the leak-detection system is not required for geomembrane liners. Our analysis suggests that the precipitant, even with a hydraulic conductivity $>1\times10^{-7}$ cm/s could efficiently plug holes and defects of the geomembrane. This analysis also suggests that, because defects and holes can be plugged with no operator intervention, a thinner geomembrane could be used, in combination or not with the leak detection system waiver. This possibility, however, needs to be confirmed by experiments and pilot tests.

On the other hand, equivalent containment can be achieved for clay liners—common in Texas—mostly by sheer accumulation of the precipitated material at the bottom of the pond. The modest thickness of at most a few inches of precipitant after a few years of operation suggests that the precipitated material needs to have a hydraulic conductivity much lower than $1\times10^{-7}$ cm/s to impart the required properties to a scaled-down liner and to be successfully substituted in part or all of the clay liner. As in the case of geomembranes, precipitant may plug small cracks that could appear throughout the life of the pond, reducing the cost of operator intervention.

In summary:

- There are no regulatory hurdles in using self-sealing evaporation ponds; however, the burden of proving the validity of the approach in each specific case is on the permit applicant.
- Calcite and gypsum are the most common mineral precipitates. Some clay mineral(s) (notably sepiolite) may also precipitate, especially if additives are added to the concentrate stream. Minerals, however, precipitate in small amounts (typically <1 inch after 5 years of operation) and may not achieve the threshold conductivity of $1\times10^{-7}$ cm/s.
- The most promising use of self-sealing properties seems to be for facilities using geomembranes if they are able to do away with the leak monitoring system requirement.

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# 1 Introduction

Evaporation ponds are a relatively simple and low-maintenance option for managing and disposing of desalination concentrate in small-scale applications. They may be particularly attractive for small communities in arid environments with level topography and where land costs are low. Typically the largest outlay for evaporation ponds is that of the constructed or manufactured liner—which might potentially leak. In some cases, the chemistry of the concentrate can be changed with additives to create a relatively impermeable layer that makes the base of the pond self sealing. This study addresses the chemical, physical, legal, and economic conditions to be met for the use of self-sealing evaporation ponds in Texas by (1) determining ranges of likely membrane concentrate compositions in Texas, (2) calculating the ability of additives to impart self-sealing characteristics to the pond walls and bottom, (3) examining any regulatory constraints to reliance on self-sealing evaporation ponds, and (4) providing cost estimates for a self-sealing evaporation pond for a 1-million-gallon-per-day (MGD) brackish groundwater desalination facility.

The present report documents results for the three tasks described in the scope of work of Contract # 2005-483-027 "*Self-sealing Evaporation Ponds*." Task 1 consisted of a mostly desktop geochemistry study aimed at understanding the technical basis behind the concept and addressed items (1) and (2) above. The geochemistry work was performed in parallel to, but independent of, similar work performed at Sandia National Laboratory (Sandia) under the direction of Dr. Patrick Brady. A study of the regulatory aspects was undertaken in Task 2. Task 3 consisted of estimating cost infrastructure and potential savings and of designing a generic self-sealing evaporation pond.

The report first gives an overview of relevant information on desalination facilities in Texas (Section 2). Section 2 also describes the scientific underpinnings of evaporation ponds and computes the net evaporation rates applicable across Texas. Section 3 lays out the sources of information for the water chemical composition and presents the general approach. Section 4 successively presents the regulatory framework in Texas and in some southwestern states and the likely composition of desalination concentrates across Texas. It then documents the geochemical numerical simulations and their results and moves on to describing design specifics and cost estimates. Lengthy and/or secondary information has been attached in several appendices (derivation of water groups, documentation on regulation, example of a permit of an evaporation pond for desalination facility, results of field sampling, information on clay minerals, a few words about those facilities with above-maximum contaminant level (MCL) arsenic, and examples and results of geochemical simulations).

# 2 Background Technical Information on Evaporation Ponds

## 2.1 Desalination Primer

All public water supply (PWS) desalination facilities in Texas use membrane technology. There are two kinds of membrane processes: pressure driven and electro-potential driven. Pressure-driven membrane processes are further described as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF and UF act only mechanically, blocking bacteria and suspended particles (10–0.05 μm) because they are too large to flow through the membrane pores. UF also blocks colloids and macromolecules (0.05–0.005 μm). In contrast, NF (0.005–0.0005 μm) blocks solutes as small as organic molecules and divalent ions. RO (0.001–0.0001 μm) blocks particles as small as monovalent ions. Both RO and NF operate mainly through diffusion and chemical interaction between membrane and solutes. NF is also called low-pressure RO, or water-softening membrane. NF removes more calcium and magnesium than chloride, resulting in softer waters. NF also removes more sulfate and bicarbonate than chloride. The two electro-potential-driven processes are electrodialysis (ED) and electrodialysis reversal (EDR). The latter process is very similar to ED, with the added benefit of reduced scaling because potentials are reversed periodically. However, ED/EDR does not remove uncharged species, such as silica. Below ~3,000 to 3,500 part per million total dissolved solids (ppm TDS), both RO and ED/EDR processes can be competitive and can produce low-salinity water at low cost. RO plants are the most widely used in the nation for desalination, with 72 % of plants using brackish-water RO, 2 % seawater RO, 15 % ED/EDR, and 11 % NF (Mickley, 2001).

Desalination concentrates are produced during removal of salts from low-quality water in RO and ED/EDR plants. The amount of concentrate as a percentage of feedwater varies according to desalination method, percentage of recovery, and chemical additives. In RO systems that produce drinking water, a typical pretreatment consists of acidification and addition of antiscalant chemicals. Disposal of the concentrate could be a major issue in siting of a new facility.

## 2.2 Desalination Facilities in Texas in 2006

A comprehensive survey of PWS desalination facilities in Texas was recently performed for the TWDB (Nicot et al., 2005). The concentrate disposal method was one of the features investigated. The number of desalination facilities in Texas has increased sharply in the past decade (Nicot et al., 2005). In 2005, the State of Texas was host to about 38 PWS facilities with a desalination design capacity of ≥0.025 million gallons a day (MGD), a cumulative desalination design capacity (DC) of ~52 MGD (Figure 2-2), and another approximately 50 facilities with smaller desalination design capacity, for a cumulative desalination design capacity of <0.5 MGD. Five facilities with a design capacity of ~34 MGD account for more than half (65 %) of the cumulative design capacity of the state. The vast majority of Texas PWS desalination facilities have adopted reverse osmosis (RO) as the desalting technique. In addition, industrial capacity amounts to roughly 60 to 100 MGD in hundreds of units, mainly in the power and semiconductor industries. Only PWS facilities offer easy-to-access data.

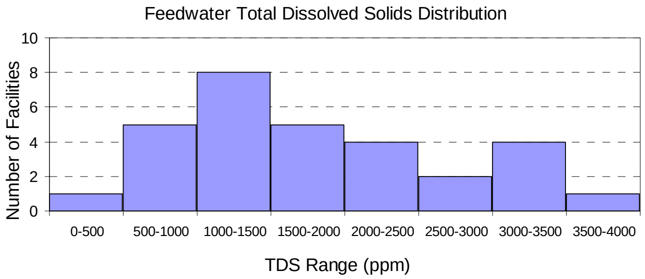
Desalination facilities have several options for disposing of the concentrate stream: evaporation pond, land application, municipal sewer, surface-water body, deep injection well (not yet practiced in Texas), and zero liquid discharge (Figure 2-3 and Table 2-1). Ten Texas facilities with a design capacity of ≥0.025 MGD (as of summer 2005) have evaporation ponds as an exclusive or nonexclusive method for disposing of concentrate (Table 2-1 and Table 2-2), to which can be added many other PWS facilities with a design capacity of <0.025 MGD (a couple are also listed in Table 2-2). Those PWS facilities with evaporation ponds are small except for that of Abilene (8 MGD DC) and Brady (1.5 MGD DC).

Feedwater TDS of current desalination facilities varies from 470 to 3,840 ppm (Figure 2-1 and Figure 2-4). An arithmetic average weighted by desalination design capacity yields a value of ~1,760 ppm, whereas an average by facility gives a similar value of ~1,870 ppm. Mode of feedwater TDS distribution is in the 1,000 to 1,500 ppm range (Figure 2-1). Source water is either a surface-water body or, more commonly, groundwater (Figure 2-5). Of 38 facilities, 8 use surface water, including the large facilities of Abilene, Sherman, and Lake Granbury Surface Water and Treatment System (SWATS). They are generally located where surface water is abundant, mainly in the northeast corner of the state, where net evaporation rates are not as favorable (Figure 2-9).

Table 2-1. Concentrate disposal method statistics (Texas PWS plants with ≥0.025 MGD DC).

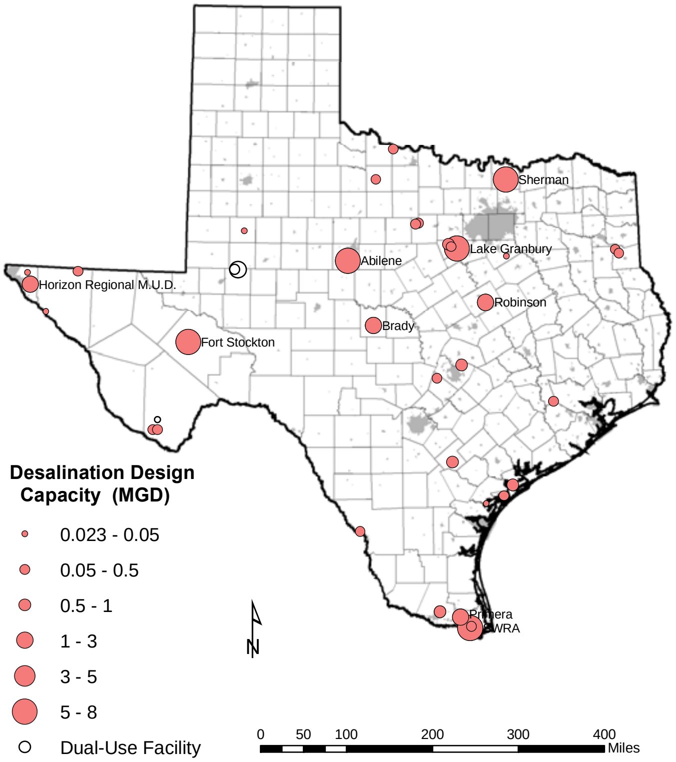
| **Method** | **Number of PWS facilities DC ≥0.025 MGD** | **Cumulative design capacity (MGD)** |
|---|---|---|
| Evaporation pond | 10 | 12.1 |
| Land application | 5 | 3.3 |
| Municipal sewer | 9 | 15.3 |
| Surface-water body | 14 | 20.7 |
| *Total* | *38* | *52.3*[A] |

[A] Sum of individual rows may differ from "Total" row owing to rounding; table valid as of summer 2005.



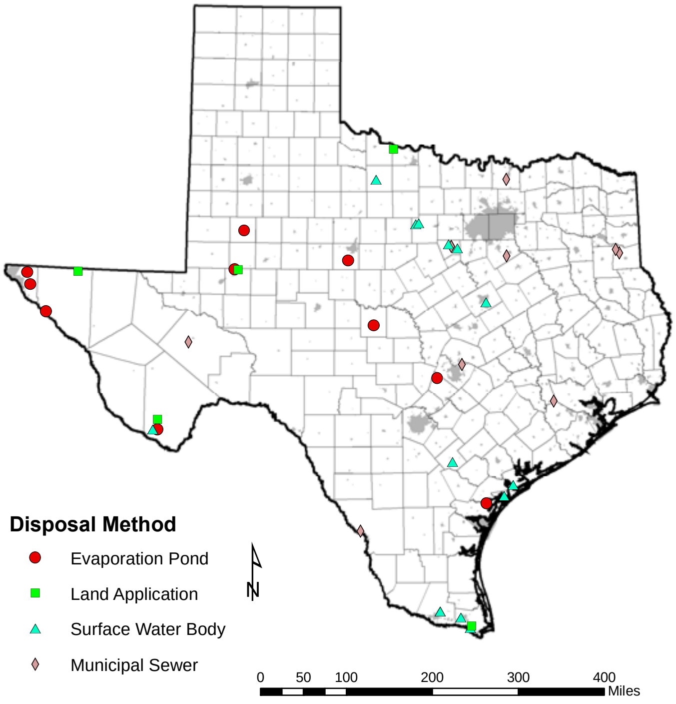
Source: Nicot et al. (2005)

Figure 2-1. Feedwater TDS distribution.



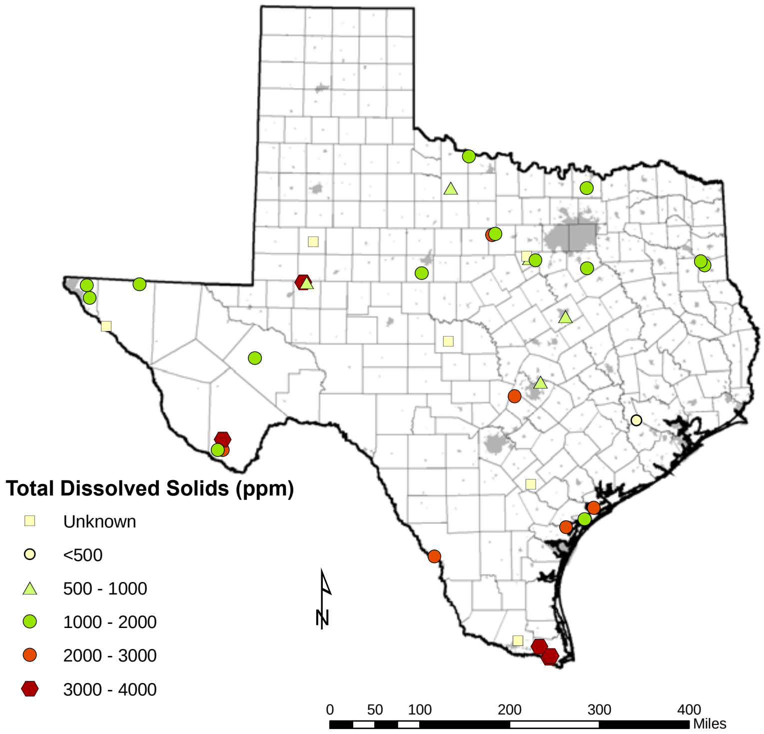
Note: Location of some facilities is only approximate; facilities with a desalination design capacity ≥1.5 MGD are named; map from Nicot et al. (2005)

Figure 2-2. Map of desalination facilities showing design capacity.



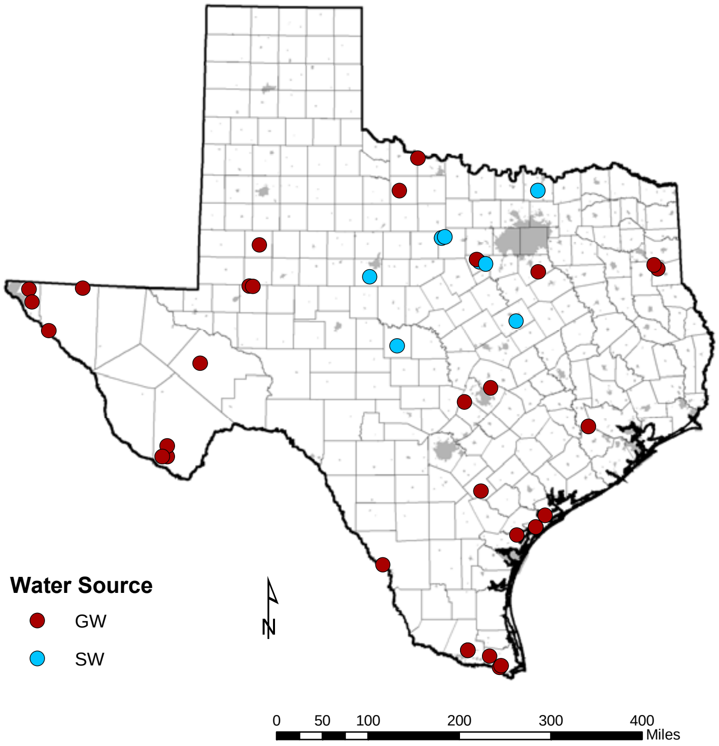
Note: Location of some facilities is only approximate; map from Nicot et al. (2005)

Figure 2-3. Map of desalination facilities (≥0.025 MGD DC) showing concentrate disposal method.



Source: Modified from Nicot et al. (2005) (unknown TDS category added)

Figure 2-4. Map of desalination facilities showing TDS of feedwater.



Source: Nicot et al. (2005), modified as noted in note D of Table 2-2; GW=Groundwater, SW=Surface water

Figure 2-5. Map of Texas desalination facilities showing feedwater origin.

Table 2-2. Characteristic summary of Texas desalination facilities with capacity ≥0.025 MGD and using evaporation pond for disposal.

| **Plant Name** | **County** | **Design Capacity (MGD)** | **Use** | **Source** | **Startup Year** | **Process** | **Blending ?** | **Disposal Method** |
|---|---|---|---|---|---|---|---|---|
| **PWS Plants with Design Capacity ~≥ 0.025 MGD** | | | | | | | | |
| City of Abilene | Taylor | 8 | DW | SW | 2004 | RO | No | EP |
| City of Brady | McCulloch | 1.5 | DW | SW[D] | 2005 | RO | Yes | EP |
| River Oaks Ranch | Hays | 0.14 | DW | GW | 1987 | RO | No | EP |
| Midland Country Club —fairways & greens[A] | Midland | 0.11 | DW/ IRR | GW | 2004 | RO | No | EP |
| Big Bend Motor Inn | Brewster | 0.072 | DW | GW | 1992 | RO | No | EP |
| City of Bayside | Refugio | 0.029 | DW | GW | 1990 | RO | No | EP |
| Horizon Regional M.U.D. | El Paso | 2.2 | DW | GW | 2001 | RO | Yes | LA/IRR/ EP |
| Haciendas Del Norte Water Improvement District | El Paso | 0.05 | DW | GW | 1981 | RO | Yes | LA/IRR/ EP |
| Esperanza Fresh Water Supply | Hudspeth | 0.023 | DW | GW | 1990 | RO | Yes | EP[B] |
| City of Los Ybanez | Dawson | 0.022[B] | DW | GW | 1991 | RO | Yes | EP[B] |
| Other Plants (not comprehensive)[C] | | | | | | | | |
| TMPA Gibbons Creek | Bryan | 0.144 | IND | SW | 1982 | RO | No | EP |
| Country View Estates | Medina | 0.014 | DW | GW | 2002 | RO | Yes | EP |

Source: Nicot et al. (2005); Mickley (2006) (see note [B])

Note: DW=drinking water; IND=industrial; GW=groundwater; SW=surface water; RO=reverse osmosis; EDR=electrodialysis reversal; EP=evaporation pond; IRR=irrigation; LA=land application

[A] Dual-use facility: public water supply and irrigation

[B] Nicot et al. (2005) did not provide disposal method for those two facilities, but Mickley (2006) did (p. 59)

[C] Survey presented in Nicot et al. (2005) does not systematically investigate plants with design capacity <0.0.25 MGD but records the information when accessible

[D] Nicot et al. (2005) listed this facility as having a GW source. However, during the interview with the operator at the plant for water sampling, it was discovered that only Lake Brady water is desalinated and then blended with GW from the Hickory aquifer

## *2.3 How Do Evaporation Ponds Operate?*

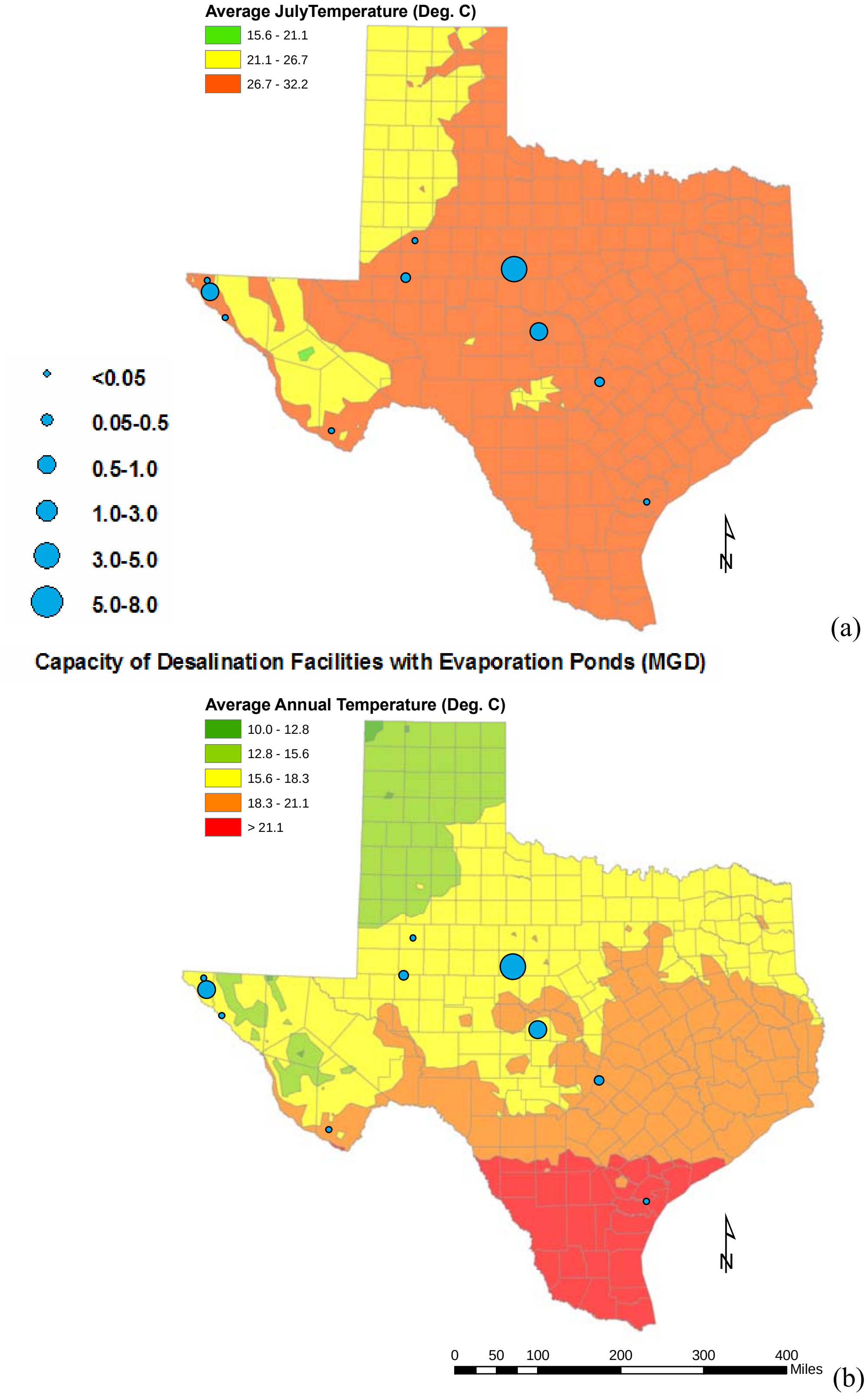
Impoundments and containment ponds are common in water/wastewater treatment and other industrial and agricultural operations. There is no fundamental difference between an evaporation pond and other types of containment ponds, except for, by design, the lack of an outlet. Regulatory requirements are similar (see Section 4.1). Typical evaporation ponds are not to be confused with sophisticated salinity-gradient solar ponds, whose principle relies on a contrast in salinity (Lu et al., 2002; Swift et al., 2002). Solar ponds function because of the large salinity/density gradient that prevents convection and mixing of the dense lower layer and dissipation of the solar energy. They are, in general, delicate to operate and fundamentally represent an energy-saving element more than a disposal feature. Solar lakes naturally functioning as solar ponds have been observed (Hudec and Sonnenfeld, 1980; Sonnenfeld and Hudec, 1980). They are, however, usually artificial, and all show a contrast in density between top and bottom of the water sheet of at least 15 g/L. The density contrast is often created by adding salt/brine at the bottom of the pond.

### 2.3.1 Evaporation Rates in Texas

Monthly precipitation and evaporation data as given by TWDB (2006a) from 1954 to 2004 are presented in detail in this section. Ambient temperature is another important parameter for geochemical modeling (Figure 2-6). Temperature data were obtained from the National Climatic Data Center (NCDC, 2006). Evaporation ponds rely on solar energy to reduce the liquid waste volume by evaporating water. The remaining liquid becomes more and more concentrated, leading to precipitation of minerals at the bottom of the ponds. The nature of precipitating minerals is site-specific and a strong function of the outfall chemical composition. Sludge may be evacuated as part of normal operations in the course of the plant's life, or it may remain at the bottom of the pond until closure of the facility. In both cases, the sludge is generally directed to a landfill. Evaporation ponds operate best in climatic environments with limited rainfall and high evaporation rates. Evaporation rates are reported in different ways: gross lake surface evaporation rate (depth that a lake surface is reduced by evaporation) and pan A evaporation rate, measured in a standard 10-inch-deep, 4-foot-diameter pan. Only the latter is directly accessible for measurement, and a correction must be applied to obtain the former, which is the parameter of interest. The correction factor, also called the *pan coefficient*, varies through the year and is location specific (0.57 to 0.92 across Texas, TWDB, 2006a). So that meaningful gross lake evaporation rates could be generated, it was decided in 1960 (Tschirhart and Rodriguez, 1998, p. 4) that the smallest practical area for evaporation calculation was a square 1° latitude and 1° longitude in size (as apparent in Figure 2-9). A total of 75 quadrangles cover Texas.

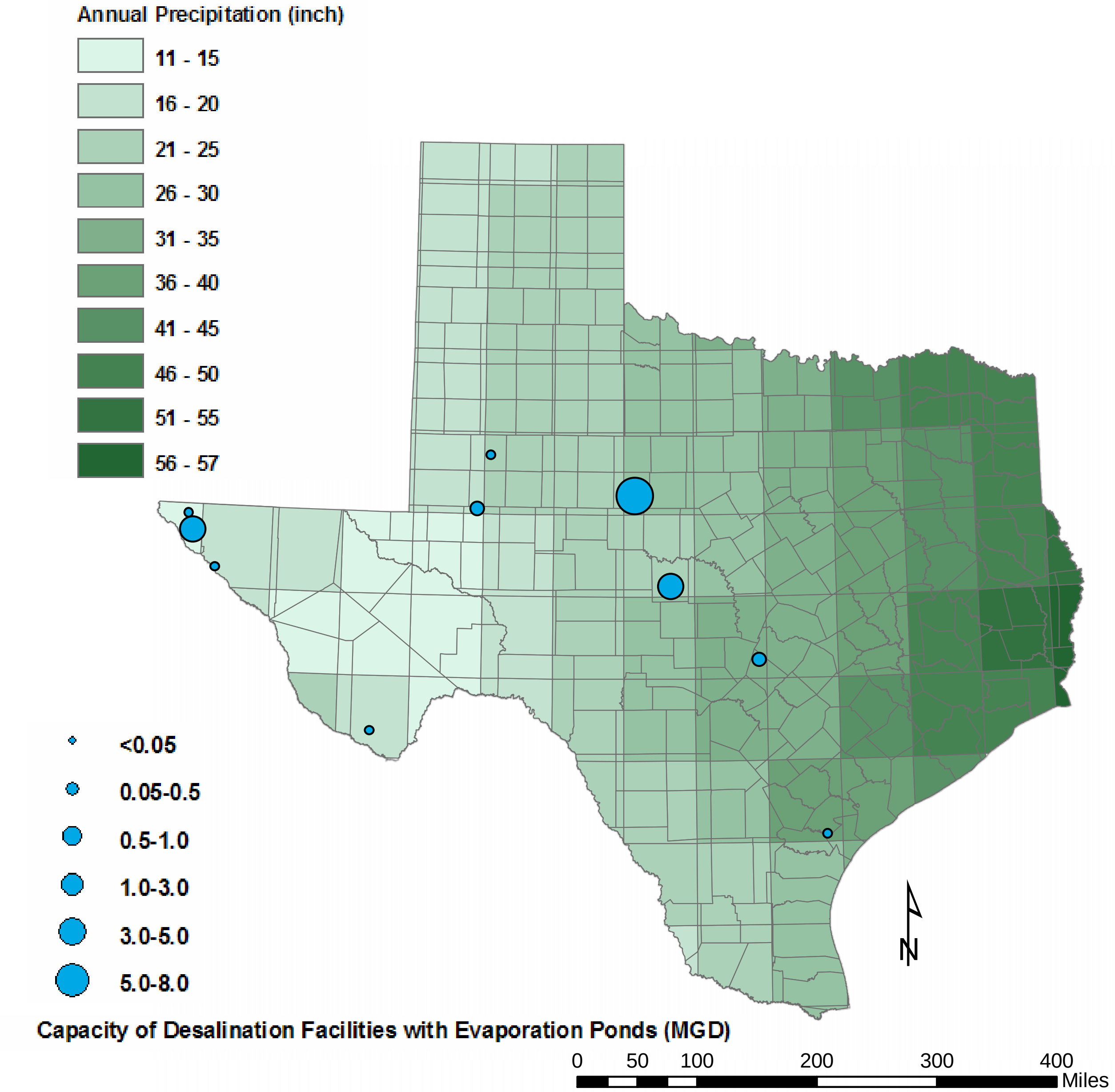
Net evaporation rate is site specific. It is positive on an annual basis when annual precipitation rate (Figure 2-7) is smaller than annual evaporation rate (Figure 2-8). Net evaporation rate follows the general weather patterns and most of Texas, and except for a limited band along the Louisiana border, net annual evaporation rates are positive (Figure 2-9). A study by Moore and Runkles (1968, figures 18–24) shows a similar pattern, although they used different pan coefficients, now out of date, resulting in different absolute values of net annual evaporation rate.

Many reports document the impact of salinity on evaporation rate (e.g., Harbeck, 1955). Mickley (2006, p. 162) suggested applying a coefficient of 0.7 to account for the salinity of the pond. When such a coefficient is applied, the areas with positive net evaporation rates are shifted somewhat to the west (Figure 2-10 and Figure 2-11). In calculation of net evaporation rates, "evaporation × salinity correction factor – precipitation" was calculated on a yearly basis then averaged and not done simply on evaporation and precipitation averages. A value of 0.7 is appropriate only if the ponds are projected to reach salt saturation during their expected lives. Our sampling of a few Texas evaporation ponds (Appendix E) suggests that they do not reach extreme salinity (that is, >30% salt by weight). A salinity correction factor of 0.9 ("low-salinity" water body—Figure 2-10) is used in the course of this work. This correction factor would be applied to salinity in the 100,000- to 150,000-ppm range (Harbeck, 1955, Fig. 2). The lower end of the concentration range corresponds to a small fresh-water evaporation rate, whereas the high end of the concentration range corresponds to an annual fresh-water evaporation rate of ~150 inches/yr (Harbeck, 1955, Fig. 2).



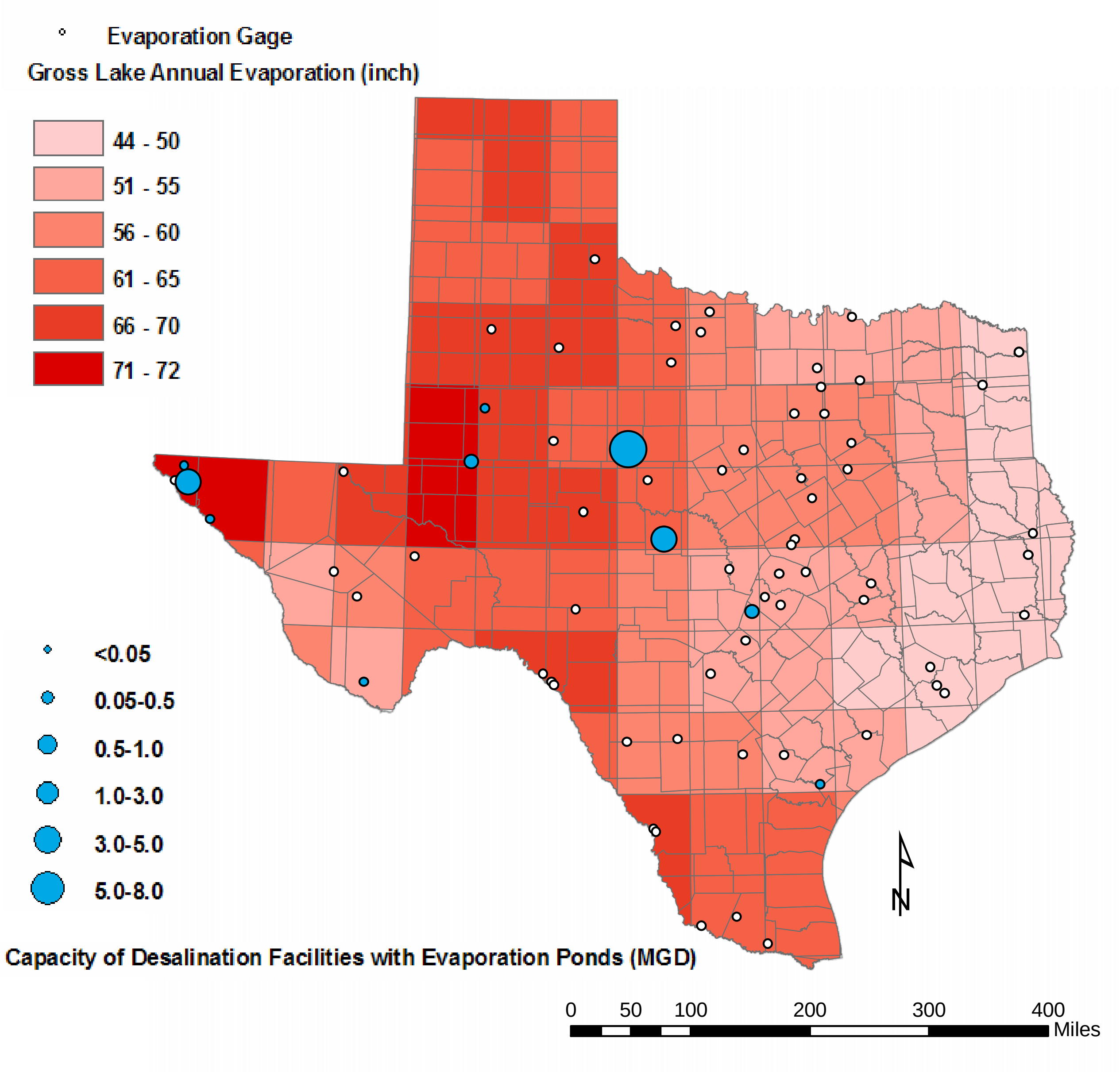
Source: NCDC Website (NCDC, 2006); desalination facility capacity from Nicot et al. (2005)

Figure 2-6. Average temperature (a) month of July, (b) annual.



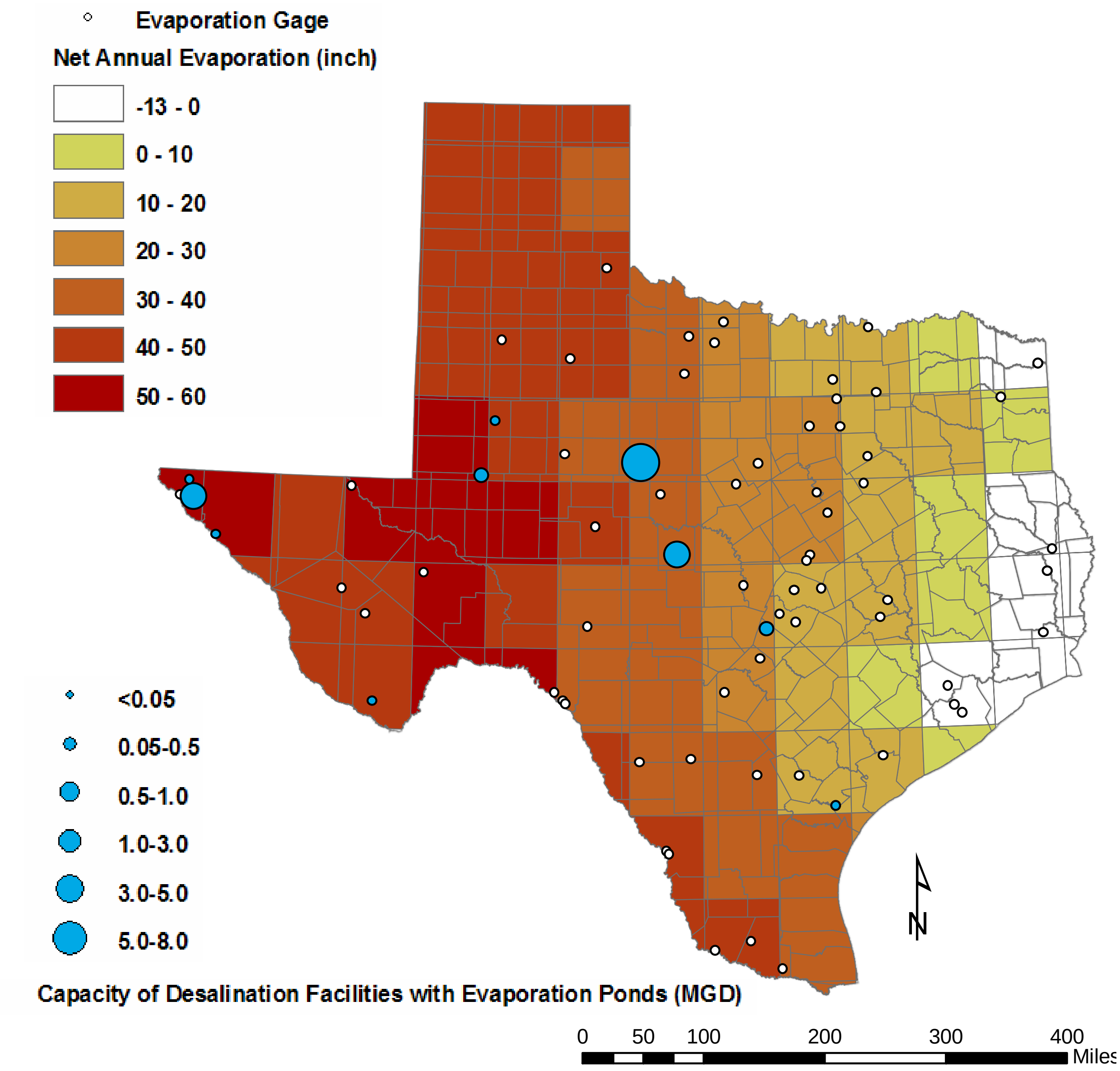
Source: Desalination facility capacity from Nicot et al. (2005); annual precipitation rate from TWDB Website (TWDB, 2006a)

Figure 2-7. Average annual precipitation rate.



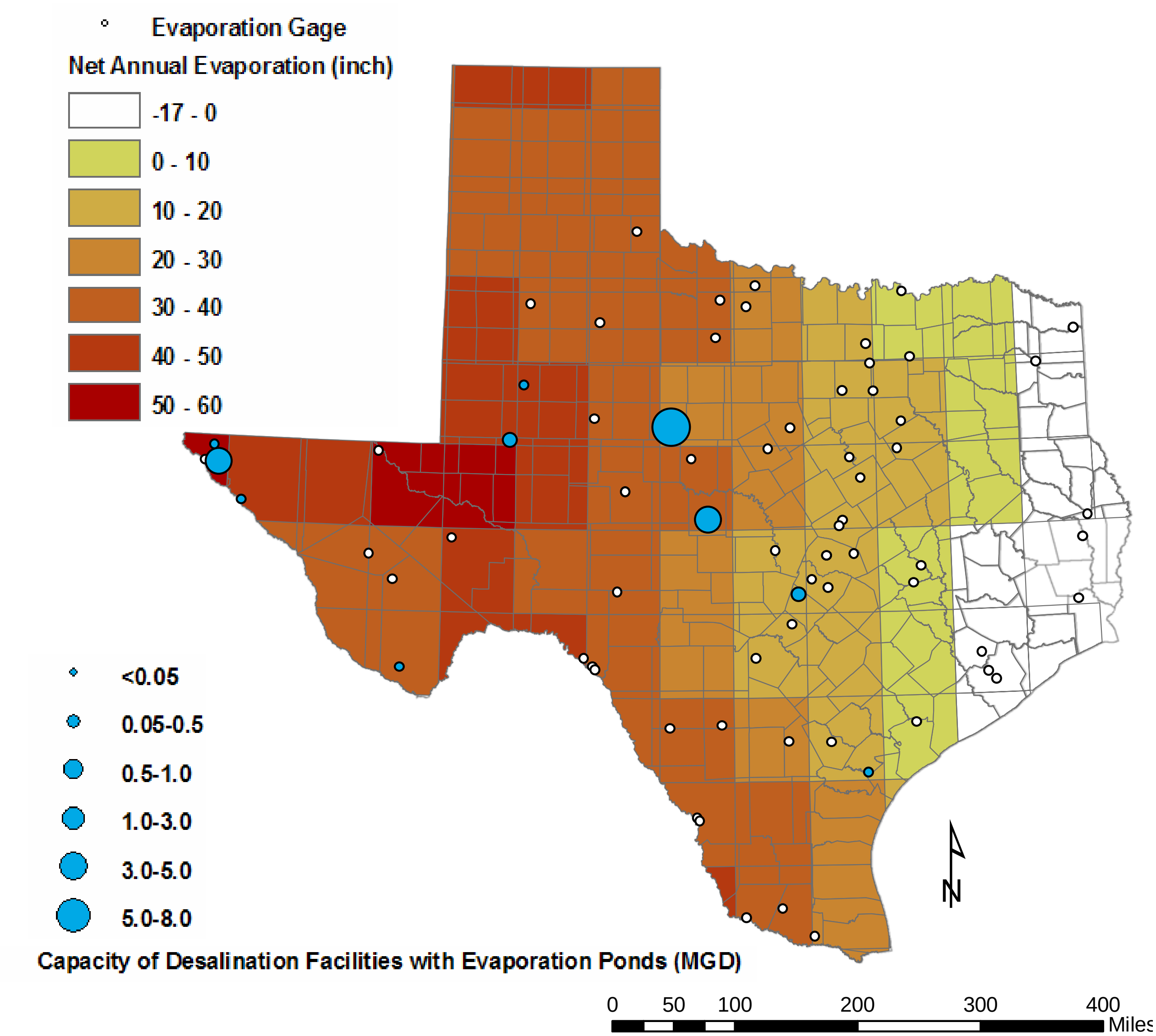
Source: Desalination facility capacity from Nicot et al. (2005); annual gross lake evaporation rate from TWDB Website (TWDB, 2006a)

Figure 2-8. Average annual gross lake evaporation rate.



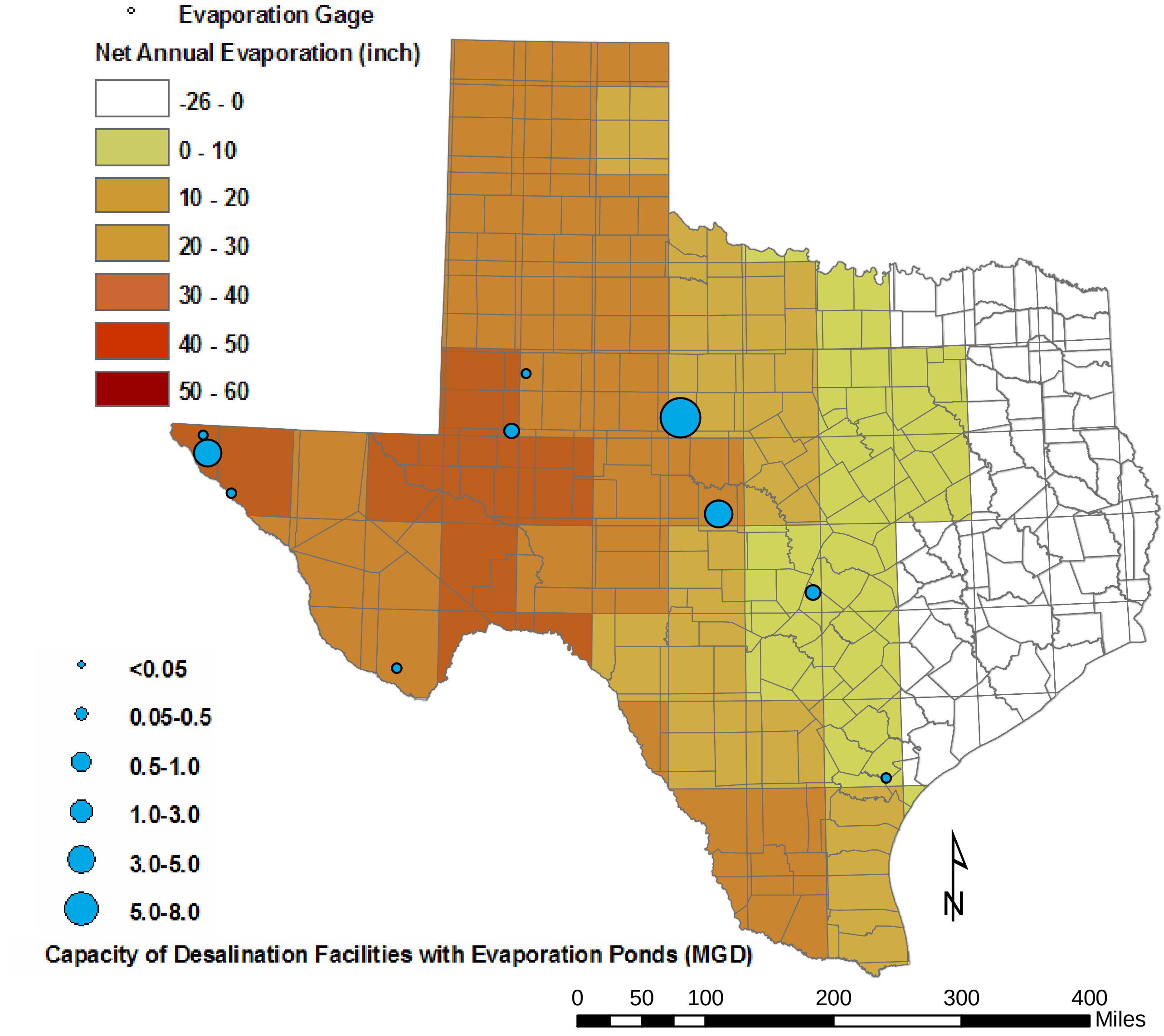
Source: Desalination facility capacity from Nicot et al. (2005); annual precipitation and gross lake evaporation rate from TWDB Website (TWDB, 2006a)

Figure 2-9. Net average annual fresh-water evaporation rates across Texas.



Source: Desalination facility capacity from Nicot et al. (2005); annual precipitation and gross lake evaporation rate from TWDB Website (TWDB, 2006a); salinity correction factor of 0.9 is applied to gross lake evaporation rate to account for the water salinity

Figure 2-10. Net average annual evaporation rates across Texas from a low-salinity water body.



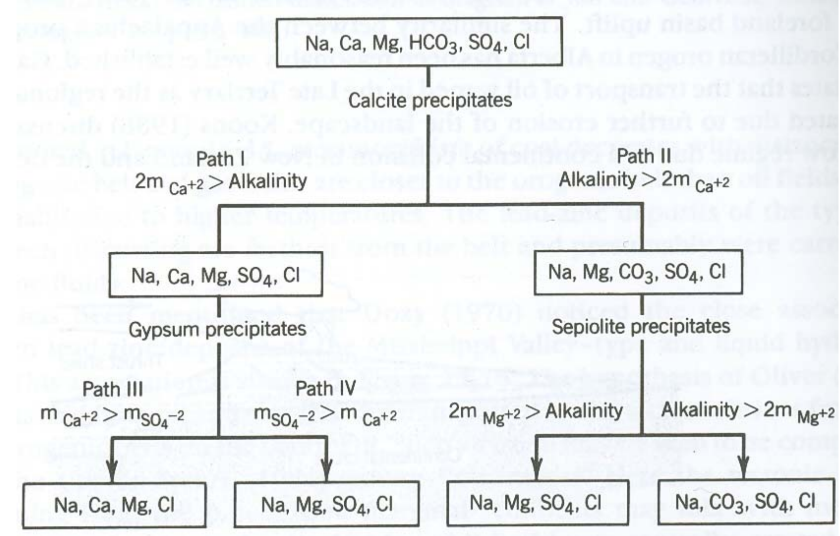
Source: Desalination facility capacity from Nicot et al. (2005); annual precipitation and gross lake evaporation rate from TWDB Website (TWDB, 2006a); multiplicative coefficient of 0.7 is applied to gross lake evaporation rate to account for the water salinity

Figure 2-11. Net average annual evaporation rates across Texas from a high-salinity water body.

### 2.3.2 Typical Mineral Suite—Chemical Divide

In the chemical evolution of an evaporation pond (with no overflow), general rules can be drawn despite the always complex chemical interactions and geochemical site specificity. Major ions making up most groundwater—fresh or saline—are $Ca^{+2}$, $Mg^{+2}$, $Na^{+}$, $K^{+}$, $SO_4^{-2}$, $HCO_3^{-}$, and $Cl^{-}$, to which $SiO_2$ can be added as a major neutral molecule. They form the bulk of the minerals precipitating when the solution is progressively concentrated. Most clay minerals require Al to precipitate. Al is generally present in minute amounts in solution but in much larger amounts as oxide/hydroxide colloids. As seen in an extensive geologic record, evaporation of seawater yields the following precipitation sequence of major minerals: calcite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$), and halite (NaCl). Calcite precipitates right away, gypsum precipitates only after approximately 80% of seawater has been removed, and halite does so when ~90% has evaporated. Because the activity of the water decreases as evaporation progresses, gypsum can be replaced by an anhydrous calcium sulfate: anhydrite ($CaSO_4$). More complex precipitation follows when about 95% of the water has been removed and when other ions start precipitating into soluble salts (e.g., sylvite—KCl; carnallite—$MgCl_2.6H_2O$). It should be noted that this salt trajectory is specific to seawater and waters of similar chemical composition.

In general, the first major minerals to precipitate are calcite and gypsum, sometimes accompanied by minor authigenic clays. Common precipitates (calcite, gypsum, and anhydrite) have a retrograde solubility; that is, their solubility decreases with temperature. It follows that in the summer, when pond water is warmer than the concentrate, precipitation can occur with no evaporation. Despite the obvious parallel that these minerals should dissolve back during the winter because of their increased solubility, the mass dissolved is typically less than the mass precipitated because fluid-mineral interactions are limited owing to the smaller surface area exposed to the aqueous environment. Such seasonal temperature variations were not addressed in this work. Evaporative concentration of groundwater follows well-known chemical pathways with multiple chemical divides. If aqueous concentrations increase, some minerals become supersaturated and start precipitating, removing ions from solution. Calcium is a prime example, and it precipitates with bicarbonate and sulfate as calcite or gypsum, respectively. However, when the system is open to the atmosphere, bicarbonate concentration cannot rise as high as that of sulfate (e.g., Boyd and Kreitler, 1986, Fig. 11) and stays more or less constant in equilibrium with atmospheric $CO_2$. Hardie and Eugster (1970) and Eugster and Jones (1979) described a generic evolution (Figure 2-12):



Source: Boyd and Kreitler (1986, p. 28) and Domenico and Schwartz (1990, p. 554)

Figure 2-12. Conceptual model of concentrate evolution.

This is the principle of chemical divide with critical points. Calcite is often the first mineral to precipitate from evaporation of groundwater (e.g., caliche layers), according to the reaction $Ca^{2+} + 2\ HCO_3^- = CaCO_3 + CO_2 + H_2O$. If calcium concentration (in equivalents) is higher than that of bicarbonate, calcium will be available to precipitate with sulfate to form gypsum. If not, most calcium will be consumed, and magnesium will then be available to precipitate as sepiolite. Sepiolite was chosen as the magnesium sink in the Hardie and Eugster (1970) model because it is consistent with observations of saline lakes of some western states. However, the chemistry of magnesium silicates is complex, and this choice may not be appropriate in all cases. Drever (1988, p. 239) stated that the most common magnesium minerals are magnesium smectites, dolomite, or magnesium-rich calcite. In this work, owing to continuous dilution of the pond water by outfall water, precipitation is limited to the most insoluble minerals, and the whole sequence of evaporites does not occur.

Other major ions, such as sodium and chloride, stay in solution longer and may precipitate together as halite. No major reaction controls sodium concentration in the way that calcium is controlled by the precipitation of calcite and gypsum. Sodium interactions with clays have, in general, a limited impact on sodium aqueous concentration. Magnesium is the third most abundant ion in seawater, although a distant third to sodium and chloride. Dolomites are a major sink, but they typically result from the interaction of limestones with magnesian brines. Potassium concentration is controlled mostly by interactions with clay minerals. At high ionic strength, it will also precipitate in sylvite (KCl) and other evaporites.

## *2.4 Geochemical Modeling Information*

The USGS-developed code PHREEQC (Parkhurst and Appelo, 1999) was used in the simulations. Several thermodynamic databases are available to the user, including Pitzer and LLNL databases. Because of the increasing ionic strength of pond water as the pond matures, the Pitzer database provided with the freeware was used. Only major ions (calcium, magnesium, sodium, potassium, chloride, sulfate, and bicarbonate) are relevant for the simulations at hand because interest is in the bulk of the precipitation and not in less common species. Thermodynamic information for relevant mineral species not present in the Pitzer database was imported from the LLNL database, especially minerals such as aluminum and/or silica in their structure. Such an addition renders results of the study more semiquantitative than if only the official Pitzer database had been used. Information about mineral molar volume was obtained from the EQ3/6 data0 database (e.g., Daveler and Wolery, 1992).

# 3 Approach and Sources of Information

In agreement with the scope of work, this project has two main objectives: (1) to determine whether any regulatory hurdle will obstruct the use of self-sealing evaporation ponds, especially in Texas, and (2) to assess the cost effectiveness of the self-sealing technique through a desktop analysis, supported by field data and a literature review. The two aspects of the project were pursued relatively independently. The regulatory analysis relied on interviews with TCEQ staff at the Austin headquarters, interviews with desalination plant operators and utility managers, and consultation of official documents (regulations, actual permits). The technical analysis could be divided into two parts. One part consisted of determining the amount and nature of the material precipitating from solution as water evaporates from the pond by using a numerical geochemical model. Unfortunately, such a desktop analysis does not provide hydraulic conductivity data; only field and laboratory experiments can do so. Instead, several publications supplied the needed information. The second part of the technical analysis involved integrating diverse regulatory options with the insights provided by modeling to quantify possible cost savings in implementing a self-sealing pond.

This section focuses mostly on the methodology used to establish composition of feedwater for desalination facilities across the state. Nature and amount of precipitates are a function of the feedwater and concentrate chemical composition. A later section (Section 4.2) will show that the chemical nature of the concentrate is not changed by RO and that it can be inferred in general terms from the feedwater chemical composition.

## *3.1 Feedwater Chemistry*

In order to produce results specific to Texas, specific water chemical composition from Texas had to be used. Desalination facility feedwater can be from either groundwater or surface water. Brackish groundwater is available across the state, but surface water is also an option in the northeast quarter of the state. Source information and preprocessing of water samples are described next. Because water chemical composition is used in geochemical modeling, stringent conditions must be applied on the set of samples retained for analysis.

### 3.1.1 Groundwater Data

The TWDB groundwater database (TWDB, 2006b) contains approximately 105,000 water-quality samples from about 55,000 unique locations across the state (including ~1,600 samples representing a mix from two aquifers). We first selected all samples with a TDS >1,000 mg/L and <5,000 mg/L, representative of possible candidate locations for desalination facilities and encompassing the salinity range of current plants (except for maybe a few with a TDS close to but below 1,000 mg/L). The following treatment was performed in this initial set.

Some of the TDS values provided in the TWDB groundwater database are not the true TDS. The TDS given in older databases (or older samples in more recent databases) is often lower than the sum of ions. It is because, in past decades, TDS was often measured as the weight of the residue after total water evaporation. In the process, about half of the bicarbonate is converted into gas during calcite precipitation, resulting in a true TDS higher than the reported TDS. The true TDS is computed as either the sum of ions or the sum of reported TDS and half of the bicarbonate concentration. This computation resulted in a total of 29,459 samples with a TDS >1,000 mg/L and <5,000 mg/L. After all samples with an electrical balance not in the -5% –5% range, with no pH data or pH outside of the 5–9.5 range, or with a TWDB-defined reliability of "01" or "02" (Nordstrom and Quincy, 1999) had been deleted, the number of acceptable samples had been reduced to 21,823. Keeping only the most recent sample for each unique location brought the number of available samples to 13,583 over Texas, to 12,835 in areas with positive net annual evaporation rates, and to 7,642 in areas with high net annual evaporation rates (Figure 3-1). Positive net evaporation rates occur when potential evaporation rates are larger than precipitation rates. They can be defined within a variety of time periods but are generally defined on an annual basis.

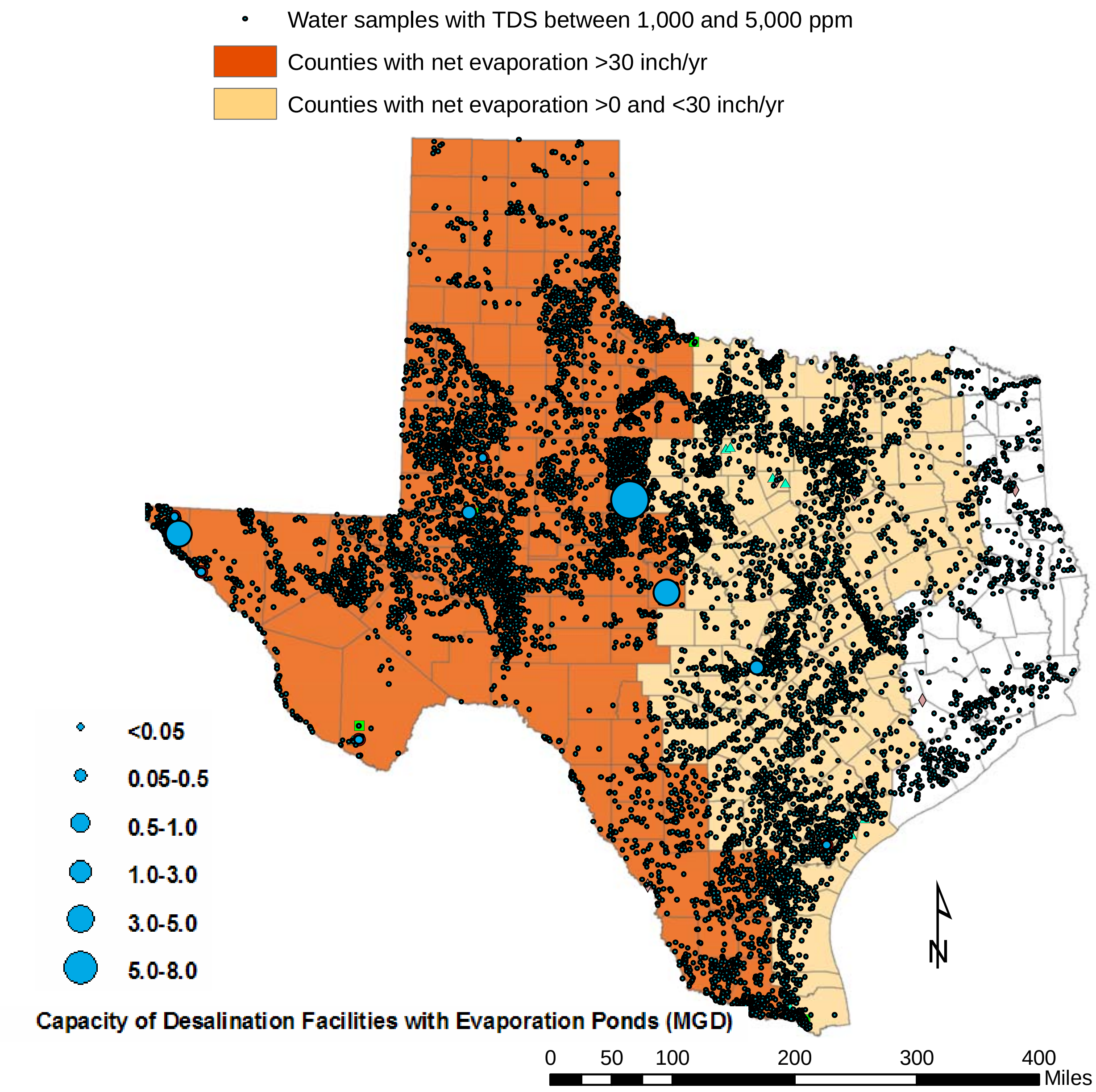
Samples are categorized according to their concentration in major ions—calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl), sulfate ($SO_4$), and bicarbonate ($HCO_3$)—to which silica ($SiO_2$) can be added, as represented on the Piper plot of Figure 8-2 (Appendix A). Given the large variety of aquifer types in Texas, it is not surprising to see that almost every type of water is present in the state. In order to have a manageable data set, we first divided the larger set up into smaller significant data sets, corresponding to the selected representative samples for each aquifer (Table 3-1). A total of 12,720 samples were distributed among 19 groundwater groups, corresponding to TWDB-defined aquifers when possible. For example, the "Eocene" group includes the Carrizo-Wilcox major aquifers and the Queen City, Sparta, and Yegua-Jackson minor aquifers, as well as other samples outside of these main formations, such as sandier facies of the Midway group (typically assumed to be the bottom confining unit of the Carrizo-Wilcox aquifer). On the other hand, the "Seymour," the "Brazos River Alluvium," and the "Ogallala" groups correspond to the Seymour, Brazos River Alluvium, and Ogallala aquifers, respectively. There is no TWDB-defined Rio Grande River Alluvium aquifer, but we defined a "Rio Grande Alluvium" group because of its specific geochemical properties. Similarly, there are several water-bearing formations of Pennsylvanian or Permian age in North-Central Texas between the TWDB-defined Ogallala and Trinity aquifers that have not been officially sanctioned by the state as minor or major aquifers. Because those groups are operationally defined mostly for the purpose of understanding their behavior in evaporation ponds, some single aquifers have been split to allow for the difference in lithology. For instance, Trinity aquifer samples have been included in either the "Cretaceous Limestone" or the "Cretaceous Sandstone" groups, depending on the nature of the host rock (e.g., Hosston Sands or Glenrose Limestone).

Geochemical characteristics of the 19 groundwater groups (and the one surface-water group discussed subsequently) are described in Appendix A. It should be noted that the geochemical nature of the brackish samples does not necessarily represent that of the fresh-water samples of the same aquifers. One can consult the water-quality section of the relevant GAM models (http://www.twdb.state.tx.us/gam/index.htm) for a better picture of the geochemistry of a given aquifer as a whole. Figure 3-2 plots the location of the central sample of each group (see Appendix A) on a Piper plot and demonstrates the wide range of the chemical composition of slightly brackish waters in the state. Out of the 20 groups, 4 stand out in their composition: Capitan Reef, Bone Spring / Victorio Peak, Permian Evaporite, and Brazos River Alluvium. Central values of all other groups occupy a relatively compact area of the Piper plot. They tend to plot toward the sodium and potassium apex, with calcium being generally second in molar concentration and toward the chloride apex and sulfate second in anion abundance. Permian Evaporite water shows a dominant calcium sulfate water, whereas Capitan Reef and Bone Spring / Victorio Peak waters also tend to a less-dominant calcium sulfate composition. Brazos River Alluvium has a strong bicarbonate imprint and tends toward a calcium carbonate water type.

Table 3-1. List of water sample groups (12,720 samples)

| Group Name | Number of Samples with TDS >1,000 and <5,000 ppm | Examples of Aquifers/Formations Included in Group* |
|---|---|---|
| Mixed Alluvium | 694 | Alluvium, Quaternary, terrace deposits |
| Brazos River Alluvium | 180 | **Brazos River Alluvium** |
| Rio Grande Alluvium | 184 | Rio Grande River Alluvium |
| Seymour | 936 | **Seymour aquifer** |
| Bolson | 316 | **Hueco, Mesilla, Presidio, Redford, Red Light Draw, and Salt Bolsons** |
| Ogallala | 1156 | **Ogallala aquifer** |
| Pecos Valley | 393 | **Pecos Valley aquifer** |
| Gulf Coast Sandstone | 1773 | Jasper, Evangeline, and Chicot aquifers; Beaumont Clay, Goliad Sand (**Gulf Coast aquifer**) |
| Eocene | 874 | **Carrizo-Wilcox aquifer, Queen City and Sparta aquifers, Yegua-Jackson aquifer,** Bigford Formation |
| Cretaceous Limestone | 1230 | **Edwards and Trinity aquifers**, Austin Chalk |
| Cretaceous Sandstone | 2373 | **Trinity aquifer, Antlers Sandstone, Blossom Sandstone, Nacatoch Sandstone, Woodbine Sandstone** |
| Triassic Sandstone | 318 | **Dockum aquifer** |
| Permian Evaporite | 465 | **Blaine aquifer, Rustler aquifer**, Whitehorse Group, Artesia Group |
| Permian Limestone | 768 | Wichita Group, Clearfork Group, Choza Formation, Arroyo Formation, Lueders Limestone |
| Permian Sandstone | 106 | San Angelo Sandstone |
| Bone Spring – Victorio Peak | 130 | **Bone Spring and Victorio Peak aquifers** |
| Capitan Reef | 27 | **Capitan Reef aquifer** |
| Pennsylvanian | 724 | Canyon Group, Cisco Group, Strawn Group, Graham Formation |
| Llano Uplift | 41 (limestone)<br>32 (sandstone) | **Marble Falls, Ellenburger, San Saba Limestones**<br>**Hickory Sandstone** |
| | | |
| Surface water | 496 | N/A |

*TWDB-recognized aquifers (minor or major) are in **bold print**



Source: Desalination facility capacity from Nicot et al. (2005); annual precipitation and gross lake evaporation rate from TWDB Website (TWDB, 2006a); multiplicative coefficient of 0.9 is applied to gross lake evaporation rate to account for the water salinity; water samples: TWDB groundwater database (TWDB, 2006b)

Note: Because quadrangle and county boundaries do not match, there is not an exact match of the 0 and 30-inch net evaporation lines

Figure 3-1. Map of counties with no, low to medium (<30 inches), and high (>30 inches) net evaporation rates and of groundwater samples with TDS >1,000 and <5,000 ppm.

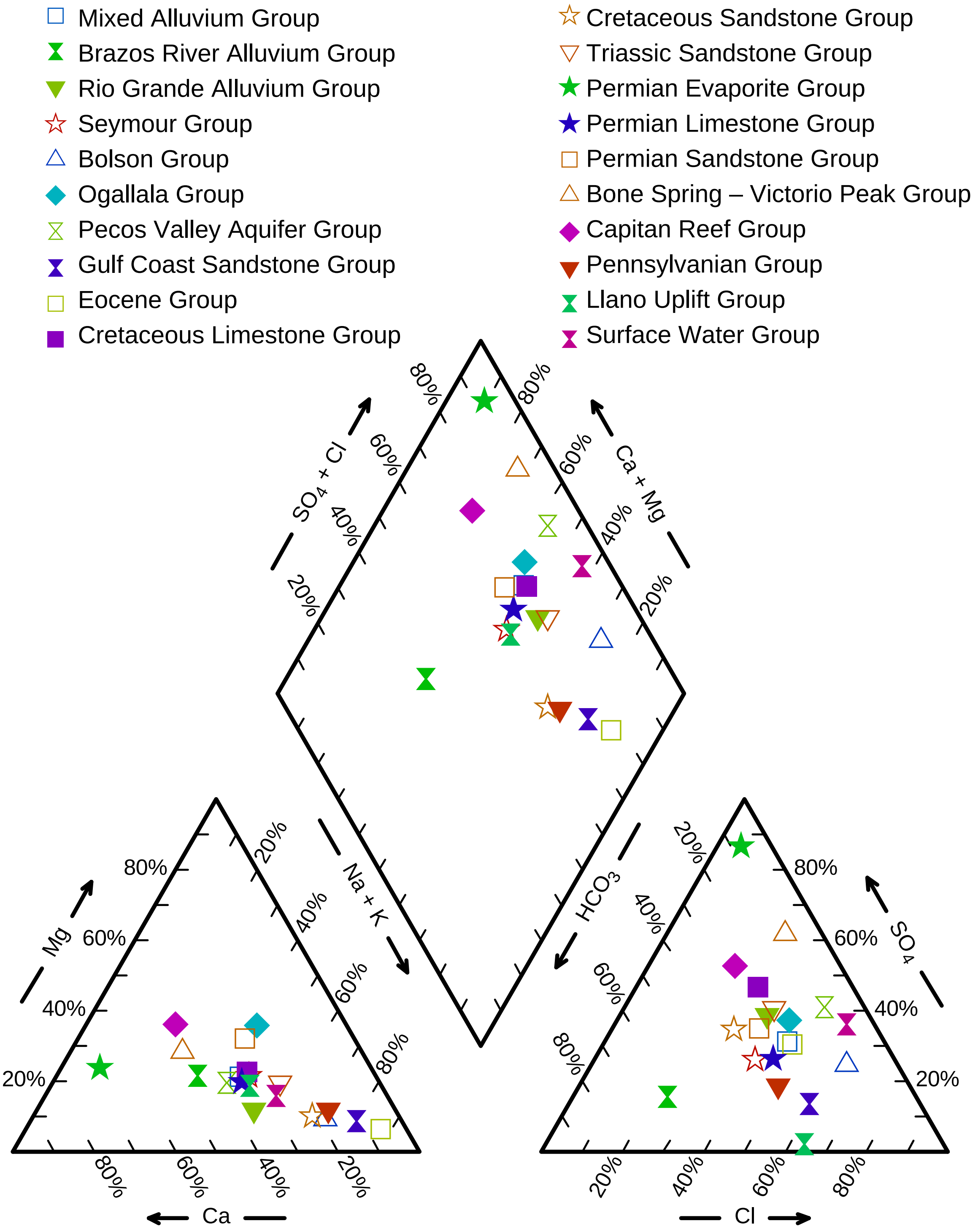
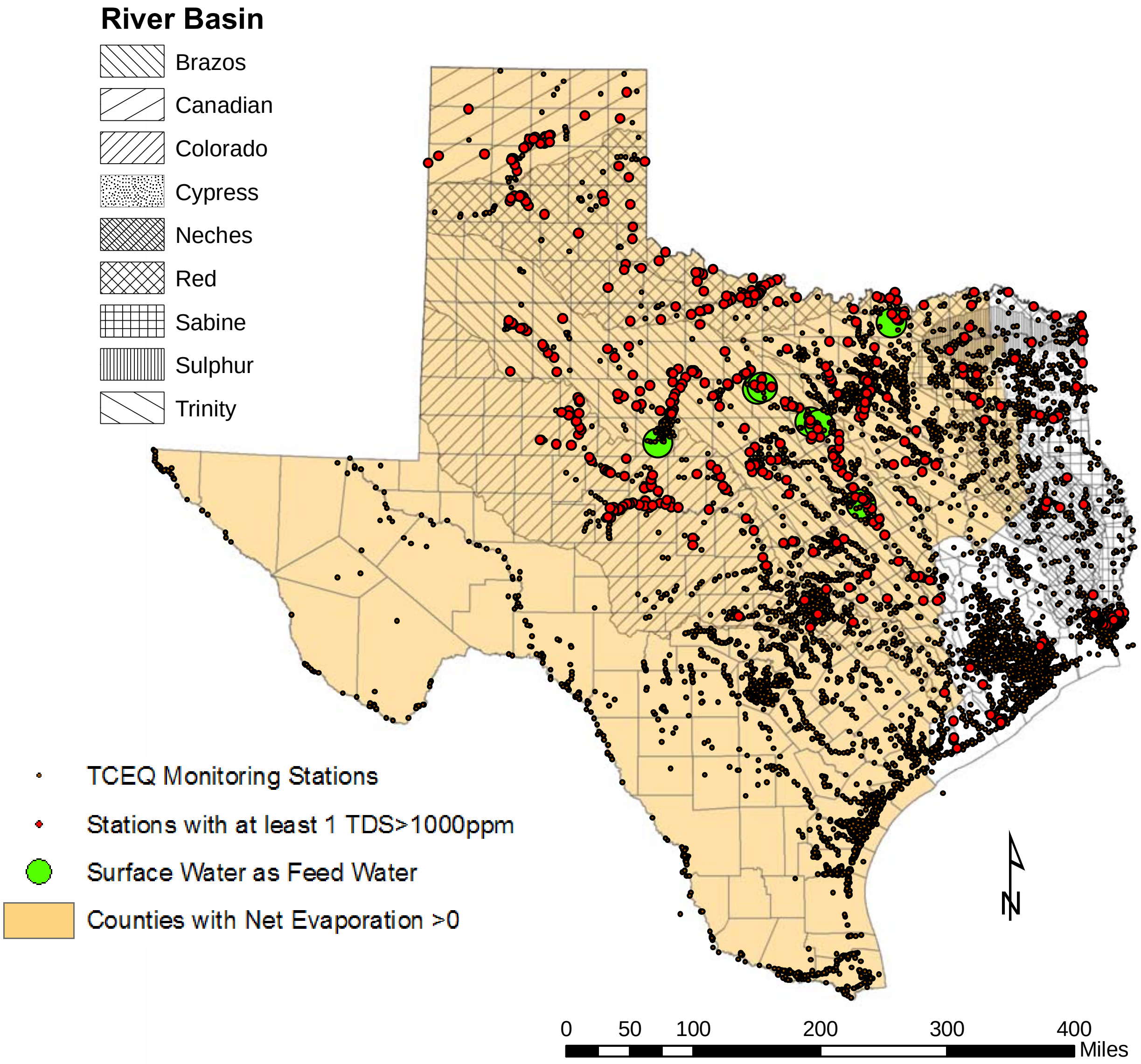


Figure 3-2. Piper plot of central values of all 20 groups.

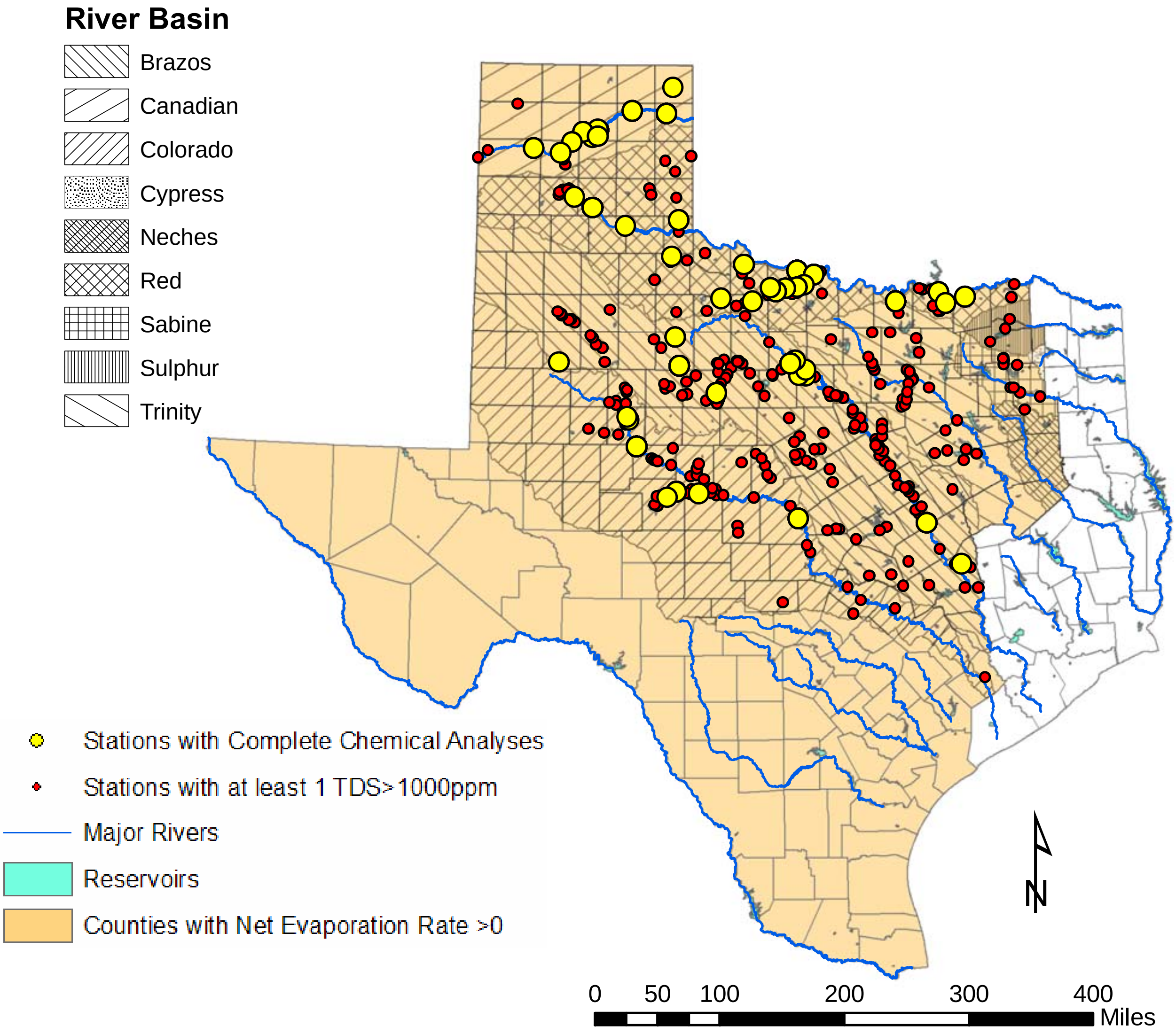
### 3.1.2 Surface-Water Data

The TCEQ surface-water database (TCEQ, 2006b) ("Texas Clean Rivers Program") contains surface-water chemical analyses dating back to 1968 in approximately 8,400 unique locations across the state, mostly in the east half of the state (Figure 3-3). Out of these, 49 stations have at least 1 complete chemical analysis (often only chloride is analyzed) with TDS >1,000 ppm and are located (Figure 3-4) in the section of river basins (Canadian, Red, Brazos, Trinity, Sabine, and Colorado) with net positive evaporation rates and where desalination facilities have historically used surface water as feedwater. The 49 stations have a combined 496 relevant chemical analyses.



Source: Feedwater from Nicot et al. (2005); station location and analyses from TCEQ (2006b)

Figure 3-3. Surface-water stations with at least one sample with a TDS >1,000 ppm.



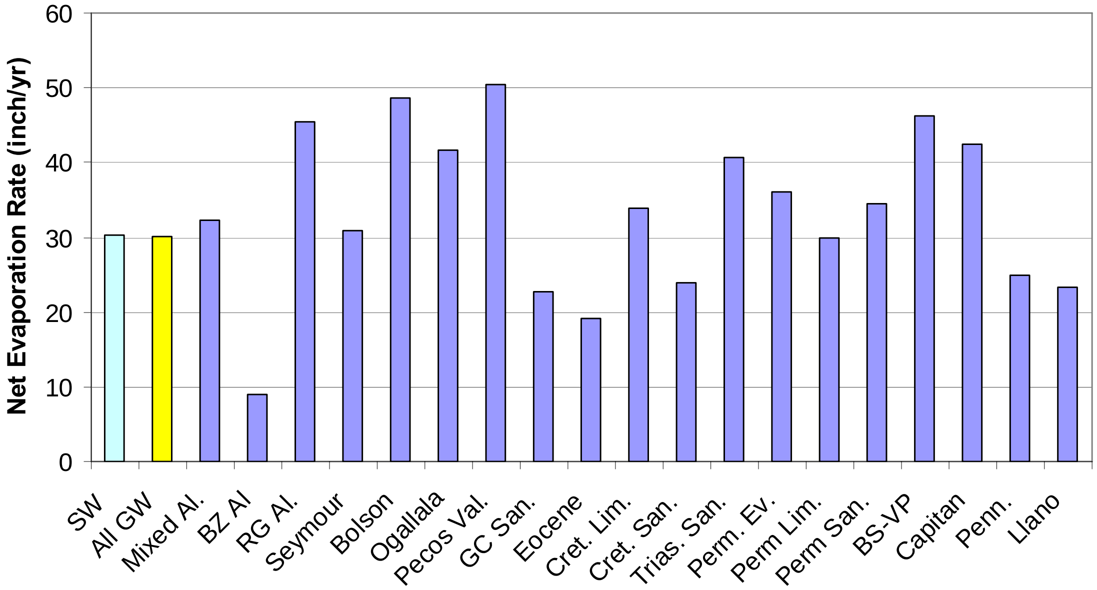
Source: Feedwater from Nicot et al. (2005); station location and analyses from TCEQ (2006b)

Figure 3-4. Surface-water stations with chemical analyses of major ions and TDS >1,000 ppm.

### 3.1.3 Feedwater Groups and Evaporation Rates

It can be observed that, in any case, net evaporation rates are high in the arid west of the state, in the 40-to 60- and 20- and 40-inch/yr range for low- and high-salinity water, respectively. These passive net evaporation rates can be enhanced by applying additional technology (at a cost), such as spraying into the atmosphere the concentrate and/or pond residual water to increase evaporative surface area (e.g., Ahmed, 2000). Such an approach has been planned for the River Oaks Ranch facility (Hays County).

A net average annual evaporation rate (Figure 3-5) was computed for each of the water groups defined in Appendix A by sampling the net annual evaporation rate at each sample location with the help of GIS software and averaging the rate over all samples. It varies from <10 inches/yr over the Brazos Alluvium aquifer to ~50 inches/yr in the Pecos Valley aquifer and the Bolson aquifer of far-west Texas. A weighted average of net evaporation rates for all samples is ~30 inches/yr.



Note: Evaporation rate assumed to be 90% of gross lake evaporation rate

Figure 3-5. Net average annual evaporation rate for each water sampling group.

## 3.2 *Regulatory Review*

The main written sources of information were articles in Title 30 of the Texas Administrative Code (TAC) dedicated to TCEQ, especially Chapter 317 "*Design criteria for sewerage systems*" and Chapter 309 "*Domestic wastewater effluent limitation and plant siting,*" as well as similar documents for neighboring states. Municipal wastewater treatment rules are used as guides for evaluation but are not strict regulatory requirements for industrial permits. Appendix B reproduces relevant subchapters and excerpts from TCEQ instructions for completing an industrial wastewater permit application (TCEQ, 2006a). To clarify how to apply these rules to self-sealing evaporation ponds, we interviewed several TCEQ staff members. In the Water Quality Division: Kelly Holligan (Team Leader, Industrial Wastewater Permits) and Michael Chadwick (Geologist) and in the Environmental Law Division: Kathy H. Brown. In addition, we obtained copies of industrial wastewater permits of two Texas facilities using evaporation ponds (River Oaks Ranch in Hays County and Brady in McCulloch County –see Appendix C).

## 3.3 *Field Sampling and Technical Interviews*

In the course of the project, opportunities to undertake field sampling materialized. For a better understanding of natural environments sharing important characteristics with evaporation ponds (that is, natural analogs) (Section 4.3.2), multiple water and sediment samples were collected in the Texas Panhandle as described in Appendix D. Water samples, bottom sediments, and, when applicable, crust samples were taken at four facilities with evaporation ponds across Texas (River Oaks Ranch in Hays County, Brady in McCulloch County, Abilene in Taylor County, and Horizon MUD in El Paso County). Those samples were useful in adjusting geochemical modeling results and in providing data about actual evaporative processes in the state of Texas.

# 4 Analysis and Results

## *4.1 Legislative Options*

This "regulatory" section (1) describes the current State and Federal regulatory limitations on self-sealing pond-liner technology; (2) lists the policy, regulatory, and statutory shifts potentially needed to overcome any existing procedural impediments to efficient permitting of this technology; and (3) makes projections on the likelihood of success of the possible shifts in permitting structure needed to allow self-sealing pond technology.

According to Federal regulations, wastewater is classified as either municipal or industrial—the former being restricted to wastewater treatment plant (WWTP) effluent that may contain microorganisms. It follows that desalination concentrates are by definition industrial wastes.

### 4.1.1 Regulatory Framework

#### 4.1.1.1 Federal Statutory and Regulatory Requirements

The Federal Clean Water Act established the National Pollutant Discharge Elimination System (NPDES) to protect the quality of all navigable waters in the United States. Any facility or operation that would result in any discharge into waters in the United States is required to obtain a permit from the U.S. Environmental Protection Agency (EPA) or a state delegated to administer the NPDES program. The Texas Commission on Environmental Quality (TCEQ) has been delegated to permit all facilities in Texas and has adopted and implemented the Texas Pollutant Discharge Elimination Program (TPDES).

The definition of navigable waters has been broadly interpreted to include lakes, rivers, streams, wetlands, and all other water bodies that are hydrologically connected that could transport pollutants into them. Thus, if evaporation ponds are effectively engineered to eliminate discharge, no Federally mandated TPDES water-quality permit would be required.

#### 4.1.1.2 Texas Statutory Requirements

The Texas State Water Code, Subtitle D, Chapter 26, Water Quality Control, describes the requirements for permitting construction, operation, and maintenance of any facility in Texas with the potential of discharging pollutants into or adjacent to waters in the state. The following is an excerpt from Chapter 26:

*Sec. 26.121. UNAUTHORIZED DISCHARGES PROHIBITED.*
*Text of section effective until delegation of NPDES permit authority*
*(a) Except as authorized a rule, permit, or order issued by the by the commission, no person may:*
*(1) discharge sewage, municipal waste, recreational waste, agricultural waste, or industrial waste into or adjacent to any water in the state;*
*(2) discharge other waste into or adjacent to any water in the state which in itself or in conjunction with any other discharge or activity causes, continues to cause, or will cause pollution of any of the water in the state…*

TCEQ administers this provision and is responsible for issuing required permits. One important distinction between State and Federal statutes is the State's requirement to permit discharges adjacent to, as well as into, waters in the state. Hence, evaporation ponds are subject to these "State-only" permit requirements.

#### 4.1.1.3 Texas Regulatory Requirements

TCEQ administers the Texas Land Application Permit (TLAP) program to regulate all discharge activities that do not directly impact waters in the state, including irrigation, evaporation, and subsurface disposal of wastewater. A State-issued permit must be obtained prior to the construction and operation of any regulated facility.

No specific rules have been adopted to regulate the permitting of industrial wastewater treatment facilities. However, detailed instructions for "*Completing the Industrial Wastewater Permit Application*" describe specific criteria for impoundments at industrial facilities, including liner information (TCEQ, 2006a), and provide help in filling out the Industrial Wastewater Permit Application (TCEQ-10411, revised 10/2004). Other documents on related topics have been released as well to facilitate applicants' tasks (e.g., TNRCC, 1994, on municipal waste liners).

Policies for industrial facilities are based primarily on provisions of the Texas Administrative Code, Title 30, Chapter 317 (30 TAC 317), Design Criteria for Sewerage Systems, for domestic wastewater treatment facilities, including no-discharge activities such as evaporation ponds. The following requirements are applicable (in full in Appendix B):

- Rule 317.4, Wastewater Treatment Facilities, includes requirements for wastewater stabilization ponds (secondary treatment ponds) on which the evaporative pond requirements are based. However, unlike the current evaporation pond requirements for industrial facilities, the criteria specified in this rule require a 2-foot-thick layer of clay soil (in situ or constructed) and geomembrane liner thickness of only 20 mils. The rule does allow for the use of "other methods with commission approval."
- Rule 317.5, Sludge Processing, includes requirements for dewatering and drying operations that would be applicable to desalination evaporative ponds.
- Rule 317.1(a)(4)(B) includes requirements for obtaining approvals for innovative and nonconforming technologies. These provisions would guide TCEQ staff in evaluations necessary to gain approval of any alternative liner or system for desalination evaporation ponds.
- Rule 309.13(d), Unsuitable Site Characteristics, includes criteria for wastewater impoundments overlying recharge zones of major and minor aquifers, including acceptable minimum liner specifications, which are more stringent than the criteria of 30 TAC 317.4. The soil liner (in situ or constructed) must be at least 3 ft thick, with a hydraulic conductivity no greater than $10^{-7}$cm/s. The minimum thickness required for a geomembrane liner is 30 mils. These standards are the basis for the requirements for evaporation ponds for industrial facilities.

These cited rules for municipal wastewater treatment, although used as guides for evaluation, are not considered to be strict regulatory requirements for industrial permits. TCEQ has considerable latitude in approving alternative permit requirements. The Waste Permit Division at TCEQ allows the option of an "alternative liner," in which the permitee submits plans for any other pond lining method. Such a case could occur when usable groundwater quality is inferior to wastewater-stream quality (alternative liner, option 1; see Appendix C). The following is a brief description of the permit process.

An evaporation pond for a desalination plant would require application for an industrial permit (TCEQ-10411) under the TLAP program. The application process is administered by the TCEQ

Water Quality Division. The following individuals may be contacted for further information and instructions.

- Wastewater Permits Section Chief—Chris Linendoll (512) 239-4515
- Municipal Permits Team Leader—Kelly Holligan (512) 239-2369

Information required in the application includes, but is not limited to,

- Facility/Site Information—nature and type of industrial activity, SIC and NAICS codes, process description, materials that may reasonably be expected to be in effluent, a facility map, siting relative to the 100-year floodplain.
- Treatment System—physical, chemical, and/or biological treatment processes to be used and a flow schematic with a water balance for each treatment unit.
- Impoundments—type of impoundment (evaporation) identifying it as a no-discharge pond and describing proposed pond-liner specifications. For alternative pond-liner technology, additional technical information must be provided demonstrating equivalent performance criteria. Minimum data for all impoundments include
  - Dimensions—length, width, and depth of water surface at capacity; depth from natural ground level, depth of freeboard.
  - Test results—liner permeability, compatibility with wastes, depth of impermeable clay soils, etc., as applicable.
  - Leak Detection—type of detection systems or groundwater monitoring wells and available data.
  - Seasonal High Water Table—depth of seasonal high water table in relation to the bottom of the impoundment.
  - USGS Quadrangle Map—map locating water supply wells and/or monitoring wells within ½ mi of the impoundment and copies of State Water Well Reports with data on depths to groundwater (TCEQ Central Records [512] 239-0900).
  - Site-Specific Data—available data pertaining to groundwater, soils, geology, etc., that can be used to assess the potential for migration of wastes from the impoundment and the contamination of ground- or surface waters.
- Outfall Information—location (latitude/longitude), flow volume, and duration of each discharge point into the impoundment.
- Pollutant Analysis—four separate analytical results as specified unless prior approval is obtained from TCEQ.
- Engineering Report—calculations for evaporation for average long-term and worse-case conditions and for storage volume.

Once the permit application has been found to be administratively and technically complete by TCEQ, all necessary public notice requirements must be satisfied. This public notice informs the public that a draft permit has been prepared for disposal of wastewater. The public may provide comments or request a public meeting or request a public hearing on the draft permit. A permit application fee and an annual water quality fee may be required.

Initial industrial wastewater permits are typically issued for a 5-year period. Renewal periods may vary from 2 to 10 years and may be adjusted to correspond to the State's basin planning cycle. Recertification of the integrity of the pond liner may be required any time materials are removed from the pond or upon renewal of the permit.

### 4.1.2 Policy Overview

The Texas Land Application Permit (TLAP) is required for all nondischarge facilities, such as evaporation ponds, to prevent any wastewater discharge that would otherwise be regulated under the Federally-mandated Texas Pollutant Discharge Elimination Program (TPDES) or that may cause contamination of groundwater. These state-only permits specify liner characteristics, freeboard height, maximum discharge rates, and other parameters to satisfy the statutory obligations to regulate discharges "adjacent to" waters in the state, including groundwater, that are not regulated by Federal requirements. Data must be provided during the application process to demonstrate compliance during typical and worst-case conditions expected for the geographic location of the proposed facility. No water-quality standards are applied to discharges into the ponds if all TLAP conditions are met.

Evaporation ponds are most appropriate in the arid areas of the state where meteorological conditions are most conducive to this technology. The following minimum design features and criteria have been established by TCEQ. The TCEQ Water Quality Permitting staff has also indicated that a leak-detection system or a groundwater monitoring system similar to that required for geomembrane liners would also be required for alternative liners until published studies verify a barrier effect under all ambient conditions.

#### 4.1.2.1 Pond Sizing

The size of an evaporation pond must be sufficient to satisfy acceptable water balance and storage-capacity calculations found in "Completing the Industrial Wastewater Permit Application, Instructions for Worksheet 3.1 – Surface Land Disposal of Effluent (Example 6)" (TCEQ, 2006a). Data for net evaporation values may be obtained from TWDB's Evaporation/Precipitation Data for Texas (TWDB, 2006a). Documentation of alternative data sources must be provided. Criteria considered include average annual rainfall and evaporation rates for the previous 25 years; worst-case rainfall and evaporation rates experienced during any year within the previous 25 years; maximum effluent flow, typically converted to inches per month per acre of surface area of the evaporation pond; and maintenance of a minimum of 2 ft of freeboard at all times (including worst-case conditions).

#### 4.1.2.2 Pond Liner

The liner of an evaporation pond must ensure a hydraulic conductivity of no greater than $10^{-7}$ cm/s and must satisfy the requirement for a surface impoundment at a domestic wastewater treatment facility described in 30 TAC Chapters 317 and 309. The following three liners are considered acceptable: in situ clay with a thickness of 3 ft or more, compacted clay with a thickness of 3 ft or more, or geomembrane liner of 30-mil thickness or more with an underground leak-detection system or groundwater monitoring system. The clay (in situ or constructed) must have >30% material passing the #200 sieve (0.074 mm), liquid limit ≥30%, and plasticity index ≥15% –information on those parameters is available in the manuals "Standard Test Methods for Amount of Material in Soils Finer than No. 200 (75-m) Sieve," D1140, and "Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils," D4318, published by the American Society for Testing and Materials (ASTM). In addition, the clay must be compacted in lifts of no more than 9 inches to 95% of its standard Proctor maximum dry density to achieve the required maximum conductivity of $10^{-7}$ cm/s.

#### 4.1.2.3 Alternative Liner Requirements

An alternative liner technology may be approved by TCEQ if it can be demonstrated to provide an equivalent degree of protection (see, for example, Appendix C, alternative liner, option 2). Requirements specified in Rule 317.1(a)(4)(B) include engineering proposals for processes, equipment, or construction materials and results of pilot or demonstration studies. Performance data from existing full-scale facilities may be submitted in addition to, or in lieu of, pilot studies, warranties, or performance bonds (2-yr) to cover the cost of removal or abandonment, and engineering reports following start-up detailing actual performance of the technology in accordance with applicants' or manufacturer's claims.

### 4.1.3 Regulatory Programs in Selected Southwestern States

Three states in the southwestern United States that have meteorological conditions similar to those of western Texas were examined to evaluate current regulatory requirements for the permitting of evaporation ponds. Pond-liner requirements are very similar to regulations in Texas and stipulate the type, thickness, hydraulic conductivity, compaction, and durability of various liner materials. However, no universal national criteria exist, and each state has adopted specific requirements and permitting mechanisms for approved liner systems. No special or unique liner requirements were identified specifically for self-sealing liner alternatives in any of the states. Approval of an alternative liner system would require technical data and testing results to demonstrate equivalency to the liner system prescribed in each state. Specification for compacted soil, soil/clay, or soil/bentonite liners may be the most appropriate benchmarks for such determinations. The following sections describe specific requirements and applicable citations in Arizona, Oklahoma, and New Mexico.

#### 4.1.3.1 Arizona

Evaporation ponds are regulated by the Arizona Department of Environmental Quality (ADEQ) under Title 49, The Environment, Chapter 2, Water Quality Control, Article 3, Aquifer Protection Permits, of the Arizona Revised Statutes (ARS). Individual or General Permits may be issued to facilities demonstrating the use of Best Available Demonstrated Control Technology (BADCT). Specific BADCT information is provided in the Arizona Mining Guidance Manual BADCT, Section 3.6, Surface Ponds, which describes the design, construction, and operational requirements for aquifer protection. Supplemental information is also found in Appendix C of the document, Liner Design Principles and Practice. Structures that are designed and constructed not to discharge and that are built on an impermeable barrier that can be visually inspected for leakage are exempt from permitting under the Aquifer Protection Program (ARS Section 49-250). Title 18, Chapter 9 of the Arizona Administrative Code includes requirements for aquifer protection permits. Type 3 General Permits for lined impoundments (R18-9-D301) may be obtained for "wastewater derived from a potable water treatment system, including clarification sludge, filtration backwash, lime and lime-softening sludge, ion exchange backwash, and reverse osmosis spent waste…." An applicant must file a Notice of Intent and a Supplemental Notice of Intent. To satisfy General Permit conditions, evaporation ponds must be designed and constructed to ensure containment of normal operating volumes plus inflow from the 100-yr, 24-h storm event and maintain at least 2 ft of freeboard. Pond liners typically consist of a prepared foundation, a combination of liners, possibly a leak detection layer, and a protection layer. Pond liners must meet the following specifications:

Soil liners must

- Ensure a seepage rate of <550 gal/acre/d (0.2 inch/day or 73 inches/year);
- Be at least 1 ft thick and compacted to a uniform density of 95% of the standard Proctor maximum dry density as defined by the "Standard Test Method for Laboratory Compaction Characteristics of Soil Using Standard Effort (12,400 ft-lbf/ft$^3$ or equivalently 600 Kn-m/m$^3$)," D698-00 Rev1 (2000) published by ASTM; and
- Resist desiccation.

Geomembrane liners must

- Be at least 30 mil thick or at least 60 mil thick if high-density polyethylene is used; or
- Be an alternative with a calculated seepage rate of <550 gal/acre/day (0.2 inch/day or 73 inches/year); and
- Be ultraviolet resistant and chemically compatible with the wastewater to prevent corrosion or degradation.

ADEQ also recognizes manufactured bentonite liners, known as geosynthetic clay liners (GCLs), as a liner component. No reference is made in the Arizona Administrative Code to self-sealing evaporation pond technologies or a mechanism for considering specific alternatives under a general permit, other than that specified for geomembrane liners. Further information may be available from the ADEQ Aquifer Protection Unit Director Michele Robertson at (602) 771-4827.

#### 4.1.3.2 Oklahoma

In Oklahoma, PWS evaporation ponds are subject to Oklahoma Department of Environmental Quality (ODEQ) Rules and Regulations, Title 252, Chapter 626, Public Water Supply Construction Standards. The Oklahoma Administrative Code (OAC) requires a permit for construction or modification of any PWS that must include a residuals management plan for the "proper disposal of WTP (water treatment plant) waste…." The regulations provide that "waste from ion exchange plants, demineralization plants, etc. that cannot be discharged to a sanitary sewer or meet discharge permit requirements without cost prohibitive treatment may be discharged to evaporation ponds meeting the requirements of OAC 252:626-13-4." Section 626-13-4, Lagoons, establishes design and operational requirements for residuals management, which stipulates that

- Two or more lagoons must be constructed with periodic removal of residuals at least every 2½ years;
- Dikes must be constructed of "relatively impervious material and compacted to at least 90% of its maximum dry standard Proctor density";
- Lagoons must be a minimum of 8 ft deep, with a minimum of 3 ft of freeboard;
- Lagoons must be capable of containing volumes based on annual average pan evaporation minus the 90th percentile annual rainfall; and
- The bottom seal must comply with the requirements of OAC 252:616.

OAC Section 252:616 describes specific requirements and appropriate uses for compacted clay liners, geomembrane liners, composite liners, soil and bentonite liners, and concrete liners. General liner requirements allow ODEQ to "consider liner systems other than those described in this Subchapter, on a case-by-case basis."

Requirements for compacted clay liners and soil and bentonite liners are most comparable to self-sealing liner alternatives and are considered to be "moderately protective." Liner materials must be compacted with a "water content-density range to assure a maximum saturated hydraulic conductivity of $1 \times 10^{-7}$ cm/sec."

- Clay liners must be applied in at least four successive "lifts" of not more than 9 inches in thickness uncompacted, and 6 inches of thickness compacted to a minimum of 2 ft of thickness. The liner at the bottom of the pond must be compacted to a water content of as much as 4% above optimum and to at least 90% of the Standard Proctor maximum dry density.
- Soil and bentonite liners must be uniformly mixing bentonite into the soil to a depth of at least 6 inches, applied at a rate at least 125% of the minimum rate determined in laboratory tests needed for stability and maximum hydraulic conductivity.
- Liners must be properly protected from freezing and desiccation and covered by at least 12 inches of soil.

Further information may be available from the ODEQ Public Water Supply Program Compliance Determination Support Team Leader, Michele Welch at (405) 702-8127.

#### 4.1.3.3 New Mexico

Very little information is available regarding regulation of evaporation ponds in New Mexico. New Mexico Administrative Code (NMAC) Title 20 Environmental Protection, Chapter 6 Water Quality, Part 2 Ground and Surface Water Protection, requires any person who discharges effluent or leachate directly or indirectly into groundwater to obtain a State permit from the New Mexico Environment Department (NMED). NMED has not received primacy for the National Pollutant Discharge Elimination System (NPDES) program. No specific requirements or exemptions for evaporation ponds are mentioned in these regulations.

Pond-liner requirements were included in the Recommended Standards for Wastewater Facilities published by the NMED Construction Programs Bureau, although they are applied only to facultative and aerated ponds. Soil/clay liners

- Must be compacted to a saturated hydraulic conductivity no greater than $1 \times 10^{-7}$ cm/sec at 90% of the Standard Proctor maximum dry density (ASTM D698) (at least half its material must pass a #200 sieve); have a Plasticity Index of no less than 10%; and contain particles no larger than 4 mm (5/32 inch).
- Must be augmented with bentonite clay if the required hydraulic conductivity limit cannot be met.
- Must be no less than 18 inches thick constructed in 6-inch lifts.
- Are not recommended for evaporation ponds that may be subject to desiccation; exposed to highly acidic, alkaline, or chemical wastewater; or located over a vulnerable aquifer.

The Natural Resources Conservation Service (NRCS) in New Mexico has also published the following series of Conservation Practice Specifications for Pond Sealing or Lining: Flexible Membrane (521A), Soil Dispersant (521B), Bentonite Treatment (521C), and Cationic Emulsion-Waterborne Sealant (521D).

Specifications for geomembrane liners and bentonite treatment methods were on the NRCS Website, but the documents for soil dispersion and cationic emission-waterborne sealant methods were not available. Specifications identifying liner thickness (30–40 mil for geomembranes and

6–24 inches for bentonite treatment) were provided, but no other limitations for conductivity, permeability, or other criteria were included. It is unclear whether these specifications would apply to evaporation ponds used in conjunction with desalination or other water-treatment facility or are limited to agricultural operations supported by NRCS. Further information may be available from the NMED Ground Water Quality Bureau at (505) 827-2918 or from the New Mexico State NRCS Office, State Conservationist, Dennis Alexander at (505) 761-4401.

### 4.1.4 Factors to Reduce Complexity and Cost in Texas

New self-sealing evaporation pond technology can make desalination facilities more affordable if it can lower costs associated with the installation and maintenance of pond liners by reducing the amount of compacted clay to less than 3 ft or replacing it entirely or by eliminating the need for a leak-detection system beneath a geomembrane liner.

#### 4.1.4.1 Liner Requirements

Deposition of precipitants from the effluent stream may reduce or eliminate the need for standard liner materials in desalination evaporation ponds. This substitution could reduce the cost of installing clay or geomembrane liners to achieve an equally effective seal. An equivalency determination would require an applicant to adequately demonstrate that (1) self-sealing methods will achieve containment capability equivalent to that of current prescriptive liners or, when combined with a geomembrane liner, will enhance containment to a degree that a leak detection system is unnecessary and (2) resulting liner material(s) will not deteriorate owing to reactivity with salinity or other compounds in the effluent stream, exposure to sunlight, exposure to expected temperature extremes, or periods of desiccation.

Support information for such a demonstration may include (1) documentation of applicable scientific reports, previously conducted research, and other literature; (2) results of recently conducted scientific and engineering studies or pilot projects; (3) monitoring data from existing operational facilities currently utilizing the proposed technology; and (4) certification by a Licensed Professional Engineer in Texas.

#### 4.1.4.2 Permit Processing

No changes to existing regulatory requirements or processes are necessary to obtain permits for self-sealing evaporation pond liners at desalination plants in Texas. Each application would be evaluated on its own merits and could receive approval upon adequate case-by-case demonstration of equivalency with current clay and geomembrane liner performance standards.

Regulatory processing for permitting of an evaporation pond could be simplified if the self-sealing technology were recognized by TCEQ as an accepted type of liner, equivalent to compacted clay or geomembrane liners. Instructions for “Completing the Industrial Wastewater Permit Application” could be modified without statutory change or rulemaking to add self-sealing liner technology to the list of acceptable liners. Such a revision may provide applicants a greater degree of regulatory certainty that a permit application will be approved if certain conditions were met. However, TCEQ may be hesitant to make such a modification, given the limited number of likely permit applications for desalination facilities.

#### 4.1.4.3 Leak Monitoring

Evaporation ponds with geomembrane liners are required to have underground leak-detection systems that lie beneath the liner for the purpose of detecting leakage through it. Alternatively, leakage from ponds can be monitored by groundwater monitoring wells (TCEQ, 2006a).

Monitoring must be conducted at least monthly and results reported to TCEQ annually. Indications of leakage require corrective action. Given that leak detection system or groundwater monitoring with the potential for corrective action is not required for ponds with in situ or compacted clay liners, facility owners may prefer the cost certainty of ponds lined with clay rather than geomembrane liners.

TCEQ staff has indicated that similar monitoring is required for alternative liner systems. Reducing or eliminating monitoring requirements would further lower costs to small municipalities or other customers interested in using evaporation ponds with a desalination system. Because self-sealing liner technology by design would automatically seal any leaks that might appear in the liner, requirements for extensive, permanent monitoring may not be necessary. Studies, pilot or demonstration projects, engineering design, and other research performed to document the integrity of self-sealing evaporation pond-liner technology should verify the effectiveness of these self-sealing properties. TCEQ may be able to modify monitoring requirements if adequate documentation can be provided that monitoring would not be necessary to protect human health or the environment.

### 4.1.5 What if Something Goes Wrong?

In order to gain some understanding of what would happen if leakage were actually detected we contacted two of the four facilities we previously visited for field sampling (see Appendix E). Their responses follow:

City of Abilene—Rodney Taylor, Assistant Director of Water Utilities:

- No specific insurance is carried on desalination plant or evaporation ponds.
- City of Abilene is self insured and would address any liability issues.
- Repairs or remediation due to a leak in the evaporation pond liner would likely be paid for by the cash reserves in the city's Enterprise Fund.

Horizon Municipal Utility District—Joe Paxton, Operations Manager [(915) 852-4465]:

- No specific insurance is carried on desalination plant or evaporation ponds.
- General insurance is obtained from the Texas Municipal League available to water districts.
- Water districts are shielded from liability in most cases.
- Repairs to clay liner, if necessary, would be covered by general operations and maintenance budget funded by consumer rates and bonds.

Implementing self-sealing evaporation ponds will not impact insurance cost for municipal utilities because they are mostly self-insured.

### 4.1.6 Regulatory Conclusions

No significant regulatory barriers exist to prevent permitting of self-sealing evaporation pond-liner technologies at desalination facilities in Texas. No-discharge facilities, such as evaporation ponds, are not required to obtain any Federal permit or authorization (i.e., TPDES permit). However, a state-only Texas Land Application Permit (TLAP) must be issued by the TCEQ Water Quality Division.

Although TCEQ has not adopted specific regulations regarding TLAP requirements for industrial wastewater treatment facilities, it uses the current requirements for municipal wastewater treatment facilities at sites that have unsuitable hydrogeologic characteristics as a guide. TCEQ has developed detailed instructions for completing a TLAP application for industrial facilities that describes these requirements. Certain pond-liner technologies that have been proven to meet minimum performance criteria for containing industrial wastewater discharges are specified in TCEQ guidance. Evaporation pond liners that are currently recognized as acceptable in Texas (called prescriptive liners in this report) include

- In situ clay, at least 3 ft thick with hydraulic conductivity of $10^{-7}$ cm/s or less,
- Compacted clay, at least 3 ft thick with hydraulic conductivity of $10^{-7}$ cm/s or less, or
- Geomembrane liner, at least 30 mil thick with an underlying leak-detection system.

Alternative liners (see Appendix C) may be approved on a case-by-case basis with adequate demonstration that the alternative can achieve an equivalent hydraulic conductivity and will have no adverse reactivity to effluent characteristics, sunlight, temperature, or desiccation.

Regulatory processes and costs related to the permitting of self-sealing pond liners could possibly be reduced if the technology were added to the list of acceptable liners and not required to undergo a case-by-case determination. No statutory change or rulemaking would be required to revise the permit instructions; however, TCEQ would require compelling scientific and engineering evidence to justify such a modification.

Costs could also be reduced if leak-detection monitoring of alternative liner systems could be reduced or eliminated. Again, scientific and engineering evidence, including the results of demonstration studies, would be necessary to show that monitoring would not be necessary to ensure protection of human health and the environment.

## 4.2 Range of Likely Membrane Concentrate Compositions

Whereas feedwater chemical composition is widely available and compiled in the TWDB groundwater database, little public information is available about membrane concentrate composition. In this report, we followed the procedure presented in Mace et al. (2006) to compute the likely range of membrane concentrate composition. The concentrate composition is a strong function of the feedwater composition to which operational imprints are added (acidification, closed system, efficiency, and recovery). As discussed in Nicot et al. (2005), RO technology is supplanting ED/EDR technology, at least in Texas. Consequently, a RO concentrate is assumed in the remainder of this work. As a first approximation, RO technology rejects anions, cations, and neutral ions at the same rate as and independently of charge density (e.g., Jordahl, 2006, p. 6–7). It is assumed that technological improvements will trend in that direction and that concentrate TDS is about four times that of the feedwater (Mace et al., 2006).

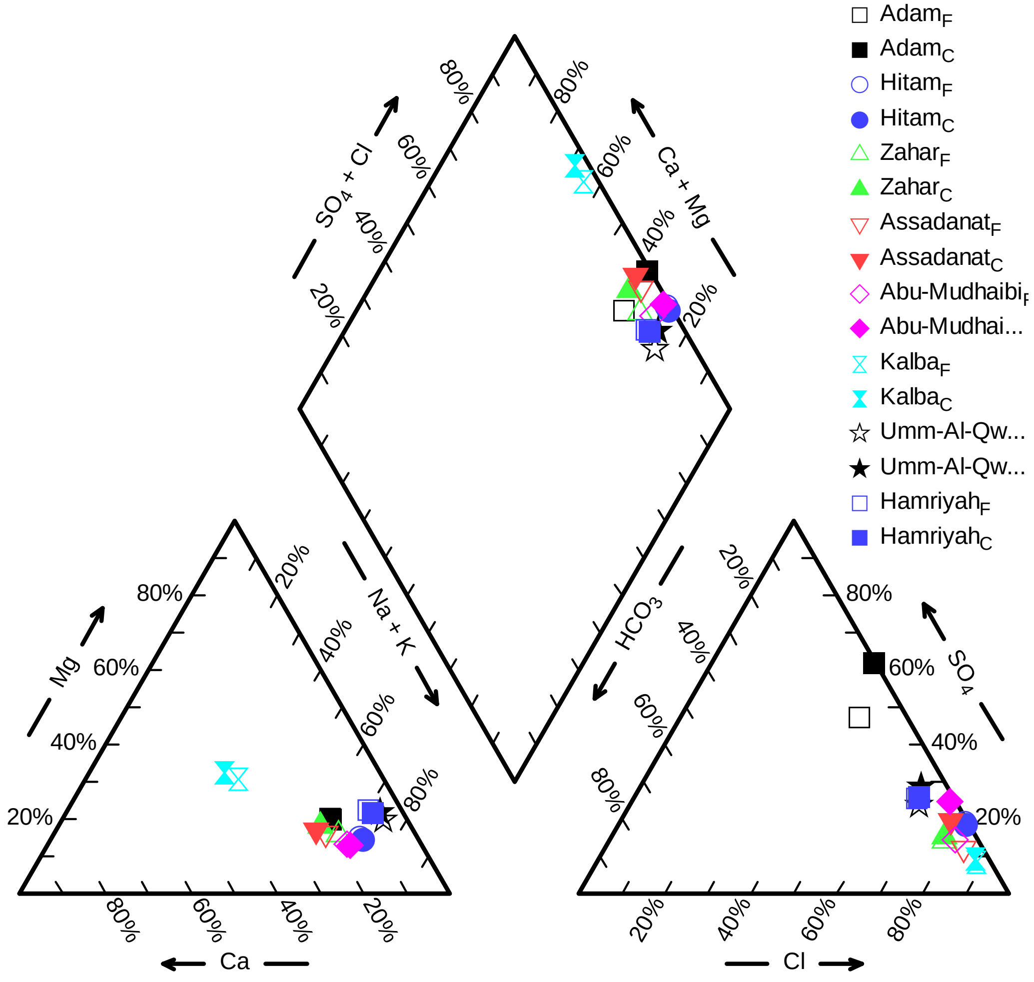
In general, divalent ions are rejected at a higher rate than monovalent ions, but the error by assuming the same rejection rate decreases as the recovery increases. It follows that this assumption is valid for the slightly brackish waters considered in this study but may not have been appropriate for seawater desalination that has a lower recovery rate. This assumption would not be valid either for NF membranes that let through most of the monovalent ions. In addition, not making that assumption for RO membranes would imply considering specific membrane varieties and using specific, sometimes proprietary, software designed by membrane vendors. RO technology allows for gases ($O_2$, $CO_2$, $H_2S$) to go through the membrane, and the resulting concentrate is gas-poor. Acidification with either hydrochloric or sulfuric acid is a widespread pretreatment technique. At least 8 out of the 38 PWS facilities presented in Nicot et al. (2005) use this approach (unpublished data).

We had limited success in contacting Texas facilities and requesting information about concentrate chemical composition. In the next section, we present information about Middle Eastern facilities whose concentrate information has been published, as well as results of field sampling of four Texas facilities conducted during this study to suggest the reasonable assumption that concentration of most ions in the concentrate is approximately four times that found in the feedwater.

### 4.2.1 Out-of-State Examples

In order to test our numerical approach to obtaining accurate concentrate compositions, we used data from Ahmed (2000) and Ahmed et al. (2001). The paper contains feedwater and concentrate data from several facilities located in the Middle East (Table 4-1 and Table 4-2), which hosts numerous desalination facilities (e.g., Wangnick, 2002). They provide a good basis for investigating feedwater/concentrate relationships. Inspection of the ratio of concentrate and feedwater concentrations for individual ions and TDS shows that ions are concentrated roughly by the same amount. This finding was confirmed when we plotted the results on a Piper plot (Figure 4-1). It shows little geochemical distance between feedwater and concentrate for all ions. It is clear that the Haima facility (Table 4-1) does not fit the general pattern (concentrate with a low pH of ~3, high concentration factor for chloride, and low concentration factor for sodium). The most likely interpretation is that hydrochloric acid is added to feedwater to control scaling. Consequently, the pH drops and the chloride concentration factor increases dramatically artificially. The Adam facility shows a similar but less pronounced pattern. Sulfuric acid is added, also to control scaling, as evidenced by the higher concentration factor and the lower pH (5.66). Acid addition translates into a drop in alkalinity (from 230 to 37 mg/L, despite an average concentration factor larger than 4). The $CO_2$/carbonic acid and bicarbonate system has a pKa of about 6.4, suggesting that little bicarbonate exists at 5.6, almost one pH cycle lower. The Haima concentrate analysis shows no bicarbonate results because there is none in solution at pH=3. The slight drop in pH in the Abu-Mudhaibi facility also suggests that scaling is controlled by acid addition (Ahmed, 2000, Table 9). In a closed system, concentrate should have a pH higher than that of feedwater because of the increase in bicarbonate ions. The Zahar and Hamriyah facilities follow this pattern. The Zahar feedwater is not acidified. Most of these facilities also received sodium metabisulfite to control chlorine when chlorination is used. Most modern membranes are not chlorine tolerant, and the water stream must be dechlorinated, typically with sodium metabisulfite.

From these observations, it can be concluded that most ions behave conservatively and mechanically increase in concentration by an amount consistent with the increase in TDS. Chloride or sulfate may not follow this pattern if acid is added. Bicarbonate concentration is a function of pH and of the open/closed status of the system. If the system is open to atmosphere, bicarbonate concentration is in equilibrium with atmospheric $CO_2$, as dictated by the solution pH. If the system is closed and no acid is added, bicarbonate follows a pattern similar to that of other ions, and the pH increases.



Source: Ahmed (2000) and Ahmed et al. (2001)

Figure 4-1. Piper plot of feedwater (F) and concentrate (C) of selected desalination facilities in the Middle East.

Table 4-1. Feedwater and concentrate chemical composition from a few Middle Eastern desalination facilities.

| **Facility** | **Ca** | **Mg** | **Na** | **K** | **Cl** | **$SO_4$** | **Sr** | **Alkalinity** | **Hardness** | **Bicarbonate** | **pH** | **TDS** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Adam** | | | | | | | | | | | | |
| FW | 103 | 70 | 410 | 12 | 506 | 773 | 3 | 195 | 548 | 230 | 8 | 2,000 |
| Conc | 417 | 280 | 1,670 | 43 | 1,964 | 4,336 | 13 | 30 | 2,211 | 37 | 5.56 | 8,747 |
| C/FW | 4.05 | 4.00 | 4.07 | 3.72 | 3.88 | **5.61** | 3.95 | **0.15** | 4.03 | 0.16 | | 4.37 |
| **Haima** | | | | | | | | | | | | |
| FW | 652 | 267 | 3,340 | 125 | 1,697 | 2,037 | 16 | 62 | 2,748 | *62* | 7 | 8,217 |
| Conc | 1,020 | 406 | 406 | 174 | 9,090 | 3,881 | 24 | *0* | *3958* | *0* | **3.07** | *14,977* |
| C/FW | 1.56 | 1.52 | 0.12 | 1.39 | **5.36** | 1.91 | 1.54 | | | | | |
| **Hitam** | | | | | | | | | | | | |
| FW | 563 | 382 | 3,400 | 124 | 7,483 | 2,366 | 13 | 125 | 2,996 | 135 | 8 | 14,451 |
| Conc | 665 | 448 | 4,250 | 145 | 8,118 | 2,466 | 15 | 142 | 3,526 | 125 | 7.66 | 16,142 |
| C/FW | 1.18 | 1.17 | 1.25 | 1.17 | 1.08 | 1.04 | 1.20 | 1.14 | 1.18 | 0.93 | | 1.12 |
| **Zahar** | | | | | | | | | | | | |
| FW | 179 | 95 | 746 | 28 | 1,408 | *337* | 5 | 244 | *777* | *244* | 7 | *3,037* |
| Conc | 612 | 315 | 1,980 | 95 | 4,367 | 1,143 | 16 | 704 | 2,846 | *704* | 7.32 | 8,990 |
| C/FW | 3.42 | 3.32 | 2.65 | 3.36 | 3.10 | *3.39* | 3.47 | 2.89 | | | | |
| **Assadanat** | | | | | | | | | | | | |
| FW | 367 | 174 | 1,290 | 12 | 2,160 | *417* | 30 | 196 | *1,521* | *196* | 8 | *4,616* |
| Conc | 923 | 413 | 2,780 | 82 | 4,532 | 1,552 | 28 | 380 | 4,041 | *380* | 7.21 | 10,553 |
| C/FW | 2.51 | 2.37 | 2.16 | 7.03 | 2.10 | *3.72* | 0.93 | 1.94 | | | | |
| **Abu-Mudhaibi** | | | | | | | | | | | | |
| FW | 294 | 137 | 1,360 | 29 | 2,151 | 515 | 8 | 200 | 1,309 | 245 | 7 | 4,651 |
| Conc | 962 | 448 | 4,630 | 101 | 7,335 | 3,296 | 27 | 168 | 4,281 | 205 | 6.03 | 16,960 |
| C/FW | 3.27 | 3.27 | 3.40 | 3.47 | 3.41 | 6.40 | 3.34 | 0.84 | 3.27 | 0.84 | | 3.65 |
| | | | | | | | | | | | | |
| **Kalba** | | | | | | | | | | | | |
| FW | 446 | 245 | 536 | 11 | 2,103 | 265 | 5 | 109 | 2,130 | 133 | 7.48 | 3,700 |
| Conc | 1,180 | 644 | 1,170 | 34 | 5,413 | 756 | 11 | 285 | 5,615 | 347 | 7.59 | 9,432 |

| Facility | Ca | Mg | Na | K | Cl | $SO_4$ | Sr | Alkalinity | Hardness | Bicarbonate | pH | TDS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C/FW | 2.65 | 2.63 | 2.18 | 3.09 | 2.57 | 2.85 | 2.12 | 2.61 | 2.64 | 2.61 |  | 2.55 |
| **Umm-Al-Qwain** |  |  |  |  |  |  |  |  |  |  |  |  |
| FW | 49 | 110 | 775 | 19 | 1,182 | 562 | 5 | 226 | 581 | 275 | 7.80 | 2,851 |
| Conc | 202 | 510 | 3,190 | 85 | 4,108 | 2,444 | 21 | 538 | 2,630 | 656 | 7.54 | 10,923 |
| C/FW | 4.12 | 4.64 | 4.12 | 4.36 | 3.48 | 4.35 | 4.23 | 2.38 | 4.53 | 2.39 |  | 3.83 |
| **Hamriyah** |  |  |  |  |  |  |  |  |  |  |  |  |
| FW | 48 | 85 | 498 | 13 | 779 | 407 | 4 | 177 | 474 | 216 | 7.31 | 1,949 |
| Conc | 173 | 311 | 1,930 | 51 | 2,933 | 1,537 | 14 | 617 | 1,730 | 753 | 7.66 | 7,350 |
| C/FW | 3.60 | 3.66 | 3.88 | 3.84 | 3.77 | 3.78 | 3.81 | 3.49 | 3.65 |  |  | 3.77 |

Note: Units are mg/L; FW=Feedwater; Conc=Concentrate; C/FW=Ratio Concentrate / Feedwater; Hardness is sensibly equivalent to $CaCO_3$ + $MgCO_3$ (weight basis); italic (and blue) cells contain data not provided in the source but calculated to approximately match TDS and electrical balance

Source: Ahmed et al. (2001) and modified from Mace et al. (2006)

Table 4-2. Facility characteristics.

| Facility | Capacity MGD - ($m^3$/day) | Disposal |
|---|---|---|
| Adam | 0.26 – (1,000) | Evaporation Pond |
| Haima | 0.0264 – (100) | Evaporation Pond |
| Hitam | 0.0264 – (100) | Shallow well bore |
| Zahar | 0.0132 – (50) | Shallow well bore |
| Assadanat | 0.0132 – (50) | Shallow well bore |
| Abu-Mudhaibi | 0.0132– (50) | Shallow well bore |
| Kalba | 3.84 – (14,550) | Ocean Discharge |
| Umm-Al-Qwain | 2.77 – (10,500) | Ocean Discharge |
| Hamriyah | 0.77 – (2,900) | Land disposal (dry creek) |

Note: All source water is brackish groundwater; source: Ahmed et al. (2001)

### 4.2.2 Texas Data

Currently in Texas no data contrasting feedwater or concentrate chemical composition are publicly available, although information about permeate composition is more readily available. In order to partly fill that data gap, we conducted a small field sampling program that included four facilities (see Appendix E). Feedwater compositions fall within the expected range (Table 4-3), which can be verified by checking their position on the Piper plots of the water groups presented in Appendix A: Figure 8-4 (Rio Grande alluvium for Horizon facility), Figure 8-20 (surface-water group for Abilene and Brady facilities), and Figure 8-11 (Cretaceous limestone group for River Oaks Ranch –ROR– facility).

Conclusions are similar to those obtained from the Middle East samples. Feedwater and concentrate fall very close to one another on a Piper plot (Figure 4-2). It should be noted that the decrease in bicarbonate concentration in the concentrate visible on Figure 4-2 has not been measured but computed from assumed equilibrium with calcite because alkalinity was not measured in the field.

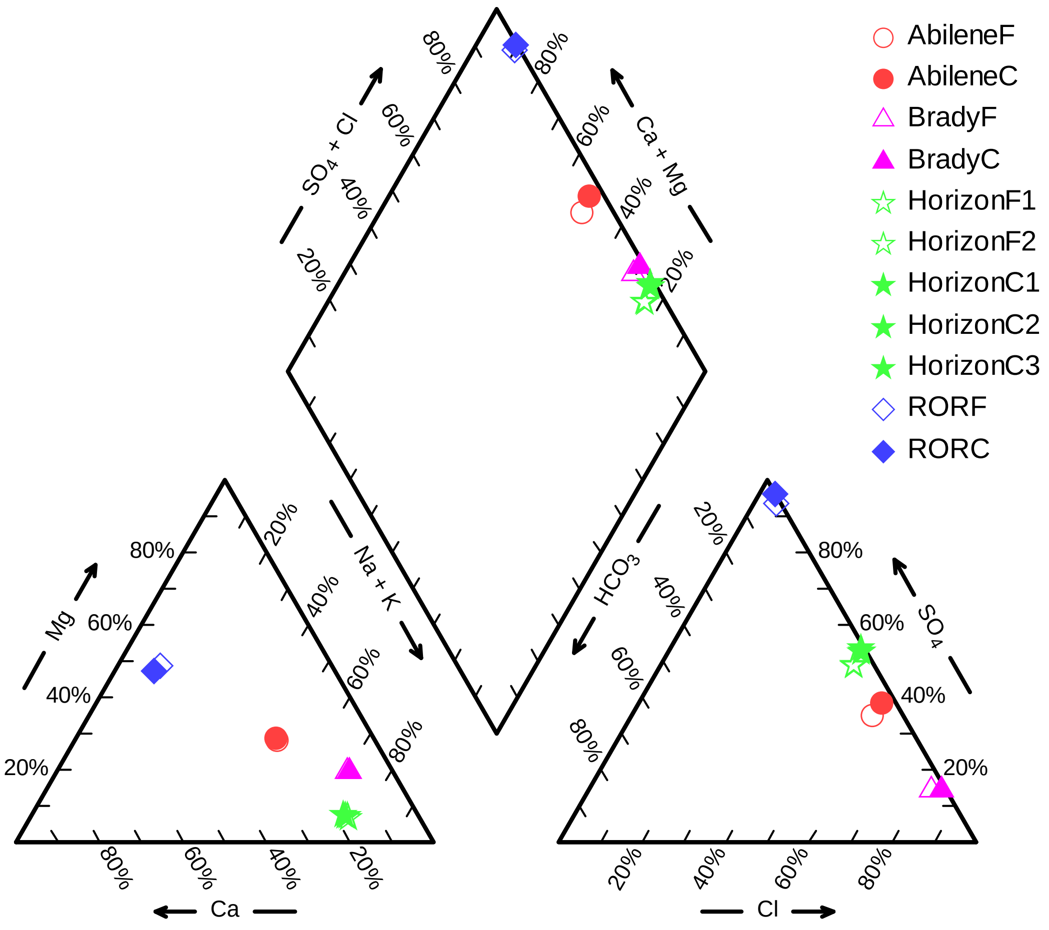


Figure 4-2. Piper plot of feedwater (F) and concentrate (C) of selected Texas desalination facilities.

Table 4-3. Feedwater and concentrate chemical composition from selected Texas desalination facilities.

| Facility | $SiO_2$ | Ca | Mg | Na | K | Cl | $SO_4$ | Sr | Alkalinity | Hardness | Bicarbonate | pH | TDS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Abilene** | | | | | | | | | | | | | |
| FW | 5.2 | 86.9 | 63.6 | 202.0 | *10.7* | 381.9 | 311.1 | NM | NM | NM | *84.4* | 7.88 | 1130 |
| Conc. | 16.0 | 279.5 | 206.0 | 638.3 | 35.0 | 1,232.2 | 1,098.1 | NM | NM | NM | *122.9* | 7.36 | 3762 |
| C/FW | 3.0 | 3.2 | 3.2 | 3.2 | | 3.2 | 3.5 | NM | NM | NM | 1.5 | | 3.3 |
| **Brady**[A] | | | | | | | | | | | | | |
| FW | 10.8 | 44.9 | 48.0 | 317.5 | 17.5 | 590.1 | 139.0 | NM | NM | NM | 42.5 | 8.40 | 1207 |
| Conc. | 26.6 | 109.9 | 124.7 | 820.5 | 46.0 | 1,596.9 | 364.6 | NM | NM | NM | 29.9 | 8.32 | 3166 |
| C/FW | 2.5 | 2.4 | 2.6 | 2.6 | 2.6 | 2.7 | 2.6 | NM | NM | NM | 0.7 | | 2.6 |
| **Horizon** | | | | | | | | | | | | | |
| FW | 23.5 | 105.7 | 27.5 | 538.4 | *10.9* | 419.0 | 595.3 | NM | NM | NM | *76.4* | ND | 1728 |
| FW | 31.6 | 95.4 | 21.7 | 479.8 | *10.9* | 415.0 | 593.1 | NM | NM | NM | *72.3* | 7.94 | 1736 |
| Conc. | 70.3 | 244.8 | 60.6 | 1202.1 | 27.1 | 997.2 | 1,519.5 | NM | NM | NM | *35.1* | 8.03 | 4230 |
| Conc. | 66.3 | 183.8 | 45.8 | 899.6 | 21.5 | 958.9 | 1,461.2 | NM | NM | NM | *52.0* | 7.96 | 3726 |
| Conc. | 106.8 | 319.8 | 79.6 | 1,523.1 | 37.3 | 1,485.9 | 2,344.5 | NM | NM | NM | *46.0* | 7.89 | 5831 |
| C/FW | 2.9 | 2.5 | 2.5 | 2.4 | | 2.8 | 3.0 | NM | NM | NM | 0.6 | | 2.7 |
| **River Oaks Ranch** | | | | | | | | | | | | | |
| FW | 12.3 | 323.9 | 231.5 | 79.2 | 24.1 | 67.3 | 1,598.4 | NM | NM | NM | *23.8* | NM | 2349 |
| Conc. | 34.7 | 1,207.7 | 796.0 | 268.9 | 64.5 | 203.7 | 6,832.0 | NM | NM | NM | *14.2* | NM | 9796 |
| C/FW | 2.8 | 3.7 | 3.4 | 3.4 | 2.7 | 3.0 | 4.3 | NM | NM | NM | 0.6 | | 4.2 |

Note: Units are mg/L; FW=Feedwater; Conc.=Concentrate; C/FW=Ratio Concentrate / Feedwater; NM= not measured; italic (and blue) cells contain data not provided in the source but calculated to approximately match TDS and electrical balance—Feedwater K computed from concentrate K by assuming average concentrate / feed ratio; bicarbonate computed with PHREEQC assuming equilibrium with calcite

[A] Concentrate obtained at the Brady facility does not represent the ultimate concentrate but its composition after one pass

### 4.2.3 Conclusions on the Range of Likely Membrane Concentrate Compositions

Because of the straightforward relationship between feedwater and concentrate composition, as demonstrated in the previous two sections, the range of concentrate composition can be well approximated by the range in composition of feedwater. Appendix A details the results of the analysis by aquifer. Texas is a large state, and thus it is not surprising that brackish-water composition varies within a large range.

## *4.3 Self-Sealing Geochemical Calculations*

Geochemical self sealing can be understood in two ways. Solution ions will provide material to grow crack-plugging material identical to that in crack walls, using the crack walls themselves as physical support (case of clay liners). Alternatively, a new material will precipitate from solution to plug the cracks regardless of the chemical nature of the opening walls (valid for both clay and geomembrane liners). In order to understand the likelihood of precipitation of self-sealing material and the amount thereof, several sets of geochemical calculations were conducted. The geochemical simulations consisted of determining what material could be self sealing, when and how it can precipitate out of solution with or without additives, and whether there is any area in Texas that would fit these criteria. To better grasp the complexity of the issue, we explored multiple ways of accessing the technical feasibility of self-sealing evaporation ponds by investigating mainly through a literature search: (1) natural analogs, (2) industrial analogs, and (3) experiments. Laboratory experiments generally provide a very short time scale (days, weeks, maybe months), whereas the geologic record provides information in the very long term (thousands to millions of years). The time frame of the chemical reactions relevant to evaporation ponds ranges from days to years.

To be efficient as a liner, precipitate should have a hydraulic conductivity $<10^{-7}$ cm/s. Muds accumulating at the bottom of the pond may not reach this threshold right away but would need to mature for a few years. Actually, it is common to observe in nature precipitation of amorphous minerals that then slowly transform themselves into a more crystalline form. Sepiolite is an interesting mineral following this pattern. Sepiolite (see Appendix F) is a clay mineral with strong water-adsorbing properties but that is not subject to volume changes when exposed to the desiccating effect of the atmosphere (in the fashion of smectite clays). Sepiolite in its disordered phase also has the advantage of precipitating fairly easily, requiring only silica and magnesium to be present in the solution. It may behave more satisfactorily than calcite or gypsum, two minerals also precipitating fairly easily. Even when sepiolite is present in a lesser amount than these two minerals, it may nevertheless provide the mineral mixture with the required properties.

### 4.3.1 Mechanics of Self Sealing

Self-sealing properties can be imparted to a defective liner in two ways. Dissolved ions can help in healing a crack, hole, or other defect by precipitating material identical to the liner and thus plugging the opening. This case applies only to a clay liner in which growth of similar clay materials could possibly be initiated from the opening walls. However, it is more likely and applicable to both geomembrane and clay liner that the precipitate will passively plug the opening, independently of the nature of the liner. When a hole appears in a geomembrane liner or a crack in a clay liner, water will flow preferentially in that direction, bringing dissolved material needed to seal the opening. There are numerous expressions for flow through a defective liner (e.g., Walton et al., 1997; Moo-Young et al., 2004; and see Section 4.4.2). Another mechanism, possibly more likely and certainly quicker, is the mechanical filling of the hole by entrainment of bottom sediments and the plugging of the opening through filtering of the particulate-rich suspension. This process was not investigated in this study.

Turner et al. (1999) categorized several sealing mechanisms by direct precipitation:
(1) deposition of a well-individualized layer on top of the pond bottom; it grows by settling of particles generated in the water; (2) clogging of the pores at the top of pond bottom; this is a variation of the previous case, in which reactions still occur in the main water body;
(3) precipitation occurs in the soil pore space, resulting in grain growth and lowering of conductivity. Previous mechanisms are applicable to both a geomembrane or clay liner because there is no chemical interaction between the liner and the solution; a simple support is needed. A fourth mechanism can be added that would consist of the solution reacting with the clay/soil matrix to generate solids of larger molar volumes, leading also to a plugging of the pores.

## 4.3.2 Literature Review of Analogs

Analogs to self-sealing evaporation ponds can be found in some industrial ponds, in saline lakes, where sepiolite naturally precipitates, and in specifically designed experiments.

### 4.3.2.1 Industrial Ponds—Lagoons

Many past tests and experiments give anecdotal evidence that precipitated materials can lead to a reduction in permeability. Jones (1983) studied the impact of sodium-chloride brines on clay permeability at an abandoned pond in Carlsbad, NM, and observed a reduction in leakage rate by one order of magnitude in approximately 20 years (p. 2 and 3). The cause of the decrease was described as unknown, but two of the four mechanisms put forward (salt deposition and ionic effects on clay) are relevant to this study. He also mentioned experiments done by the Bureau of Reclamation to seal clay liners by spraying sodium salts before use.

Industrial ponds of exotic chemical composition also illustrate the different mechanisms presented earlier. A large pond in the Crimea of southern Ukraine on the Black Sea developed a thick crust of natrojarosite, gypsum, and iron oxides, as evidenced by the large pH contrast on each side of the crust (Schuiling and van Gaans, 1997). The process started when acidic waste fluid reacted with the calcareous clay liner. This approach of having fluids of contrasting nature react to produce a precipitate can be engineered. Ding et al. (2003) proposed mixing fly ash (alkaline by nature) with acidic fluids to precipitate. Shi and Booth (2005) and Yoon et al. (2003) demonstrated the feasibility of such an approach when the two reactants are contained within a single liner system. A liner rupture will liberate the reactants, which will then react to heal the defect. The approach, however, does not make use of the pond fluid (except maybe water) and does not satisfy the requirement of cost effectiveness sought in this work.

### 4.3.2.2 Sepiolite

This section describes characteristics of sepiolite and palygorskite (also called attalpugite in the past). They are relatively common silica-rich clay minerals occurring in soils and sediments (Jones and Galan, 1988; Singer, 1989; Galan, 1996). They present a fibrous morphology different from that of other clay minerals, which generally have a more platy structure (see Appendix F). Sepiolite and palygorskite have a limited cation exchange capacity (4–40 meq/100g, compared with >100 meq/100g for smectites but 3–15 meq/100 g for kaolinite, in line with that of illites and chlorites). These attributes translate into having properties relatively independent of solution salinity; that is, they do not flocculate under a change in salinity or ionic make up. Smectites typically shrink at higher salinity. On the other hand, their specific surface area is large (300 to 600 $m^2/g$, Galan, 1996) compared with >600 $m^2/g$ for smectites and <20 $m^2/g$ for kaolinite. This property explains their industrial use as a sorbent (e.g., cat litter), especially in controlling odors.

Sepiolite precipitates directly from solution rather than from precursor minerals (e.g., Birzoy, 2002; Zaaboub et al., 2005). Saponite and other smectites seem good precursor candidates, but the energy barrier for inverting the clay sheets to go from a smectite to a sepiolite structure is high (Singer, 1989, p. 864). Transformational relationships have nevertheless been described (as cited in Birzoy, 2002). It seems that in magnesium-rich environments, palygorskite may form through interaction of magnesium with illite and other clays, but much less so for sepiolite. In any case, sepiolite has been produced repeatedly in the laboratory from solution. Its precipitation is controlled by pH and magnesium, silica, and aluminum activities. Other magnesium clays (palygorskite, saponite) have also been interpreted as having sometimes precipitated directly from solution (e.g., Galan and Castillo, 1984; Akbulut and Kadir, 2003). Authigenic growth of other magnesium-consuming clays such as montmorillonite has also been observed (Parry and Reeves, 1968, p. 519). Other authigenic magnesian phyllosilicates (talc, chlorite) have been observed, but they generally derive from alteration of dolomite by silica-rich waters (e.g., Isphording, 1984, p. 66). Palygorskite evolves generally from the modification of other clays.

Sepiolite is composed of only silicon and magnesium, with the following chemical formula $Mg_4Si_6O_{15}(OH)_2(OH_2)_2.4H_2O$, also written $Mg_4Si_6O_{15}(OH)_2.6H_2O$. However, it appears that most sepiolites do contain a small amount of aluminum. If too much Al is present, a smectite will precipitate instead (e.g., montmorillonite, saponite). If pH is too low, sepiolite will not precipitate. High pH ensures a high silica activity (silica is much more soluble at high pH values). If pH is too high, another magnesium-rich phase, such as brucite ($Mg(OH)_2$) could precipitate even if aluminum is present. High pH (>9), high magnesium activity, and aluminum in sufficient amount will favor precipitation of Mg-smectites (Galan and Castillo, 1984, p.115; Keith, 2000, p. 105) and talc (Velde, 1985, p. 31) rather than that of sepiolite. Similarly, high salinity decreases silica activity and is not as favorable for sepiolite precipitation.

Poorly crystallized sepiolite precipitates readily in alkaline solutions. Wollast et al. (1968) mixed sodium metasilicate ($Na_2SiO_3$) and magnesium chloride ($MgCl_2$) to precipitate sepiolite. Further experiments showed that sepiolite precipitates readily from seawater with the addition of silica. In both cases, a poorly crystalline gel of sepiolite composition is obtained. They also observed that the sepiolite precipitation rate depended on pH. Singer (1989, p.851) cited several other authors' experiments leading to the same results. Several studies have consistently determined the reaction constant for sepiolite precipitation (Wollast et al., 1968; Stoessell, 1988). Wollast et al. (1968) also determined the formation reaction constant for the poorly crystalline form of sepiolite that has been observed to precipitate in laboratory experiments rather than the crystalline form. Precipitation rates seem fast (Brady, 1992) when adequate ions are present (Si and Mg) in sufficient concentration.

#### 4.3.2.3 Natural Analogs

Many saline lakes in the western U.S. behave like natural evaporation ponds. The groundwater they receive is equivalent to pond feedwater. One difference, though, is the possibility of liquid water exiting the lake through an outlet or by infiltration. Saline lakes help in our understanding of the set of minerals likely to precipitate and, possibly, their sealing efficiency. Saline lakes are typically discharge features. Saline lakes of the Texas Panhandle receive groundwater influx from the Ogallala aquifer that is concentrated by evaporation (as opposed to the thousands of small circular depressions called playas that are lined by clays but are the avenue for recharge to the Ogallala aquifer). That same groundwater has a relatively high TDS concentration and is a possible feedwater source for Panhandle communities located west and south of Lubbock. Glass et al. (1973) studied analogous saline-lake clay deposits in eastern New Mexico and the Texas Panhandle and observed the occasional presence of sepiolite and palygorskite among the most common clays (illite, kaolinite, and montmorillonite). They noted that appearance of sepiolite was generally correlated with a loss in montmorillonite. Montmorillonite is not stable in Mg-rich waters favoring sepiolite diagenetic deposition (Parry and Reeves, 1968). They also observed abundant sepiolite in Mound Lake (p. 523), especially above a thin dolomitic layer and in Tahoka Lake. In both cases, sepiolite was confined to the surface or a few feet from the surface. Other researchers have also observed sepiolite in the High Plains (e.g., Allen et al., 1972). The later basin (see Appendix D) was also sampled in the course of our work with no detectable sepiolite. However, our samples were taken on the lake edge. Sepiolite is often described as more abundant in the middle of the basin/lake rather than on its edges because of the influx of aluminous detrital clay (e.g., Keith, 2000, p. 96). Even without detrital input, this observation still holds. In the largest world deposit of sepiolite, accumulated in a lacustrine environment in Spain during the Tertiary period, spatial transition (from proximal to distal) from Mg-smectite to palygorskite to sepiolite has been described (Galan and Castillo, 1984, p. 113). Sampling of the sediments of nine saline lakes (Appendix D) failed to provide evidence of large-scale sepiolite precipitation but did show traces of the mineral. Bottom sediments are mostly detrital (abundant quartz and some illite, feldspars, kaolinite, and smectites), with a generally small fraction of chemical origin (calcite, gypsum, halite). Except in one case with a TDS >300 g/L, all water samples have TDS <50 g/L.

Farther west, Boyd and Kreitler (1986, p. 16) described sediments of a salt basin in far west Texas as composed mostly of gypsum with (a few feet below ground) calcite, dolomite, magnesite, halite, and native sulfur with no significant clay material. The presence of native sulfur suggests reducing conditions (biomediated sulfate reduction). Dolomite and magnesite are not common minerals in evaporative ponds; they formed because of the high magnesium concentration in the brine. In general, magnesium carbonates, such as magnesite, are unusual in recent sediments (Langmuir, 1997, p. 195; Deocampo, 2005). In the geologic record dolomite is generally understood to be a result of the long and slow interaction of calcite with high-magnesium brines (either of marine or evaporative lake origin). Sepiolite should have also precipitated but did not because of a lack of silica in solution.

It can be concluded that sepiolite does precipitate in natural conditions analogous to those of evaporation ponds and that it can be expected to precipitate in the ponds if environmental conditions are right.

#### 4.3.2.4 Experiments

No experiments were performed in the course of this study, but several researchers and technologists have performed tests and experiments on self-sealing materials. Wollast et al. (1968) mixed sodium metasilicate and magnesium chloride to precipitate sepiolite. They did not investigate the flow properties of the precipitate. Donahe (2006) and Brady (P.V. Brady, 2006, personal communication) observed the precipitation of sepiolite gel by mixing the same ingredients. Only two natural clays have been observed to precipitate directly from solution under laboratory conditions: kaolinite (Nagy, 1995) and sepiolite (Brady, 1992). Turner et al. (1999) observed the precipitation of calcite and gypsum in laboratory experiments and during a pilot scale test in the El Paso area. In laboratory experiments, solid calcium carbonate and calcium sulfates were obtained by mixing synthetic calcium chloride, diammonium sulfate, and sodium carbonate brines in such proportions that supersaturation of these solid compounds resulted. The column experiments were set to occur in a soil matrix of variable composition (sand, sand bentonite), and precipitation occurs within the pore system with repeated addition of new batches. The desired conductivity of $10^{-7}$ cm/s was reached in only 1 case out of 16 experiments. Field experiments proceeded along the same lines with the mixing of two solutions: the membrane concentrate rich in sodium, chloride, and sulfate with a calcium and a magnesium-rich solution—a product of the regeneration of ion exchange columns also used in the desalination process. The resulting solution was then applied to a variety of matrix types held by large field containers submitted to natural evaporation. Hydraulic conductivity reduction was achieved but not to the extent desired. In another study, conductivity of a preparation containing 20% sepiolite was measured at values of approximately $10^{-6}$ cm/s (Keith, 2000, p. 230), that is, in the vicinity of and above the required threshold for a prescriptive liner but possibly sufficient to develop containment equivalence (see Section 4.4.2). Ca-bentonite yielded similar values under the same laboratory experimental conditions, mimicking a pond liner.

Donahe (2006) evaluated the feasibility of sodium silicate as a precursor material for a self-forming evaporation pond liner. Sodium metasilicate would react with the magnesium and calcium present in the pond concentrate to produce a low-permeability layer rich in sepiolite or similar material. He used soils sampled near the Tularosa Basin National Desalination Research Facility in New Mexico, to which he added solutions of different chemical composition to test changes in permeability. His data suggest that sepiolite was produced with an observable decrease in vertical permeability of the soil but still not meeting regulatory requirements.

#### 4.3.2.5 Additives

Wollast et al. (1968) used magnesium chloride and sodium metasilicate, both being laboratory and industrial compounds. A source of magnesium, magnesium chloride has a high solubility and is typically extracted from bitterns. Its cost is in the \$0.15 to 0.20/lb range (USGS, 2006), not including transport costs. Its molar weight is ~95 g/mol, which translates into a price of \$0.031 to 0.042/mol Mg. Magnesium chloride is not regulated and is widely available. Epsom salt ($MgSO_4.7H_2O$) is an alternative magnesium source. Sodium metasilicate ($Na_2SiO_3$—hydrated or not) could be a source of silica. Sodium metasilicate can be used only in alkaline pH conditions because it is a regulated hazardous material. Current uses include detergent components and anticorrosion agents. An approximate cost is \$1.50/lb, which is \$ 0.40 /mol Si. Each mole of sepiolite contains 3 moles of Si and 2 moles of Mg (~\$1.30 / mol) for a molar volume of 143 $cm^3$/mol.

A slightly different angle, often taken in the industry, would be to treat the water. Many additives could gel the water. For example, methyl cellulose is used as a thickening agent for aqueous preparations. Other polymers as well are used in the oil industry to increase viscosity of aqueous preparations. However, cost remains an obstacle.

### 4.3.3 Geochemical Simulation Parameters

In this section, we discuss numerical input to the self-sealing geochemical model. Numerous books present geochemistry fundamentals (e.g., Drever, 1988; Stumm and Morgan, 1996; Langmuir, 1997). Bethke (1996, Chapter 1) gives a good general introduction to geochemical modeling. There are several geochemical software codes available as well, and the USGS-developed freeware PHREEQC (Parkhurst and Appelo, 1999) version 2.12 was used, whose family of software products originated in the late 1970's. PHREEQC contains capabilities such as speciation-solubility and kinetically controlled reaction pathway features, which are found in many geochemical software packages. It also includes surface complexation, ion exchange, absorption and solid solutions, and a versatile treatment of rate laws. In addition, PHREEQC has transport features with handling of dispersion and diffusion in a double-porosity medium. It also has inverse modeling capabilities. PHREEQC supports the use of Davies and B-dot equations (e.g., Bethke, 1996, p. 109; Langmuir, 1997, Chapter 4), as well as Pitzer formalism for activity coefficients (Langmuir, 1997, Chapter 4). Pitzer formalism and the corresponding Pitzer database are particularly well suited to modeling high ionic strength solutions resulting from evaporation (that is, approximately more saline than seawater). At lower ionic strength, Pitzer formalism is equivalent to classic widespread formalisms. As in any geochemical software, a thermodynamics database must be provided. Geochemical simulation results are always a function of the thermodynamics database used and of its consistency. Downloaded software offers a choice of five databases. Our work uses the Pitzer database, complemented by minerals and elements imported from the LLNL database (see Appendix E).

Geochemical reactions are driven not by ion concentrations but by activities. Activity coefficients are computed by empirical or semiempirical models. A model used in many geochemical codes is the B-dot model, which is approximately valid up to the ionic strength (~salinity) of seawater (~35,000 ppm). Geochemical modeling beyond the salinity of seawater requires more sophisticated activity models such as the Pitzer model. The classic B-dot approach assumes no specific interaction between ions or same-interaction coefficient for all ions. The Pitzer model goes further in the analysis and develops a set of binary interaction coefficients specific to a pair of ions (e.g., $Na^+$ and $Cl^-$ or $Na^+$ and $SO_4^{2-}$). Another important aspect of geochemical modeling is the assumption of equilibrium or, alternatively, the introduction of precipitation or dissolution kinetics. Thermodynamics can only suggest final equilibrium phases. It can specify neither geochemical path nor time to reach equilibrium. It has often been observed that amorphous phases precipitate first, followed by a slow maturation to more crystalline, less soluble phases. In another example, talc may be thermodynamically favored over sepiolite (talc is also composed of only Mg and Si, $Mg_3Si_4O_{10}(OH)_2$), but sepiolite precipitates because of faster kinetics.

Numerical geochemical modeling consists of mimicking the operation of an evaporation pond. Evaporation is modeled by retrieving water from the system, assumed for convenience and by default by PHREEQC at 1 kg of water, while keeping all the dissolved solids in solution. Because the pond design assumes constant water depth on average, the evaporated water mass is replaced by the exact same mass of concentrate ("mixing parameter"), increasing in effect the dissolved solid loading of the system.

#### 4.3.3.1 Balance of Influx and Evaporation Rates

This section describes how the abstraction of water and the addition of concentrate to mimic evaporation pond operation are modeled. Pond TDS increases owing to evaporation and then stabilizes/plateaus because of mineral precipitation. To measure evaporation progress, we first assume no mineral precipitation. A simple mass balance approach can then quantify the concentration factor *CF*, defined as the ratio of the concentrate concentration $C_0$ to the pond concentration $C$. *CF* measures evaporation progress. Mass balance on the water is

In–Out = change in storage:

$$Q_t - E_t = \frac{dV_t}{dt}$$

where $Q_t$ is the concentrate flow rate and $V_t$ is the volume of water contained in the pond, all at time *t*. $E_t$ is the net evaporation rate computed from fresh-water evaporation $E_f$ and precipitation rate *P*, $E_t = c \times E_f - P$, where *c* is the salinity correction coefficient (taken as 0.9 in this work). Assuming constant flow and net evaporation rates, the equation becomes

$$Q_t t - E_t t = V_t \qquad (1)$$

that is, $Q_t \cong E_t$ as *t* becomes large. Similarly, a mass balance on a generic conservative solute yields

$$Q_t t C_0 - E_t t \times 0 = V_t C \qquad (2)$$

Substituting (1) into (2) yields

$$(V_t + E_t t)C_0 = V_t C \text{ or } 1 + \frac{E_t t}{V_t} = \frac{C}{C_0} \qquad (3)$$

If *S* is the pond surface area and *h* the time-averaged depth (*h* and *S* are designed so that the pond has the desirable characteristics of holding winter output and precipitation; we assume that the pond is rightly sized and that the pond volume is approximately constant), *E*=*eS* where *e* is the specific net evaporation rate [L] and *V*=*hS*. Equation (3) then becomes

$$CF = \frac{C}{C_0} = 1 + \frac{eSt}{hS} = 1 + \frac{et}{h} \qquad (4).$$

If the pond is 10 inches deep and the local evaporation rate is 50 inches/yr, after 10 years the concentration factor 1+50× 10/10=51, still assuming no mineral precipitation. A feedwater of 1,500 ppm will yield a concentrate of 6,000 ppm and a pond concentration of 300,000 ppm after 10 years (assuming no precipitation). Sanford and Wood (1991) examined the case in which some outflow is allowed from a closed basin and concluded that the *CF* tends toward a steady-state level.

Numerical geochemical modeling works simply and assumes that evaporation rate is constant throughout the year. Volume *Vx*, where *x* is the mixing parameter, is added to the pond at every period, should be equal to the amount retrieved by evaporation. For numerical reasons a monthly period is chosen (Figure 4-3).

Mixing parameter *x* is related to the parameter *CF* by $\frac{C}{C_0} = CF = \frac{C_n}{C_0} = 1 + nx$. The group *et* defined in equation 4 becomes a discretization of the equation $ne_{per}$, where *n* is the number of periods (e.g., month) and $e_{per}$ the evaporation for a unit surface area during that period. It ends up that the mixing parameter is equivalent to $x = e_{per}/h$. For example, the average evaporation rate for the surface-water group is 30.3 inches/yr (Figure 3-5), that is, $e_{per}$=2.53 inches/month. Assuming a pond depth of 12 inches, the mixing parameter *x* is *x*=0.2106 (Table 4-4). PHREEQC assumes a default mass of water of 1 kg in the system. It was checked using conservative solutes that the PHREEQC behaves properly under that scheme.

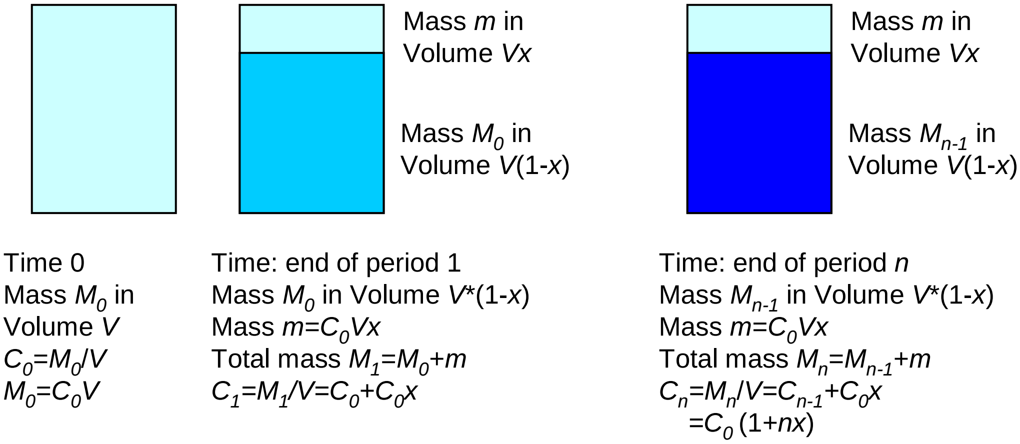


Figure 4-3. Mixing scheme of numerical modeling.

Table 4-4. Mixing parameter for monthly periods

| Group Name | Fraction Evaporated in 1 Period or Mixing Parameter (=$x$) | Amount of Water to Be Added in 1 Period |
|---|---|---|
| Mixed Alluvium | 0.2238 | 12.4238 |
| Brazos River Alluvium | 0.0617 | 3.4279 |
| Rio Grande Alluvium | 0.3151 | 17.4943 |
| Seymour | 0.2142 | 11.8917 |
| Bolson | 0.3377 | 18.7514 |
| Ogallala | 0.2897 | 16.0831 |
| Pecos Valley | 0.3496 | 19.4107 |
| Gulf Coast Sandstone | 0.1575 | 8.7452 |
| Eocene All Samples | 0.1333 | 7.4034 |
| Eocene Mixed | 0.1333 | 7.4034 |
| Eocene Na Dominant | 0.1333 | 7.4034 |
| Cretaceous Limestone | 0.2351 | 13.0523 |
| Cret. Sandst. All samples | 0.1663 | 9.2349 |
| Cret. Sandst. Mixed | 0.1663 | 9.2349 |
| Cret. Sandst. Na Dominant | 0.1663 | 9.2349 |
| Triassic Sandstone | 0.2822 | 15.6666 |
| Permian Evaporite | 0.2506 | 13.9160 |
| Permian Limestone | 0.2082 | 11.5601 |
| Permian Sandstone | 0.2398 | 13.3145 |
| Bone Spring – Victorio Peak | 0.3208 | 17.8105 |
| Capitan Reef | 0.2947 | 16.3607 |
| Pennsylvanian | 0.1736 | 9.6398 |
| Llano Uplift | 0.1618 | 8.9843 |
| | | |
| Surface Water | 0.2106 | 11.6912 |

Note: It can check that the ratio of column 3 to column 2 is equal to the molar density of water (~55.5 moles/kg)

### 4.3.3.2 Minerals Allowed to Precipitate

As in all predictive geochemical simulations, the modeler has the difficult choice of deciding which minerals are allowed to precipitate. This choice has a large impact on results and is guided by experience, conservatism relative to expected results, and consideration of analogs. To assess the impact of precipitation of some minerals, particularly clays, sensitivity analyses where varying minerals are allowed to precipitate were performed. Some minerals are thermodynamically stable but will not precipitate because of kinetics reasons. Others, less stable, called metastable minerals, will precipitate instead then evolve at a very slow rate to a more stable form (Ostwald's step rule, e.g., Bethke, 1996, p. 301). A list of allowed and suppressed minerals is provided in Table 4-5. For example, dolomite ($CaMg(CO_3)_2$) can use up all magnesium present in solution and keep sepiolite from reaching favorable precipitation conditions. In this particular case, it is generally recognized that dolomite does not precipitate in evaporation pond conditions because precipitation kinetics are too slow (e.g., Bethke, 1996, p. 86; Drever, 1988, p.65). It would, however, be plausible to consider dolomitization of calcite in a magnesium-enriched brine, seeing as how it occurs in nature. Because of the focus on sepiolite in this work, the geochemistry of magnesium-rich minerals is important. Magnesium-rich minerals relevant to this work can be categorized into two groups: magnesium carbonates and magnesium-rich phyllosilicates/clays. Magnesium sulfates and chlorides are more soluble and require evaporation levels not reached in this work to precipitate.

Precipitation rates of magnesium-containing carbonates seem to be inversely related to their magnesium content (calcite > magnesian calcites > dolomite > magnesite) (Arvidson and Mackenzie, 2000; Palandri and Kharaka, 2004). Pokrovsky and Schott (1999) estimated magnesite precipitation rate to be at least three orders of magnitude lower than that of calcite. This difference in rate allows dissolved magnesium to be used for precipitation of other minerals of faster kinetics, such as sepiolite. Smith et al. (1995) observed magnesite precipitation in only 1 sample out of 47 in a sampling of three Central Valley evaporation ponds in California. Consequently, no dolomite or magnesite is allowed to precipitate in any run of this work. Hydromagnesite ($Mg_5(CO_3)_4(OH)_2.4H_2O$) and artinite ($Mg_2CO_3(OH)_2.3H_2O$) are generally associated with serpentine deposits, although hydromagnesite has been observed in caves. In similar modeling exercises (e.g. Alai et al., 2005, p. 34; Banks et al., 2004, p. 1923, Huff, 2004, p. 287; Smith et al., 1995, p. 133), dolomite, hydromagnesite, and magnesite were not allowed to precipitate. On the other hand, some hydrated magnesium carbonates are allowed to precipitate because hydrated forms generally precipitate first. Nesquehonite ($Mg(HCO_3)OH.2H_2O$) is found in dry lakes (e.g., Owens Lake in California—Levy et al., 1999) and more generally in evaporites when magnesium is available (Kloprogge et al., 2003). If magnesium sulfates do not precipitate at the salinity level reached in the simulations, calcium and potassium sulfates such as gypsum, anhydrite, syngenite ($K_2Ca(SO_4)_2.H_2O$), and other minor minerals do.

Another large group of minerals that could use up magnesium before sepiolite had any chance to precipitate is the smectite group and allied minerals. Appendix F gives a succinct description of clay mineralogy. Estimating neoformed clay mineralogy through geochemical modeling is notoriously difficult, and the approach taken in this work is to assume that mostly sepiolite clay will precipitate. It gives an upper bound on the amount of nonswelling clay that can precipitate. Minerals included in some of the simulations are Ca-montmorillonite (with some magnesium in it), celadonite (e.g., Parry and Reeves, 1968; Hover, 2003), talc, and saponite (e.g., Akbulut and Kadir, 2003)—all as individual representatives of different clay/phyllosilicate families. Chemical formulae are given in Table 4-5. Many minor silicates could also be formed (e.g., albite), but their addition to the mineral suite would not add much insight to the results. The focus of the sensitivity runs is on taking magnesium away from sepiolite and not aluminum or silica from magnesium-rich minerals. In most simulations, no silica is allowed to precipitate as quartz, low-temperature phases, or amorphous silica to favor clay precipitation. A sensitivity run was done with amorphous silica.

Table 4-5. Important allowed ("A") and suppressed ("S") minerals

| Status | Mineral Name | Formula | Comments |
|---|---|---|---|
| A | Anhydrite | $CaSO_4$ | |
| S | Artinite | $Mg_2CO_3(OH)_2.3H_2O$ | Serpentine alteration products |
| A/S | Brucite | $Mg(OH)_2$ | |
| A | Calcite / Aragonite | $CaCO_3$ | Ubiquitous mineral |
| A/S | Ca-montmorillonite | $Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$<br>$Ca_{0.165}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$ | In phreeqc.dat<br>In LLNL.dat—used in numerical simulations |
| A/S | Celadonite | $KMgAlSi_4O_{10}(OH)_2$ | Celadonite usually includes Fe in its structure. We assume that Fe does substitute for Al and Si but that the proxy formula accurately represents major ion consumption. |
| S | Chlorite | $Mg_5Al_2Si_3O_{10}(OH)_8$ | |
| S | Dolomite | $CaMg(CO_3)_2$ | |
| A | Gypsum | $CaSO_4.2H_2O$ | |
| S | Hydromagnesite | $Mg_5(CO_3)_4(OH)_2.4H_2O$ | Mostly serpentine alteration products |
| S | Magnesite | $MgCO_3$ | |
| A | Nahcolite | $NaHCO_3$ | |
| A | Nesquehonite | $MgCO_3.3H_2O$ or $Mg(HCO_3)OH.2H_2O$ | |
| A | Sepiolite | $Mg_4Si_6O_{15}(OH)_2.6H_2O$ | Precipitate from alkali saline waters in arid environments |
| A | Syngenite | $K_2Ca(SO_4)_2.H_2O$ | |
| A/S | Talc | $Mg_3Si_4O_{10}(OH)_2$ | |
| A/S | Ca-saponite | $Ca_{0.165}Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2$ | |

#### 4.3.3.3 Simulation Parameters

Geochemical simulations made use of water samples, whose composition is available from the TWDB (groundwater) and TCEQ (surface water) Websites. All data available were winnowed down to a single representative sample for each of the groups defined and explained in Appendix A. This simplification was needed to obtain a manageable set of samples to analyze.

PHREEQC input corresponding to net evaporation rates is provided in Table 4-4. Although atmospheric temperature information is available on a fine time and spatial scale (Figure 2-6), all simulations assume a pond temperature of 25°C. The lack of thermodynamic data for other temperatures largely guided this choice. Because of time and budget constraints, no seasonal variation in evaporation or temperature is accounted for. Average annual temperature varies from ~10$^{o}$C in the northern Panhandle to >20$^{o}$C in the valley at the Mexican border. During the summer ( July taken as representative), the daily average temperature varies from 20$^{o}$C to more than 30$^{o}$C. Evaporation occurs mostly in the summer, and pond temperature rises to 25$^{o}$C or above. Evaporation pond temperature is sensitive to atmospheric temperature variations because the large aspect ratio of the fluid volume favors easy heat exchange with the atmosphere (by design). Despite the nonlinearity of thermodynamic systems with temperature and accounting for all other assumptions and uncertainties, assuming a constant temperature of 25$^{o}$C is thought to yield reasonably accurate results.

Assumption of an open/closed system could also potentially bring different sets of results. The system is obviously open for water, but the gas-phase behavior is not as clear. The fact that reducing or low-$O_2$ conditions have been observed in the sampled ponds and in other Texas closed water bodies suggests that exchange between the pond bottom, where mineral precipitation is most likely to take place, and the atmosphere is sometimes slow. Some ponds (e.g., Horizon MUD and Abilene) show abundant marshland vegetation, whose decay explains the low dissolved oxygen (DO) reading. Others (e.g., River Oaks Ranch and Brady) display slimy surfaces, suggesting algal and microbial activity. The evaporation-driven-precipitation mechanism suggests that redox reactions are of minor importance and that DO concentration is not of direct interest. However, DO can be used as a surrogate to estimate rates of $CO_2$ exchange with atmosphere. Large biomass/water coefficients will generate high daily $CO_2$ variations. The interest in $CO_2$ buildup or lack thereof proceeds from the potential uptake of dissolved magnesium to precipitate magnesium-rich carbonates. Bicarbonate/$CO_2$ concentrations also control solution pH, and pH has a large impact on the precipitation sequence. Huff (2004, p. 287) assumed a constant $CO_2$ partial pressure. Banks et al. (2004, p. 1925) also found that the assumption of equilibrium with atmospheric $CO_2$ in geochemical modeling of saline lakes and rivers matches well with the data. $CO_2$, as a gas, is gradually less soluble in water as salinity increases, explaining the rise in pH, as $H^+$ is consumed according to $HCO_3 + H+ = CO_2 + H_2O$. A study of African lakes (Deocampo, 2005) expectedly showed that biological activity, through its control on $CO_2$ activity, itself controlling pH, affects sepiolite and other magnesium silicate stability. However, until further studies determine $CO_2$ and $O_2$ gradients in ponds, the uncertainty is addressed in our work through a sensitivity analysis. Two cases were considered: (1) bicarbonate/$CO_2$ being free to evolve with no interaction with the atmosphere (base case) and (2) bicarbonate concentration being controlled by atmospheric $CO_2$ concentration ($\log P_{CO2} = -3.42$ or 380 ppm).

Another important parameter is dissolved aluminum concentration. Sources of aluminum could be windblown dust or material from clay liners. Dissolved aluminum is difficult to determine because colloidal aluminum that is not stopped by common laboratory filters (e.g., Hitchon et al., 1999, p. 43 and p. 191; Bethke, 1996, p. 25 and p. 92) could lead to an overestimation of dissolved concentration. Dissolved aluminum concentration, in general low, is controlled by colloids and other small aluminum oxyhydroxide particles (AlOx). Common AlOx phases are gibbsite ($Al(OH)_3$), boehmite (AlOOH), and diaspore (AlOOH). Apps et al. (1988, p. 82) stated that diaspore is the most stable phase. In our work, when clays are added to the list of minerals allowed to precipitate, the aqueous phase is assumed in equilibrium with diaspore. Other workers have used a similar approach. Drever (1988, p. 210) assumed equilibrium with gibbsite, whereas Langmuir (1997) did so with kaolinite in a different context. Drever (1988, p. 211) also suggested that aluminum could originate from cation exchange from detrital clays or clays lining the bottom of the pond. Precipitation of aluminum-containing clays (i.e., all of them but sepiolite) can scavenge magnesium and silica, limit sepiolite precipitation, and generate desiccation-sensitive clays.

Another parameter of importance, pH, is intrinsically linked to $CO_2$ partial pressure. $P_{CO2}$, pH, and $HCO_3$ are uniquely determined through the equilibrium constant of the following reaction: $CO_2(g) + H_2O = HCO_3^- + H^+$ but are also impacted by salinity of the solution through activity of water and activity of aqueous components. Values of pH depend on biological activity, kinetics of $CO_2$ diffusion, and carbonate chemistry—all factors hard to model in the current scoping analysis. Sampled ponds suggest that pond pH is always higher than that of concentrate (Table 12-2). Smith et al. (1995, p. 133 & ff), in a study of three California ponds also reported that the ponds had a higher pH than that of the inflow water (inflow pH = 7.63–pond pH = 9.05; 7.32–8.26; 7.61–8.25). In order to maximize sepiolite precipitation during the modeling exercise, pH is set to the middle of the sepiolite stability pH range at a value of 8.5 by adding either caustic soda (NaOH) if the pH is too low or hydrochloric acid (HCl) if the pH is too high. In most simulations, acid generally has to be added.

In some circumstances, some minerals may not precipitate despite thermodynamics suggesting otherwise and become supersaturated. Natural waters are usually supersaturated relative to calcite (e.g., Langmuir, 1997, p. 219); however, many potential precipitation nuclei are present in a pond, and it is assumed that calcite and all other minerals will precipitate at a saturation index (SI) $SI=0$. Another important aspect, already touched upon, is the impact of kinetics and crystallinity of the precipitates. Poorly crystalline phases precipitate first, followed by an aging process. Poorly crystalline sepiolite (“sepiolite(d)”) is assumed to precipitate in all runs.

Many other geochemical processes, possibly relevant to the problem at hand, were not incorporated into the simulations. Solid solutions (e.g., precipitation of magnesian calcite when magnesium precipitates within the calcite structure), cation exchange, or sorption are not included in this scoping study. Similarly, a lack of data and budget constraints hamper a more realistic geochemical understanding, in which interactions with the clay liner and with the windblown dust would be accounted for. Nucleation is another important process not studied in this work. Direct precipitation from solutions generally requires nucleation sites. A significant fraction of the windblown dust is clay particles that could provide support for the initial clay precipitate. Addition of crystal seeds of sepiolite/palygorskite to the pond water could also enhance precipitation of the right minerals. Fate of chemicals added to the feedwater stream may also impact (favorably or not) the self-sealing process. Donahe (2006) investigated the presence of an antiscalant (Nalco PermaTreat PC-191) on the precipitation rate of sepiolite. He found that the antiscalant did not impact nucleation but generated smaller precipitant particles, leading to an increase in permeability reduction, as opposed to the lack of increase in the case with no antiscalant. In the modeling runs, pond water is assumed to be well mixed, with no concentration gradient; this assumption may not be realistic because $O_2$ gradient was observed in several of the sampled ponds.

#### 4.3.3.4 Scaling of PHREEQC results

Mineral precipitation volume must be scaled from PHREEQC direct results. Three aspects are relevant: nature and proportions of precipitates and total volume of precipitates. Results of simulation runs are presented in terms of concentration factor/evaporation progress, which is a linear function of time and evaporation rate and an inverse function of pond depth (recall that one of the basic assumptions of the model is that the pond is well designed and that its depth is approximately constant through time). An additional feature is that the PHREEQC simulations are framed so that the amount of precipitation is for 1 kg. In view of the number of major assumptions, 1 kg of water is equated to 1 L of water in the postprocessing of results. Let $M_i$ be the amount in moles of mineral *i* precipitating from 1 kg of water at some time *t* and $MV_i$ is its molar volume ($cm^3$/mol). Total volume precipitated is then

$$\theta \sum_i M_i MV_i$$

where $\theta$ is the average porosity of the mix of minerals.

PHREEQC results are given for 1 L/1 kg of solution as a function of $CF=1+et/h$, where *h* is pond depth, *e* is net evaporation rate, and *t* is time. Precipitant is distributed over surface area *A* so that $Ah=10^{-3}$ $m^3$ (all SI units). It follows that the amount of precipitation per unit area is $M_i/A = 10^3 \times M_i h$ (mol/$m^2$, *h* in m). The customary unit for molar volume is $cm^3$/mol, and the volume of precipitation per unit area is then (*h* in m, $MV_i$ in $cm^3$/mol)

$$10^{-3} \times \theta h \sum_i M_i MV_i \ \ \mathrm{m^3/m^2}$$

Mickley (2006, p. 162) summarized pond depth constraints to be in the 1- to 18-inch range. Evaporation rate is not impacted much by pond depth, and a shallow depth carries the risk of frequent exposure to the atmosphere and subsequent drying and cracking. In the processing of simulation results, we assumed a pond depth of either 3 or 12 inches.

A quick calculation can be done to estimate maximum amount of precipitates, assuming that the dissolved amount can be neglected. By construction, net evaporation rate is equal to concentrate flow rate. The mass on a unit surface area at time *t* is $C_{TDS} \times e \times t$ (× 1 $m^2$); that is, with a feedwater concentration of 1,500 mg/L, $C_{TDS}$ = 6 kg/$m^3$, and a net evaporation rate of 30 inches/year for 30 years, ~137 kg/$m^2$. If material density is ~2,400 kg/$m^3$, it translates to ~5.7 cm, or 8.2 cm if one assumes a porosity of 30%. This calculation is consistent with a plot provided in Mickley (2006, p. 164) and results presented in the next section.

### 4.3.4 Geochemical Simulation Results

In order to test several environmental conditions, several sets of geochemical runs were done (Appendix H); each set is composed of 24 runs: the 20 groups (Appendix A) + 2 subgroups (Na-dominant and mixed) added to Eocene and Cretaceous Sandstones groups.

As a general rule, the following minerals precipitate:

- calcite (carbonate with little solubility)
- gypsum (an additional sink for calcium)
- a soluble magnesium carbonate
- a clay or claylike mineral

Calcite is a sink for calcium and is fully or partly replaced by gypsum when sulfate concentration is high enough. The specific magnesium carbonate is sensitive to the composition of the aqueous phase. It could be nesquehonite, huntite, syngenite…. Each of these minerals occurs in specific natural conditions. For example, it seems that huntite is typically generated by magnesium brines the same way dolomite is generated from calcite. It was checked, however, that some kind of magnesium precipitation occurs independently of the species specified in the geochemical simulations and in molar amounts sensibly equivalent. The nature of the clay depends on Al availability, although most clay minerals have aluminum in their structure. In sensitivity runs (some are presented in Appendix H), we assumed that a magnesium member of clay groups known to precipitate in saline lakes was allowed to precipitate along with sepiolite. Diaspore (AlOOH) is assumed to be present in all clay sensitivity runs and to control aqueous aluminum concentrations. We tested celadonite from the illite group, Ca-montmorillonite, with some magnesium from the trioctahedral smectite group, and Ca-saponite, which also contains magnesium, from the dioctahedral smectite group. In presence of aluminum, one of these minerals generally precipitates instead of sepiolite. In general, saponite is the most likely to precipitate, strongly limiting or preventing sepiolite deposition. In contrast, sepiolite precipitates preferentially to talc and kaolinite and often times Ca-montmorillonite. The same is true of Ca-montmorillonite, even if its precipitation has been made more likely by increasing the reaction constant by three orders of magnitude.

Base-case accumulations were computed with no clay minerals other than sepiolite allowed to precipitate (by setting no aluminum in solution), a fixed pH of 8.5, and $CO_2$ partial pressure free to drift. Because these conditions maximize sepiolite precipitation, results represent an upper bound of the likely outcome and are sensitive to the concentrate chemical composition (Table 4-6). Results of some geochemical simulations are presented in Appendix H. For the purpose of comparing results from different groups, durations of 5 and 30 years after facility opening are retained; 30 years represents a reasonable life span for a pond and 5 years corresponds to a time interval at which benefits of self sealing should have occurred. With no additives, the average amount of precipitate at the bottom of a pond is 0.15 inch, with a sepiolite fraction of 7%. The average hides large discrepancies across the state (Table 4-6). Bone Spring – Victorio Peak brackish water, as well as Permian Evaporite groups, has the highest accumulation (0.7–0.8 inch) after 5 years, but with a small sepiolite fraction. This statistic is due partly to high feedwater TDS (Table 8-1) and to a lesser degree to their high local evaporation rates. In addition, a higher sepiolite fraction corresponds to smaller accumulation thickness, and relative accumulation between groups after 30 years parallels that of 5 years. Average accumulation depth is ~1 inch in thickness, with a sepiolite fraction of ~6%. Largest accumulations are produced by Bone Spring – Victorio Peak brackish water and Permian Evaporite groups once again (5.6 and 4.6 inches, respectively), still with little sepiolite. These accumulation thickness values do not, however, account for porosity.

A set of runs with the addition of a large amount of sepiolite precursor (0.01 mol/L of a blend of $MgCl_2$ and $Na_2SiO_3$ in 2:3 proportions, which translates into an approximate doubling of the concentrate TDS) was performed (see Appendix H), with clear improvement in accumulation thickness (Figure 4-4) and sepiolite fraction (Table 4-7 and Table 4-8). In these runs, if amorphous silica is allowed to precipitate, it does so in only two subgroups (Na-dominant samples from the Eocene and Cretaceous Sandstone groups) and in minor quantities, most likely because silica solubility is high at alkaline pH's. This number of sepiolite precursors corresponds to an areal loading of 513 tons/acre over 30 years (338 tons/acre of sodium metasilicate) and 85 tons/acre after 5 years. Donahe (2006, p. 65) noted that, in his laboratory experiments, at the application rate of 35 to 40 tons/acre of sodium silicate, the self-forming liner is capable of supplying an added resistance to the soil equivalent to 6 inches of native soil on average.

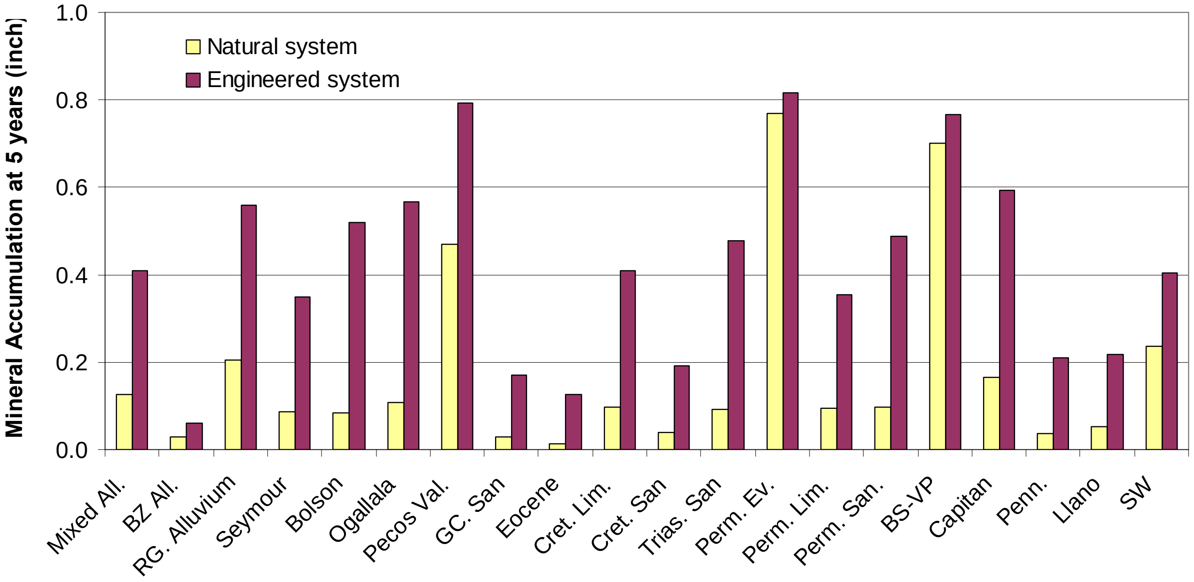


Figure 4-4. Comparison of total mineral accumulation (inches) at 5 years for nonengineered ("natural") and engineered (addition of sepiolite precursor) systems.

### 4.3.5 Conclusions on Self-Sealing Geochemical Calculations

The most likely self-sealing mechanism is precipitation of neoformed materials from the solution. The most volumetrically abundant minerals to precipitate are calcite, gypsum, and, if engineered correctly, sepiolite. The locus of precipitation is not an output of the geochemical modeling, but it is likely to initiate on the geomembrane liner or within the first few millimeters of the clay liner, at least initially. Nevertheless, the amount of precipitated material remains low, especially early in the life of the pond and, despite considerable geographic variability, typically only a fraction of an inch. Addition of chemical additives to the concentrate stream does help in producing a thicker accumulation in proportions commensurate to the added amount. Adding approximately 0.01 mol of sepiolite precursors to 1 L of concentrate is equivalent to 1.3¢ for 3 L of potable water, that is, an increased cost of ~1.5¢/gal attributable to chemical product purchase, notwithstanding operational costs. In the most favorable case, adding such amount of additives will cost over $1/1,000 gal.

Previous laboratory and field experiments have suggested that precipitation of these compounds does reduce hydraulic conductivity but not to the requested limit of $10^{-7}$ cm/s. The additional reduction in conductivity could, however, help the permittee in requesting an alternative pond-lining method (alternative liner, option 2; see Appendix C). In summary, the following observations can be made:

- the most abundant minerals to precipitate are calcite, gypsum, and, if engineered correctly, sepiolite
- the total amount of precipitate is small (<1 inch/unit surface area)
- addition of additives is cheap
- previous laboratory and field experiments suggest that conductivity of precipitate is above regulatory threshold.

Table 4-6. Average mineral accumulation thickness and sepiolite fraction at 5 and 30 years in a 3-inch-depth pond in nonengineered conditions (assumes a porosity of 0%).

| **Groups** | **At 5 years** | | **At 30 years** | |
|---|---|---|---|---|
| | **Acc. Depth (inches)** | **Fraction Sepiolite (%)** | **Acc. Depth (inches)** | **Fraction Sepiolite (%)** |
| Mixed Alluvium | 0.12 | 9.2 | 0.81 | 8.3 |
| Brazos River Alluvium | 0.03 | 9.4 | 0.16 | 10.3 |
| Rio Grande Alluvium | 0.21 | 11.8 | 1.74 | 8.3 |
| Seymour | 0.09 | 16.3 | 0.58 | 14.3 |
| Bolson | 0.08 | 31.8 | 0.92 | 17.2 |
| Ogallala | 0.11 | 34.4 | 0.64 | 33.6 |
| Pecos Valley | 0.47 | 5.2 | 3.85 | 3.8 |
| Gulf Coast Sandstone | 0.03 | 28.0 | 0.26 | 18.6 |
| Eocene All Samples | 0.01 | 27.2 | 0.08 | 27.2 |
| Eocene Mixed | 0.06 | 17.7 | 0.43 | 14.6 |
| Eocene Na Dominant | 0.00 | 31.3 | 0.02 | 41.2 |
| Cretaceous Limestone | 0.10 | 9.6 | 0.63 | 8.8 |
| Cret. Sandst. All Samples | 0.04 | 13.4 | 0.30 | 10.5 |
| Cret. Sandst. Mixed | 0.09 | 5.3 | 0.63 | 4.7 |
| Cret. Sandst. Na Dominant | 0.00 | 51.5 | 0.13 | 15.0 |
| Triassic Sandstone | 0.09 | 8.6 | 0.57 | 8.2 |
| Permian Evaporite | 0.77 | 1.2 | 4.61 | 1.2 |
| Permian Limestone | 0.09 | 8.6 | 0.65 | 7.5 |
| Permian Sandstone | 0.10 | 12.1 | 0.61 | 11.3 |
| Bone Spring – Victorio Peak | 0.70 | 1.9 | 5.60 | 1.4 |
| Capitan Reef | 0.17 | 7.1 | 1.02 | 6.8 |
| Pennsylvanian | 0.04 | 11.6 | 0.42 | 6.3 |
| Llano Uplift | 0.05 | 7.6 | 0.37 | 6.6 |
| Surface Water | 0.24 | 2.1 | 1.81 | 1.6 |
| | | | | |
| Simple Average | 0.15 | 15.1 | 1.12 | 12.0 |
| Weighted Average | | 7.0 | | 5.8 |

Table 4-7. Average mineral accumulation thickness and sepiolite fraction at 5 years in a 3–inch-depth pond in nonengineered and engineered conditions (assumes a porosity of 0%).

| **Groups** | **Nonengineered Conditions** | | **Engineered (Mg+Si) Conditions** | |
|---|---|---|---|---|
| | **Acc. Depth (inches)** | **Fraction Sepiolite (%)** | **Acc. Depth (inches)** | **Fraction Sepiolite (%)** |
| Mixed Alluvium | 0.12 | 9.2 | 0.41 | 56.1 |
| Brazos River Alluvium | 0.03 | 9.4 | 0.06 | 57.9 |
| Rio Grande Alluvium | 0.21 | 11.8 | 0.56 | 61.0 |
| Seymour | 0.09 | 16.3 | 0.35 | 63.7 |
| Bolson | 0.08 | 31.8 | 0.52 | 70.4 |
| Ogallala | 0.11 | 34.4 | 0.57 | 57.6 |
| Pecos Valley | 0.47 | 5.2 | 0.79 | 47.5 |
| Gulf Coast Sandstone | 0.03 | 28.0 | 0.17 | 88.1 |
| Eocene All Samples | 0.01 | 27.2 | 0.13 | 93.1 |
| Eocene Mixed | 0.06 | 17.7 | 0.18 | 69.4 |
| Eocene Na Dominant | 0.00 | 31.3 | 0.12 | 98.6 |
| Cretaceous Limestone | 0.10 | 9.6 | 0.41 | 58.6 |
| Cret. Sandst. All Samples | 0.04 | 13.4 | 0.19 | 82.4 |
| Cret. Sandst. Mixed | 0.09 | 5.3 | 0.25 | 63.5 |
| Cret. Sandst. Na Dominant | 0.00 | 51.5 | 0.16 | 98.7 |
| Triassic Sandstone | 0.09 | 8.6 | 0.48 | 60.4 |
| Permian Evaporite | 0.77 | 1.2 | 0.82 | 31.2 |
| Permian Limestone | 0.09 | 8.6 | 0.35 | 58.5 |
| Permian Sandstone | 0.10 | 12.1 | 0.49 | 50.6 |
| Bone Spring – Victorio Peak | 0.70 | 1.9 | 0.77 | 43.6 |
| Capitan Reef | 0.17 | 7.1 | 0.59 | 51.7 |
| Pennsylvanian | 0.04 | 11.6 | 0.21 | 79.5 |
| Llano Uplift | 0.05 | 7.6 | 0.22 | 69.7 |
| Surface Water | 0.24 | 2.1 | 0.40 | 51.8 |
| | | | | |
| Simple Average | 0.15 | 15.1 | 0.38 | 65.1 |
| Weighted Average | | 7.0 | | 57.5 |

Table 4-8. Average mineral accumulation thickness and sepiolite fraction at 30 years in a 3-inch-depth pond in nonengineered and engineered conditions (assumes a porosity of 0%).

| **Groups** | **Nonengineered Conditions** | | **Engineered (Mg+Si) Conditions** | |
|---|---|---|---|---|
| | **Acc. Depth (inches)** | **Fraction Sepiolite (%)** | **Acc. Depth (inches)** | **Fraction Sepiolite (%)** |
| Mixed Alluvium | 0.81 | 8.3 | 3.18 | 45.1 |
| Brazos River Alluvium | 0.16 | 10.3 | 0.51 | 67.0 |
| Rio Grande Alluvium | 1.74 | 8.3 | 5.99 | 34.6 |
| Seymour | 0.58 | 14.3 | 2.98 | 46.5 |
| Bolson | 0.92 | 17.2 | 5.99 | 37.3 |
| Ogallala | 0.64 | 33.6 | 4.88 | 40.8 |
| Pecos Valley | 3.85 | 3.8 | 11.21 | 18.6 |
| Gulf Coast Sandstone | 0.26 | 18.6 | 1.88 | 53.2 |
| Eocene All Samples | 0.08 | 27.2 | 1.24 | 65.8 |
| Eocene Mixed | 0.43 | 14.6 | 1.41 | 60.9 |
| Eocene Na Dominant | 0.02 | 41.2 | 1.38 | 58.3 |
| Cretaceous Limestone | 0.63 | 8.8 | 4.03 | 37.0 |
| Cret. Sandst. All Samples | 0.30 | 10.5 | 1.96 | 53.1 |
| Cret. Sandst. Mixed | 0.63 | 4.7 | 1.96 | 53.0 |
| Cret. Sandst. Na Dominant | 0.13 | 15.0 | 2.12 | 48.6 |
| Triassic Sandstone | 0.57 | 8.2 | 4.66 | 38.1 |
| Permian Evaporite | 4.61 | 1.2 | 5.56 | 28.6 |
| Permian Limestone | 0.65 | 7.5 | 2.89 | 45.6 |
| Permian Sandstone | 0.61 | 11.3 | 3.71 | 41.4 |
| Bone Spring – Victorio Peak | 5.60 | 1.4 | 10.93 | 18.8 |
| Capitan Reef | 1.02 | 6.8 | 6.94 | 27.0 |
| Pennsylvanian | 0.42 | 6.3 | 2.23 | 48.3 |
| Llano Uplift | 0.37 | 6.6 | 1.94 | 51.7 |
| Surface Water | 1.81 | 1.6 | 5.70 | 23.0 |
| | | | | |
| Simple Average | 1.12 | 12.0 | 3.97 | 43.4 |
| Weighted Average | | 5.8 | | 34.8 |

## *4.4 Design Specifics and Cost Estimates*

In previous sections of Chapter 4, we analyzed the regulatory environment, determined the likely composition of the concentrate, and estimated amount and nature of pond bottom sediments. In this section, we examine design specifics and cost. It is important to note that, by design, self-sealing evaporation ponds have no specific operational features. Additives can be injected in the concentrate stream as any other additive, such as antiscalant or acid. They could be added within the plant itself rather than being spread over the pond. At this point of the study, there is no firm conclusion on the need for a mixing system to homogenize the pond water because it is unclear whether a concentration gradient is helpful. Additional features to accelerate evaporation, such as, for example, evaporation nets or a Turbo-mist type of evaporator, may lead to earlier and more abundant sepiolite precipitation, but again it is unlikely to be achieved at a cost lower than that of the current technology. TCEQ (2006a), Ahmed et al. (2000), and Mickley (2006) gave general guidelines for constructing evaporation ponds. The purpose of this section is to present the design of a generic evaporation pond for outfall from a 1-MGD desalination facility sited in Texas. The cost difference between using prescriptive liner technology for the pond and using an alternative liner that incorporates self-sealing technology is also presented.

### 4.4.1 Pond Sizing

The size of the pond is calculated using procedures outlined for surface land disposal of effluent (TCEQ, 2006a) and described previously in Section 4.1.2.1. As described by Mickley (2006), the surface area required for a pond primarily depends on evaporation rate. The required pond depth is a function of its required liquid storage capacity, storage capacity for precipitant, and freeboard for precipitation and wave action. Whereas evaporation rates may be somewhat higher for shallower ponds, very shallow ponds may dry and allow liners to become exposed to the environment. Clay liners exposed to wetting and drying cycles are more likely to desiccate and crack than clay liners protected by an insulation layer, such as a soil layer (Bonaparte et al., 2002). Geomembrane liners exposed to ultraviolet radiation and high temperatures will lose antioxidants and/or plasticizers faster than geomembrane liners protected from these conditions and will have a reduced service life.

For this report, the following assumptions are made for sizing the generic evaporation pond:

- 30% of the water treated at the desalination facility is reject water that is disposed of in the evaporation pond;
- A salinity correction factor of 0.9 is appropriate for evaluation of evaporation from Texas ponds (see Section 3.3.1);
- The pond can be sized using a monthly water balance that considers the past 25 years of monthly precipitation and lake evaporation data;
- The pond should have no accumulation of liquid under average conditions and should be able to store excess liquid generated under the critical condition of maximum annual precipitation and minimum evaporation;
- Maximum depth of water in a pond should be less than 2 ft, and the minimum pond freeboard is 2 ft; and
- The pond must have sufficient capacity to store precipitant until it is removed or the pond has reached the end of its design life; for the report, it is assumed that ~1 inch of precipitant

is generated over the 30-year design life of the pond (see Table 4-8); this amount of precipitant is considered to be negligible with respect to pond storage.

Pond sizes were calculated for the 1° quadrangles with the four facilities having evaporation ponds visited in this study (River Oaks Ranch in Hays County—quadrangle 709, as defined by TWDB (2006a), Brady in McCulloch County—quadrangle 608, Abilene in Taylor County—quadrangle 508, and Horizon MUD in El Paso County—quadrangle 601. Pond-design spreadsheets are presented in Table 4-10 to Table 4-13. The smallest pond, with an area of 70.5 acres and depth (including freeboard) of 45 inches, was calculated for quadrangle 601 (Horizon MUD) (Table 4-9). Pond designs for the other three quadrangles ranged from 126.6 to 175.5 acres in surface area, with a depth of 48 inches. They cover a representative sample of net evaporation conditions expected across the state. As expected, calculated pond size is proportional to net evaporation rate. A representative evaporation pond area for a 1-MGD desalination facility can be estimated at 125 acres.

Table 4-9. Generic pond size for 1-MGD facilities located near the sampled ponds

| **Public Utility** | **Pond Area (acres)** | **Representative of USGS Quadrangle** |
|---|---|---|
| River Oaks Ranch | 175.5 | 709 |
| Brady | 135.6 | 608 |
| Abilene | 126.6 | 508 |
| Horizon MUD | 70.5 | 601 |

Table 4-10. Pond water balance for quadrangle 709, representing the River Oaks Ranch site

**PRECIPITATION AND EVAPORATION DATA (1980-2004) FROM TWDB** (http://hyper20.twdb.state.tx.us/Evaporation/evap.html)

TEXAS QUADRANGLE NUMBER 709
MAX. ANNUAL PRECIPITATION 44.94 (in.) MIN. ANNUAL EVAPORATION 48.47 (in.)

**POND AREA** 175.50 **acres**
**POND FREEBOARD** 24 **in.**
**DISPOSAL RATE** 0.3 **MGD**
**POND EVAPORATION : LAKE EVAPORATION (SALINITY CORRECTION FACTOR)** 0.9

**AVERAGE CONDITION**

| MONTH | APPLIED EFFLUENT (in.) | MEAN MONTHLY PRECIP. (in.) | TOTAL LIQUID TO POND (in.) | MEAN MONTHLY LAKE EVAP. (in.) | Δ POND STORAGE (in.) | ACCUM. POND STORAGE (in.) |
|---|---|---|---|---|---|---|
| JAN | 1.9 | 1.69 | 3.6 | 2.35 | 1.2 | 1.2 |
| FEB | 1.9 | 2.23 | 4.1 | 2.52 | 1.6 | 2.8 |
| MAR | 1.9 | 2.37 | 4.3 | 3.74 | 0.5 | 3.3 |
| APR | 1.9 | 2.06 | 3.9 | 4.69 | -0.7 | 2.6 |
| MAY | 1.9 | 4.11 | 6.0 | 5.24 | 0.8 | 3.4 |
| JUN | 1.9 | 4.44 | 6.3 | 6.55 | -0.2 | 3.1 |
| JUL | 1.9 | 2.03 | 3.9 | 7.69 | -3.8 | -0.6 |
| AUG | 1.9 | 1.85 | 3.7 | 7.59 | -3.9 | -4.5 |
| SEP | 1.9 | 2.83 | 4.7 | 5.72 | -1.0 | -5.5 |
| OCT | 1.9 | 3.62 | 5.5 | 4.62 | 0.9 | -4.6 |
| NOV | 1.9 | 2.88 | 4.8 | 3.39 | 1.4 | -3.2 |
| DEC | 1.9 | 2.18 | 4.1 | 2.38 | 1.7 | -1.5 |

**CHECK ACCUM. POND STORAGE AT END OF YEAR < 0** **-1.5** in.

**CRITICAL CONDITION**

| MONTH | APPLIED EFFLUENT (in.) | MEAN MONTHLY PRECIP. (in.) | MEAN PRECIP. DISTRIB. (%) | MAX. MONTHLY PRECIP. (in.) | TOTAL LIQUID TO POND (in.) | MEAN MONTHLY LAKE EVAP. (in.) | MEAN EVAP. DISTRIB. (%) | MIN. MONTHLY POND EVAP. (in.) | Δ POND STORAGE (in.) | ACCUM. POND STORAGE (in.) |
|---|---|---|---|---|---|---|---|---|---|---|
| JAN | 1.9 | 1.69 | 5% | 2.35 | 4.2 | 2.35 | 4% | 1.82 | 2.4 | 2.4 |
| FEB | 1.9 | 2.23 | 7% | 3.10 | 5.0 | 2.52 | 4% | 1.95 | 3.0 | 5.5 |
| MAR | 1.9 | 2.37 | 7% | 3.30 | 5.2 | 3.74 | 7% | 2.89 | 2.3 | 7.8 |
| APR | 1.9 | 2.06 | 6% | 2.87 | 4.8 | 4.69 | 8% | 3.62 | 1.1 | 8.9 |
| MAY | 1.9 | 4.11 | 13% | 5.72 | 7.6 | 5.24 | 9% | 4.05 | 3.6 | 12.5 |
| JUN | 1.9 | 4.44 | 14% | 6.18 | 8.1 | 6.55 | 12% | 5.06 | 3.0 | 15.5 |
| JUL | 1.9 | 2.03 | 6% | 2.83 | 4.7 | 7.69 | 14% | 5.94 | -1.2 | 14.2 |
| AUG | 1.9 | 1.85 | 6% | 2.57 | 4.5 | 7.59 | 13% | 5.86 | -1.4 | 12.8 |
| SEP | 1.9 | 2.83 | 9% | 3.94 | 5.8 | 5.72 | 10% | 4.42 | 1.4 | 14.3 |
| OCT | 1.9 | 3.62 | 11% | 5.04 | 6.9 | 4.62 | 8% | 3.57 | 3.4 | 17.6 |
| NOV | 1.9 | 2.88 | 9% | 4.01 | 5.9 | 3.39 | 6% | 2.62 | 3.3 | 20.9 |
| DEC | 1.9 | 2.18 | 7% | 3.03 | 4.9 | 2.38 | 4% | 1.84 | 3.1 | 24.0 |

**CHECK MAX. ACCUM. POND STORAGE < 2 FEET** **24.0** in.

NOTES:
APPLIED EFFLUENT = DISPOSAL RATE / (12 MONTHS/YEAR) / POND AREA
MEAN PRECIPITATION DISTRIBUTION = 100 (MEAN MONTHLY PRECIPITATION / MEAN ANNUAL PRECIPITATION)
MAXIMUM MONTHLY PRECIPITATION = MAXIMUM ANNUAL PRECIPITATION X MEAN PRECIPITATION DISTRIBUTION
TOTAL LIQUID TO POND = APPLIED EFFLUENT + MONTHLY PRECIPITATION
MEAN EVAPORATION DISTRIBUTION = 100 (MEAN MONTHLY EVAPORATION / MEAN ANNUAL EVAPORATION)
MINIMUM MONTHLY POND EVAPORATION =
MINIMUM ANNUAL POND EVAPORATION X MEAN EVAPORATION DISTRIBUTION X SALINITY CORRECTION FACTOR
CHANGE IN POND STORAGE = TOTAL LIQUID TO POND - MONTHLY POND EVAPORATION
ACCUMULATED POND STORAGE = ACCUMULATED POND STORAGE FOR MONTH i-1 + CHANGE IN POND STORAGE FOR MONTH i

Table 4-11. Pond water balance for quadrangle 608, representing the Brady site.

**PRECIPITATION AND EVAPORATION DATA (1980-2004) FROM TWDB** (http://hyper20.twdb.state.tx.us/Evaporation/evap.html)

TEXAS QUADRANGLE NUMBER 608

MAX. ANNUAL PRECIPITATION 38.82 (in.) MIN. ANNUAL EVAPORATION 53.75 (in.)

**POND AREA** 135.60 **acres**

**POND FREEBOARD** 24 **in.**

**DISPOSAL RATE** 0.3 **MGD**

**POND EVAPORATION : LAKE EVAPORATION (SALINITY CORRECTION FACTOR)** 0.9

**AVERAGE CONDITION**

| MONTH | APPLIED EFFLUENT (in.) | MEAN MONTHLY PRECIP. (in.) | TOTAL LIQUID TO POND (in.) | MEAN MONTHLY LAKE EVAP. (in.) | Δ POND STORAGE (in.) | ACCUM. POND STORAGE (in.) |
|---|---|---|---|---|---|---|
| JAN | 2.4 | 1.14 | 3.6 | 2.49 | 1.1 | 1.1 |
| FEB | 2.4 | 1.87 | 4.3 | 3.16 | 1.2 | 2.2 |
| MAR | 2.4 | 1.79 | 4.2 | 5.2 | -1.0 | 1.3 |
| APR | 2.4 | 1.57 | 4.0 | 6.93 | -2.9 | -1.6 |
| MAY | 2.4 | 3.46 | 5.9 | 8.29 | -2.4 | -4.0 |
| JUN | 2.4 | 3.87 | 6.3 | 9.53 | -3.2 | -7.2 |
| JUL | 2.4 | 1.74 | 4.2 | 8.77 | -4.6 | -11.8 |
| AUG | 2.4 | 1.97 | 4.4 | 7.34 | -2.9 | -14.7 |
| SEP | 2.4 | 2.94 | 5.4 | 6.09 | -0.7 | -15.5 |
| OCT | 2.4 | 2.73 | 5.2 | 4.87 | 0.3 | -15.1 |
| NOV | 2.4 | 1.82 | 4.3 | 3.11 | 1.2 | -14.0 |
| DEC | 2.4 | 1.46 | 3.9 | 2.44 | 1.5 | -12.5 |

**CHECK ACCUM. POND STORAGE AT END OF YEAR < 0** **-12.5** in.

**CRITICAL CONDITION**

| MONTH | APPLIED EFFLUENT (in.) | MEAN MONTHLY PRECIP. (in.) | MEAN PRECIP. DISTRIB. (%) | MAX. MONTHLY PRECIP. (in.) | TOTAL LIQUID TO POND (in.) | MEAN MONTHLY LAKE EVAP. (in.) | MEAN EVAP. DISTRIB. (%) | MIN. MONTHLY POND EVAP. (in.) | Δ POND STORAGE (in.) | ACCUM. POND STORAGE (in.) |
|---|---|---|---|---|---|---|---|---|---|---|
| JAN | 2.4 | 1.14 | 4% | 1.68 | 4.1 | 2.38 | 3% | 1.69 | 2.4 | 2.4 |
| FEB | 2.4 | 1.87 | 7% | 2.75 | 5.2 | 2.55 | 4% | 1.81 | 3.4 | 5.8 |
| MAR | 2.4 | 1.79 | 7% | 2.64 | 5.1 | 4.36 | 6% | 3.09 | 2.0 | 7.8 |
| APR | 2.4 | 1.57 | 6% | 2.31 | 4.8 | 5.92 | 9% | 4.20 | 0.6 | 8.4 |
| MAY | 2.4 | 3.46 | 13% | 5.10 | 7.5 | 6.34 | 9% | 4.50 | 3.0 | 11.4 |
| JUN | 2.4 | 3.87 | 15% | 5.70 | 8.1 | 7.33 | 11% | 5.20 | 2.9 | 14.4 |
| JUL | 2.4 | 1.74 | 7% | 2.56 | 5.0 | 8.57 | 13% | 6.08 | -1.1 | 13.3 |
| AUG | 2.4 | 1.97 | 7% | 2.90 | 5.3 | 8.00 | 12% | 5.67 | -0.3 | 13.0 |
| SEP | 2.4 | 2.94 | 11% | 4.33 | 6.8 | 6.17 | 9% | 4.38 | 2.4 | 15.4 |
| OCT | 2.4 | 2.73 | 10% | 4.02 | 6.5 | 4.91 | 7% | 3.48 | 3.0 | 18.3 |
| NOV | 2.4 | 1.82 | 7% | 2.68 | 5.1 | 3.39 | 5% | 2.40 | 2.7 | 21.1 |
| DEC | 2.4 | 1.46 | 6% | 2.15 | 4.6 | 2.37 | 3% | 1.68 | 2.9 | 24.0 |

**CHECK MAX. ACCUM. POND STORAGE < 2 FEET** **24.0** in.

NOTES:
APPLIED EFFLUENT = DISPOSAL RATE / (12 MONTHS/YEAR) / POND AREA
MEAN PRECIPITATION DISTRIBUTION = 100 (MEAN MONTHLY PRECIPITATION / MEAN ANNUAL PRECIPITATION)
MAXIMUM MONTHLY PRECIPITATION = MAXIMUM ANNUAL PRECIPITATION X MEAN PRECIPITATION DISTRIBUTION
TOTAL LIQUID TO POND = APPLIED EFFLUENT + MONTHLY PRECIPITATION
MEAN EVAPORATION DISTRIBUTION = 100 (MEAN MONTHLY EVAPORATION / MEAN ANNUAL EVAPORATION)
MINIMUM MONTHLY POND EVAPORATION =
MINIMUM ANNUAL POND EVAPORATION X MEAN EVAPORATION DISTRIBUTION X SALINITY CORRECTION FACTOR
CHANGE IN POND STORAGE = TOTAL LIQUID TO POND - MONTHLY POND EVAPORATION
ACCUMULATED POND STORAGE = ACCUMULATED POND STORAGE FOR MONTH i-1 + CHANGE IN POND STORAGE FOR MONTH i

Table 4-12. Pond water balance for quadrangle 508, representing the Abilene site.

**PRECIPITATION AND EVAPORATION DATA (1980-2004) FROM TWDB** (http://hyper20.twdb.state.tx.us/Evaporation/evap.html)
TEXAS QUADRANGLE NUMBER 508
MAX. ANNUAL PRECIPITATION 39.67 (in.) MIN. ANNUAL EVAPORATION 52.33 (in.)

**POND AREA** 126.60 **acres**
**POND FREEBOARD** 24 **in.**
**DISPOSAL RATE** 0.3 **MGD**
**POND EVAPORATION : LAKE EVAPORATION (SALINITY CORRECTION FACTOR)** 0.9

**AVERAGE CONDITION**

| MONTH | APPLIED EFFLUENT (in.) | MEAN MONTHLY PRECIP. (in.) | TOTAL LIQUID TO POND (in.) | MEAN MONTHLY LAKE EVAP. (in.) | Δ POND STORAGE (in.) | ACCUM. POND STORAGE (in.) |
|---|---|---|---|---|---|---|
| JAN | 2.6 | 1.15 | 3.8 | 2.33 | 1.4 | 1.4 |
| FEB | 2.6 | 1.82 | 4.4 | 2.51 | 1.9 | 3.4 |
| MAR | 2.6 | 1.90 | 4.5 | 4.26 | 0.3 | 3.6 |
| APR | 2.6 | 1.89 | 4.5 | 5.62 | -1.1 | 2.5 |
| MAY | 2.6 | 3.47 | 6.1 | 5.92 | 0.2 | 2.7 |
| JUN | 2.6 | 3.75 | 6.4 | 7.17 | -0.8 | 1.9 |
| JUL | 2.6 | 1.94 | 4.6 | 8.22 | -3.7 | -1.8 |
| AUG | 2.6 | 2.32 | 4.9 | 7.73 | -2.8 | -4.6 |
| SEP | 2.6 | 2.73 | 5.3 | 5.94 | -0.6 | -5.2 |
| OCT | 2.6 | 2.95 | 5.6 | 5.02 | 0.5 | -4.6 |
| NOV | 2.6 | 1.84 | 4.5 | 3.45 | 1.0 | -3.6 |
| DEC | 2.6 | 1.57 | 4.2 | 2.33 | 1.9 | -1.8 |

**CHECK ACCUM. POND STORAGE AT END OF YEAR < 0** **-1.8** in.

**CRITICAL CONDITION**

| MONTH | APPLIED EFFLUENT (in.) | MEAN MONTHLY PRECIP. (in.) | MEAN PRECIP. DISTRIB. (%) | MAX. MONTHLY PRECIP. (in.) | TOTAL LIQUID TO POND (in.) | MEAN MONTHLY LAKE EVAP. (in.) | MEAN EVAP. DISTRIB. (%) | MIN. MONTHLY POND EVAP. (in.) | Δ POND STORAGE (in.) | ACCUM. POND STORAGE (in.) |
|---|---|---|---|---|---|---|---|---|---|---|
| JAN | 2.6 | 1.15 | 4% | 1.67 | 4.3 | 2.33 | 4% | 1.81 | 2.5 | 2.5 |
| FEB | 2.6 | 1.82 | 7% | 2.64 | 5.3 | 2.51 | 4% | 1.95 | 3.3 | 5.8 |
| MAR | 2.6 | 1.90 | 7% | 2.76 | 5.4 | 4.26 | 7% | 3.32 | 2.1 | 7.8 |
| APR | 2.6 | 1.89 | 7% | 2.74 | 5.4 | 5.62 | 9% | 4.37 | 1.0 | 8.8 |
| MAY | 2.6 | 3.47 | 13% | 5.04 | 7.7 | 5.92 | 10% | 4.61 | 3.0 | 11.9 |
| JUN | 2.6 | 3.75 | 14% | 5.44 | 8.1 | 7.17 | 12% | 5.58 | 2.5 | 14.4 |
| JUL | 2.6 | 1.94 | 7% | 2.82 | 5.4 | 8.22 | 14% | 6.40 | -1.0 | 13.4 |
| AUG | 2.6 | 2.32 | 8% | 3.37 | 6.0 | 7.73 | 13% | 6.02 | 0.0 | 13.4 |
| SEP | 2.6 | 2.73 | 10% | 3.96 | 6.6 | 5.94 | 10% | 4.62 | 2.0 | 15.3 |
| OCT | 2.6 | 2.95 | 11% | 4.28 | 6.9 | 5.02 | 8% | 3.91 | 3.0 | 18.3 |
| NOV | 2.6 | 1.84 | 7% | 2.67 | 5.3 | 3.45 | 6% | 2.69 | 2.6 | 20.9 |
| DEC | 2.6 | 1.57 | 6% | 2.28 | 4.9 | 2.33 | 4% | 1.81 | 3.1 | 24.0 |

**CHECK MAX. ACCUM. POND STORAGE < 2 FEET** **24.0** in.

NOTES:
APPLIED EFFLUENT = DISPOSAL RATE / (12 MONTHS/YEAR) / POND AREA
MEAN PRECIPITATION DISTRIBUTION = 100 (MEAN MONTHLY PRECIPITATION / MEAN ANNUAL PRECIPITATION)
MAXIMUM MONTHLY PRECIPITATION = MAXIMUM ANNUAL PRECIPITATION X MEAN PRECIPITATION DISTRIBUTION
TOTAL LIQUID TO POND = APPLIED EFFLUENT + MONTHLY PRECIPITATION
MEAN EVAPORATION DISTRIBUTION = 100 (MEAN MONTHLY EVAPORATION / MEAN ANNUAL EVAPORATION)
MINIMUM MONTHLY POND EVAPORATION =
MINIMUM ANNUAL POND EVAPORATION X MEAN EVAPORATION DISTRIBUTION X SALINITY CORRECTION FACTOR
CHANGE IN POND STORAGE = TOTAL LIQUID TO POND - MONTHLY POND EVAPORATION
ACCUMULATED POND STORAGE = ACCUMULATED POND STORAGE FOR MONTH i-1 + CHANGE IN POND STORAGE FOR MONTH i

Table 4-13. Pond water balance for quadrangle 601, representing the Horizon MUD site.

**PRECIPITATION AND EVAPORATION DATA (1980-2004) FROM TWDB** (http://hyper20.twdb.state.tx.us/Evaporation/evap.html)
TEXAS QUADRANGLE NUMBER 601
MAX. ANNUAL PRECIPITATION 19.41 (in.) MIN. ANNUAL EVAPORATION 61.07 (in.)

**POND AREA** 70.50 **acres**
**POND FREEBOARD** 24 **in.**
**DISPOSAL RATE** 0.3 **MGD**
**POND EVAPORATION : LAKE EVAPORATION (SALINITY CORRECTION FACTOR)** 0.9

**AVERAGE CONDITION**

| MONTH | APPLIED EFFLUENT (in.) | MEAN MONTHLY PRECIP. (in.) | TOTAL LIQUID TO POND (in.) | MEAN MONTHLY LAKE EVAP. (in.) | Δ POND STORAGE (in.) | ACCUM. POND STORAGE (in.) |
|---|---|---|---|---|---|---|
| JAN | 4.7 | 0.72 | 5.4 | 2.49 | 2.9 | 2.9 |
| FEB | 4.7 | 0.77 | 5.5 | 3.16 | 2.3 | 5.2 |
| MAR | 4.7 | 0.53 | 5.2 | 5.2 | 0.0 | 5.3 |
| APR | 4.7 | 0.48 | 5.2 | 6.93 | -1.7 | 3.5 |
| MAY | 4.7 | 0.69 | 5.4 | 8.29 | -2.9 | 0.6 |
| JUN | 4.7 | 1.16 | 5.9 | 9.53 | -3.7 | -3.0 |
| JUL | 4.7 | 1.47 | 6.2 | 8.77 | -2.6 | -5.6 |
| AUG | 4.7 | 1.57 | 6.3 | 7.34 | -1.1 | -6.7 |
| SEP | 4.7 | 1.43 | 6.1 | 6.09 | 0.0 | -6.7 |
| OCT | 4.7 | 1.03 | 5.7 | 4.87 | 0.9 | -5.8 |
| NOV | 4.7 | 0.88 | 5.6 | 3.11 | 2.5 | -3.3 |
| DEC | 4.7 | 1.04 | 5.7 | 2.44 | 3.3 | 0.0 |

**CHECK ACCUM. POND STORAGE AT END OF YEAR < 0** **0.0** in.

**CRITICAL CONDITION**

| MONTH | APPLIED EFFLUENT (in.) | MEAN MONTHLY PRECIP. (in.) | MEAN PRECIP. DISTRIB. (%) | MAX. MONTHLY PRECIP. (in.) | TOTAL LIQUID TO POND (in.) | MEAN MONTHLY LAKE EVAP. (in.) | MEAN EVAP. DISTRIB. (%) | MIN. MONTHLY POND EVAP. (in.) | Δ POND STORAGE (in.) | ACCUM. POND STORAGE (in.) |
|---|---|---|---|---|---|---|---|---|---|---|
| JAN | 4.7 | 0.72 | 6% | 1.19 | 5.9 | 2.49 | 4% | 2.01 | 3.9 | 3.9 |
| FEB | 4.7 | 0.77 | 7% | 1.27 | 6.0 | 3.16 | 5% | 2.55 | 3.4 | 7.3 |
| MAR | 4.7 | 0.53 | 5% | 0.87 | 5.6 | 5.2 | 8% | 4.19 | 1.4 | 8.7 |
| APR | 4.7 | 0.48 | 4% | 0.79 | 5.5 | 6.93 | 10% | 5.58 | -0.1 | 8.6 |
| MAY | 4.7 | 0.69 | 6% | 1.14 | 5.8 | 8.29 | 12% | 6.68 | -0.8 | 7.8 |
| JUN | 4.7 | 1.16 | 10% | 1.91 | 6.6 | 9.53 | 14% | 7.68 | -1.1 | 6.7 |
| JUL | 4.7 | 1.47 | 12% | 2.42 | 7.1 | 8.77 | 13% | 7.07 | 0.1 | 6.8 |
| AUG | 4.7 | 1.57 | 13% | 2.59 | 7.3 | 7.34 | 11% | 5.91 | 1.4 | 8.1 |
| SEP | 4.7 | 1.43 | 12% | 2.36 | 7.1 | 6.09 | 9% | 4.91 | 2.2 | 10.3 |
| OCT | 4.7 | 1.03 | 9% | 1.70 | 6.4 | 4.87 | 7% | 3.92 | 2.5 | 12.8 |
| NOV | 4.7 | 0.88 | 7% | 1.45 | 6.2 | 3.11 | 5% | 2.51 | 3.6 | 16.4 |
| DEC | 4.7 | 1.04 | 9% | 1.72 | 6.4 | 2.44 | 4% | 1.97 | 4.5 | 20.9 |

**CHECK MAX. ACCUM. POND STORAGE < 2 FEET** **20.9** in.

NOTES:
APPLIED EFFLUENT = DISPOSAL RATE / (12 MONTHS/YEAR) / POND AREA
MEAN PRECIPITATION DISTRIBUTION = 100 (MEAN MONTHLY PRECIPITATION / MEAN ANNUAL PRECIPITATION)
MAXIMUM MONTHLY PRECIPITATION = MAXIMUM ANNUAL PRECIPITATION X MEAN PRECIPITATION DISTRIBUTION
TOTAL LIQUID TO POND = APPLIED EFFLUENT + MONTHLY PRECIPITATION
MEAN EVAPORATION DISTRIBUTION = 100 (MEAN MONTHLY EVAPORATION / MEAN ANNUAL EVAPORATION)
MINIMUM MONTHLY POND EVAPORATION =
MINIMUM ANNUAL POND EVAPORATION X MEAN EVAPORATION DISTRIBUTION X SALINITY CORRECTION FACTOR
CHANGE IN POND STORAGE = TOTAL LIQUID TO POND - MONTHLY POND EVAPORATION
ACCUMULATED POND STORAGE = ACCUMULATED POND STORAGE FOR MONTH i-1 + CHANGE IN POND STORAGE FOR MONTH i

### 4.4.2 Containment Equivalence

TCEQ provides exemptions from the prescriptive clay liner or geomembrane required for municipal wastewater but only suggested for industrial waste (see regulatory section). Such an alternative liner system that incorporates self-sealing technology must provide equivalent containment capability to the liners prescribed by TCEQ (alternative liner, option 2; see Appendix C).

#### 4.4.2.1 Equivalence to Clay Liner

The prescriptive clay liner must be at least 3-ft thick, with a maximum hydraulic conductivity of $1\times10^{-7}$ cm/s. The leakage rate through the saturated soil liner can be calculated using Darcy's equation: $Q / A = k\ i$, where $Q$ is the leakage rate per pond area $A$, $k$ is the hydraulic conductivity of the clay liner, and $i$ is the hydraulic gradient defined by $i = (h + t)/t$, where $h$ is the average head of liquid in pond and $t$ is thickness of clay liner. For values of $k = 1\times10^{-7}$ cm/s, $h = 1.1$ inch (the average pond depth calculated in Table 4-10 to Table 4-13), and $t = 3$ ft, $i \sim 1$ because $h$ is small relative to $t$, and $Q/A= k\ i = 3.4\times10^{-3}$ inches/day or 1.2 inches/year.

The precipitant generated in evaporation ponds may be hydraulically equivalent to a clay liner if the thin precipitant layer can limit leakage to 1.2 inches/year. Considering that the average accumulation depth of precipitant generated in the evaporation ponds was calculated to be about 0.15 inch after 5 years of pond operation (Table 4-7), the effective hydraulic conductivity of this layer at 5 years would have to be $<1\times10^{-8}$ cm/s to provide equivalent containment capability. It will be difficult for sepiolite, let alone calcite or gypsum, to meet this hydraulic conductivity criterion. Even if the thickness of the precipitant layer is increased by chemical amendment of the outfall waters (Table 4-7), thereby increasing the thickness of the layer to about 0.38 inch, the effective hydraulic conductivity of this layer at 5 years would have to be $<2\times10^{-8}$ cm/s. If the average pond depth is much higher, for example, on the order of 1 ft, as it is permissible in many cases, the equivalent containment capability must also be higher because of the increased head. In this case, the leakage rate with the prescriptive liner is $3.4\times10^{-3}$ inches/day ($i = 1.33$) whereas the effective hydraulic conductivity of the precipitant layer would be $<1\times10^{-9}$ cm/s.

In the above calculations, it is assumed that the hydraulic conductivity of the soil layer will be no greater than $1\times10^{-7}$ cm/s. In reality, a clayey soil exposed to wetting and drying cycles has the potential of developing desiccation cracks. Because of this macrostructure imposed by these cracks, hydraulic conductivity of exposed clay liners has been measured at two or more orders of magnitude higher than that of clay liners prior to exposure. Considering that equilibrium hydraulic conductivity of the exposed clay liner may be on the order of $1\times10^{-5}$ cm/s (despite being $<1\times10^{-7}$ cm/s at end of construction), effective hydraulic conductivity of a precipitant layer at 5 years would have to be $<1\times10^{-6}$ cm/s to provide equivalent containment capability. This value may be achievable for evaporation ponds in Texas (see Section 4.3.2.4). Self-sealing processes could help in mitigating clay liner aging. At a minimum, the precipitant from evaporation ponds can fill cracks that develop in exposed clay liners.

#### 4.4.2.2 Equivalence to Geomembrane Liner with a Leak-Detection System or Groundwater Monitoring System

The prescriptive geomembrane liner is at least 30 mil thick (60 mil if a high density polyethylene geomembrane is used). Unlike clay liners, when a geomembrane is selected as a pond liner, TCEQ requires that the containment capability of the geomembrane liner be monitored by a leak-detection system or groundwater monitoring system. The primary mechanism for leakage through a geomembrane is flow through geomembrane defects (rather than permeation through geomembrane holes) that are inflicted during installation or operation. Leakage through a hole in a geomembrane overlain and underlain by relatively high permeability material can be evaluated using Bernoulli's equation (Giroud and Bonaparte, 1989):

$$Q = 0.6a(2gh)^{0.5}$$

where $Q$ is leakage rate through one geomembrane hole ($m^3/s$), $a$ is the area of the circular hole ($m^2$), $g$ is the acceleration of gravity ($m/s^2$), and $h$ is the hydraulic head on top of the geomembrane liner (m). For values of two to four geomembrane holes per acre, $a = 1.08\times10^{-3}$ $ft^2$, $g = 32.2$ $ft/s^2$, and $h = 1.1$ inch (the average pond depth calculated in Table 4-10 to Table 4-13), the calculated leakage rates range from 27 to 55 inches/year (~14 inches/hole/year). If pond-water depth is higher, the leakage rate is higher too (~45 inches/hole/year with a water depth of 1 ft).

Flow through a geomembrane hole can be impeded if the hole is overlain or underlain by a relatively low permeability material, that is, either a composite geomembrane liner (that goes beyond TCEQ requirements) or a prescriptive geomembrane liner and a precipitant layer. Assuming good contact between the geomembrane and the overlying precipitant, leakage through a geomembrane hole of a precipitant/geomembrane or composite geomembrane liner can be calculated using an equation developed by Giroud (1997):

$$Q = 0.204[1 + 0.1(h/t)^{0.95}]d^{0.2}h^{0.9}k^{0.74}$$

where $Q$ is leakage rate through one geomembrane hole ($m^3/s$), $h$ is the hydraulic head on top of the composite liner (m), $t$ is the thickness of the precipitant component of the composite liner (m), $d$ is the diameter of the circular hole (m), and $k$ is the hydraulic conductivity of the precipitant component of the composite liner (m/s). This equation is not dimensionally homogeneous and must be used with the specified units.

The following input parameters were used in the analysis: $h = 0.028$ m (1.1 inches), $t = 0.0038$ m, $d = 0.011$ m (corresponds to hole area $a = 1.08\times10^{-3}$ $ft^2$), $k = 1\times10^{-6}$ to $1\times10^{-4}$ cm/s, and two to four geomembrane holes per acre. With these input parameters, the calculated leakage rates range from 0.004 to 0.25 inches/year (0.002 and 0.06 inches/hole/year for $k = 1\times10^{-6}$ and $1\times10^{-4}$ cm/s, respectively). For a water depth of 1 foot, calculated leakage becomes 0.08 and 2.4 inches/hole/year, respectively. These rates are low and significantly lower than leakage through the prescriptive clay liner (1.2 inches/year) or the prescriptive geomembrane liner overlain and underlain by relatively high permeability material (Table 4-14).

### 4.4.3 Conclusions on Containment Equivalence

Table 4-14 summarizes the calculations developed in the previous sections on equivalence. A thin precipitant by itself is unlikely to substitute for a clay liner: it may, however, help in allowing a facility from using a reduced clay liner thickness rather than the prescriptive thickness of 3 ft. In the case of a geomembrane liner, the precipitated material could have a large impact in reducing leakage through defects even if its hydraulic conductivity is above that required for a clay liner. It can be seen that a single hole (~1-cm diameter) in a geomembrane will generate a much higher overall leakage rate than that of a prescriptive clay liner. Conversely, an undamaged geomembrane will have no leakage. On the other hand, a defective prescriptive geomembrane liner acting as a composite geomembrane liner, thanks to a layer of precipitant, could behave much better than a prescriptive clay liner.

Table 4-14. Containment equivalence summary

| Equivalent Containment Type | If Minimum Pond Depth (1.1 inch) | If Possible Pond Depth (1 foot) |
|---|---|---|
| Clay liner | ***Rate must be <1.2 inches/yr***<br>— 123 $m^3$/yr/acre<br>= 0.0001 MGD/acre—<br>Translates into a single precipitant layer with $k<1\times10^{-8}$ cm/s | Precipitant $k<1\times10^{-9}$ cm/s |
| Prescriptive geomembrane liner (order of magnitude)<br>3 holes per acre | Rate is 14 inches/yr/hole distributed over 1 acre<br>N/A with precipitant – defective liner<br>— ~4,300 $m^3$/yr/acre<br>= 0.003 MGD/acre— | Rate is 45 inches/yr/hole distributed over 1 acre<br>N/A with precipitant – defective liner<br>— ~13,900 $m^3$/yr/acre<br>= 0.01 MGD/acre — |
| 0.15 inches of precipitant with $k = 1\times10^{-4}$ to $1\times10^{-6}$ cm/s and geomembrane liner<br>(order of magnitude)<br>3 holes per acre | Rate is 0.002 to 0.06 inches/yr/hole distributed over 1 acre<br>— ~0.6 to 18.5 $m^3$/yr/acre<br>= 0.45 to 13.4 gal/D/acre— | Rate is 0.08 to 2.4 inches/yr/hole distributed over 1 acre<br>— ~25 to 740 $m^3$/yr/ acre<br>= 18 to 536 gal/D/acre— |

### 4.4.4 Cost Analysis

Although cost of evaporation pond is highly site specific (e.g., Mickley, 2006, p. 163), the following analysis attempts to determine the financial advantages of having a self-sealing pond. Inspection of the design of a general evaporation pond (see Appendix J) and understanding of the regulatory requirements for self-sealing evaporation ponds led to the conclusion that there is no difference between the facilities infrastructure of a regular pond (either with geomembrane or clay liner) and that of a self-sealing pond. The differences reside mainly in the chemical nature of pond inflow (in particular, chemicals added to the concentrate stream as it leaves the plant but before it enters the pond). Operations should remain the same, with the possible additional cost of chemical additives. Capital (that is, construction) costs could be reduced if some legal requirements, such as those for municipal wastewater ponds (prescriptive clay liner at least 3 ft thick with appropriate flow properties or prescriptive geomembrane of appropriate thickness and leak/groundwater monitoring system), are waived. In this section, we assumed that the self-sealing properties of the evaporating concentrate will let TCEQ authorize the "alternative liner" path (Appendix C). Such a path is permissible if the permittee can show that concentrate is no worse than the first occurrence of the local groundwater (option 1) or if the permittee can demonstrate equivalent protective measures (option 2) or if the permittee will monitor the groundwater below the pond for the lifetime of the facility (and will clean it up if problems arise—option 3). Examples of such cost-saving measures are

- thinner geomembrane (less thick than the required 30 mil—for most materials—required for municipal wastewater),
- no leak-detection system or groundwater monitoring system if a geomembrane is used, and

- two or three clay lifts (9 inches thick each) instead of the four lifts (that is, 3 ft) generally required for constructed clay liners.

Order of magnitude capital costs can be found in Mickley (2006) and, when not provided in Mickley's document, are complemented by standard costs as practiced in the industry. The general capital cost of an evaporation pond is mostly a function of its size (area and depth). As displayed in Table 4-9, area varies as a function of net evaporation rate. Mickley (2006, p. 162) suggested pond depths ranging from 1 to 18 inches, to which a minimum freeboard (heavy precipitation and wave action combined) of 24 inches should be added (Mickley, 2006, p. 163). Major contributing costs are land, earthwork, lining, possibly monitoring system installation, and miscellaneous costs (access roads, fences, etc.).

Operational costs for conventional and self-sealing ponds are essentially the same. However, cost of additives (Section 4.3.2.5), not included in the discussion on capital costs, could be prohibitive. Land and earthwork costs are not significantly different for conventional and self-sealing ponds. The most gain can be made by doing away in full or in part with liners and/or leak-detection systems. Additional costs may be incurred by disposal of pond residuals if they are classified as hazardous material (heavy metals, arsenic). This possibility, however, seems remote (see Appendix I). Engineered self-sealing ponds, with their additional material, result in a thicker layer of bottom sediments and, thus, a reduced toxicity, which could be at a slight advantage. However, most residuals will be accepted by regular landfills, and cost differentials related to such an issue are not relevant in the high-level analysis presented in this section.

Mickley (2006, p. 171) proposed the rule of thumb of \$0.01/mil thickness /ft$^2$, that is, ~\$0.30/ft$^2$ or ~\$13,000/acre for a 30-mil geomembrane. Mickley (2006, p. 183) also proposed a simplified regression model, mostly valid from 10 to 100 acres, to estimate capital costs of an evaporation pond (no seepage monitoring included):

$$\$Cost = CI \times S \times \left(5406 + 465 \times mil + 1.07 \times LC + 0.931 \times LCC + 217.5 \times DH\right) \times \alpha$$

$$\text{with } \alpha = \left(1 + 0.155 \times DH \times S^{-1/2}\right)$$

where *S* is the pond surface area in acres, *mil* is the geomembrane thickness in mils, *LC* is the land cost per acre, *LCC* is the land clearing cost per acre, *DH* is the dike height in feet (includes excavation costs), and *CI* is the contingency factor. We set land cost at \$0, and clearing costs at a minimum of \$1,000/acre. Dyke height is taken as 8 ft. The cost can then be written as:

$\$Cost = CI \times S \times \left(8077 + 465 \times mil\right) \times \left(1 + 1.24 \times S^{-1/2}\right)$, that is, for a 125 acre pond the cost per acre is at most:

$$\$Cost/acre = 1.11 \times CI \times \left(8077 + 465 \times mil\right)$$

Focusing on the geomembrane itself and not on the other capital costs that need to be incurred anyway in all cases ("8077" for construction costs and $1.11 \times CI$ for facilities and access construction), the geomembrane cost reverts to the ~0.01/mil thickness /ft$^2$.

It can then be determined that the percentage of the liner cost is about two-thirds the total cost:

$$\%Cost = \frac{465 \times mil}{8077 + 465 \times mil} = \frac{mil}{17.4 + mil} = \frac{30}{17.4 + 30} = 63\%$$

It follows that, in the described conditions, a 30-mil membrane will cost about two thirds of the capital costs.

The cost to supply and install a state-of-the-art geocomposite (that is, with an additional layer of high-permeability granular material) leak detection system can be estimated at $\$0.75/ft^2$ (Duffy, 2005) or $33,000/acre. A more adhoc system, for example a sloping surface just beneath the geomembrane leading to a sump, would cost much less. It can be estimated at a maximum of $\$0.20/ft^2$ or $8,500/acre. The cost to construct a clay liner with suitable soil excavated from the site can be estimated as $\$10/yd^3$ (Duffy, 2005), that is, $\$1.11/ft^2$ or $48,400/acre for a 3-foot thick clay liner or $12,000/acre for each 9-inch lift.

Table 4-15 illustrates that costs of prescriptive clay or geomembrane liners are approximately equivalent (this, however, may not be true for some specific cases). With the values provided above, estimated costs to construct the prescriptive liners are:

- 3-foot thick clay liner: $48,000/acre; and
- 30-mil thick geomembrane liner with geocomposite leak detection system: $46,000/acre.

After adding other costs (land clearing, excavation, construction, etc), the approximate total capital cost applicable to both liner types is $54,000/acre. As explained above, liner construction costs could be reduced for self-sealing ponds if certain regulatory requirements for liners are waived. Examples of such waivers are:

- use of a 2-foot thick clay liner rather than a 3-foot thick clay liner, which results in an estimated savings of $16,000/acre;
- use of a geomembrane liner with a simple leak detection system, which results in an estimated savings of $33,000 - $8,500 = $24,500/acre;
- use of a geomembrane liner without a leak detection system, which results in an estimated savings of $33,000/acre;
- use of a 40-mil thick HDPE geomembrane rather than a 60-mil thick HDPE geomembrane, which results in an estimated savings of $8,700/acre; and
- use of an excavation utilizing the natural soil as a liner with no other work required as suggested by Appendix C (alternative Liner, Option 2). Savings are approximately 90% of the capital cost of a prescriptive liner.

The key requirement for all these waivers is the containment equivalence as detailed in Section 4.4.2.

Table 4-15. Summary of approximate costs and cost savings features for generic evaporation ponds

| | **Approximate Cost/(Saving) per Acre** | **Percentage Saved Relative to Prescriptive Liner** |
|---|---|---|
| **Cost independent of liner type** | | |
| Land cost | $0 | |
| Land clearing, excavation, construction | $8,000 | |
| | | |
| **Cost specific to prescriptive liners** | | |
| Prescriptive clay liner | | |
| 3-ft-thick liner | $48,000 | |
| Prescriptive geomembrane | | |
| 30-mil-thick geomembrane | $13,000 | |
| Leak-detection system | $32,700 | |
| | | |
| **TOTAL prescriptive liner (regardless of the type)** | **~$54,000** | **0%** |
| | | |
| **Alternative approaches** | | |
| 2-ft-thick clay liner | ($16,000) | 30% |
| 20-mil-thick geomembrane | ($9,000) | 17% |
| 30-mil-thick geomembrane and *simple* leak detection system | ($33,000 - $8,500) | 46% |
| 30-mil-thick geomembrane and *no* leak detection system | ($33,000) | 61% |
| Alternative liner, option 1 (Appendix C) | ($48,000) | 89% |
| Alternative liner, option 2 (Appendix C) | ($48,000) | 89% |

# 5 Conclusions, Recommendations, and Future Work

In this section, we summarize conclusions on both the regulatory and technical feasibility of self-sealing evaporation ponds. No significant regulatory barriers exist to prevent approval of self-sealing evaporation pond-liner technologies at desalination facilities in Texas. The permitting of an evaporation pond is strictly a State issue and TCEQ has considerable latitude for approving alternative permit requirements. Rules for municipal wastewater treatment are used as guides for the evaluation of industrial permits but do not impose strict regulatory requirements. Currently approved pond liners include a 3-foot-thick layer of in situ clay or compacted clay or a geomembrane liner (PVC, HDPE, butyl rubber, polypropyle, etc.) of 30 mils (0.76 mm) or more having leak-detection monitoring. An alternative liner may be approved by TCEQ if it can be demonstrated to achieve and maintain *equivalent containment* to the prescriptive liners and the resulting liner material(s) will not deteriorate because of reactivity with salinity or other compounds in the effluent stream or other ambient conditions. The geochemical analysis performed in this work suggested that at most a few inches (but typically <1 inch) of material precipitates at the bottom of the pond after 5 years of operation. Simple engineering of the system may control the nature of the precipitate and increase its amount. For example, in this work we looked at sepiolite, a clay mineral that does not share with other clay minerals the usual properties of volume change under changing conditions. Other common minerals are calcite and gypsum, as observed both in field sampling and in geochemical simulations. This study did not perform hydraulic conductivity analyses but other investigators have been unable to this point to demonstrate that the precipitant can achieve the prescribed maximum conductivity value of $10^{-7}$ cm/s.

Technical feasibility is closely associated with cost. The evaporation pond coupled with a generic 1-MGD desalination facility has an average surface area of approximately 5 acres. A rough estimation of capital costs associated with the construction of the pond yields ~$50,000/acre, not accounting for land purchase. This preliminary stage of the research does not suggest that a cost-effective self-sealing process could be implemented right away at any evaporation pond. The amount of material that can be engineered to precipitate is too small and of uncertain, but likely too high, hydraulic properties. This conclusion applies particularly to clay liners.

The regulation section of this study showed that the practical way to make use of self-sealing properties is to exercise option to demonstrate that the alternative liner will achieve equivalent containment. The greatest cost savings seem to be associated with obtaining a waiver for leak detection / groundwater monitoring systems that generally accompany a geomembrane liner. Our analysis suggests that the precipitant, even with a hydraulic conductivity $>1\times10^{-7}$ cm/s could efficiently plug holes and defects of the geomembrane. This plugging ability, however, needs to be confirmed by experiments and pilot tests. On the other hand, equivalent containment can be achieved for clay liners mostly by sheer accumulation of the precipitated material at the bottom of the pond. The modest thickness of at most a few inches of precipitant after a few years of operations suggests that the precipitated material needs to have a hydraulic conductivity much lower than $1\times10^{-7}$ cm/s to impart the required properties to a scaled-down liner and to be substituted successfully for part or all of the clay liner.

An immediate benefit of self-sealing properties could be increased confidence in permitting an evaporation pond constructed to municipal wastewater standards and located in an environmentally sensitive area (such as above a shallow groundwater source of potable water). However, self sealing technology does not seem able to create the sought-after repair effect at a cost smaller than traditional techniques in these sensitive areas. At the opposite end of the environmental spectrum, if the effluent is nonhazardous and local groundwater quality poor, a self-forming single liner may be appropriately constructed by, for example, forcing precipitation of sepiolite through an initially high loading of sepiolite precursors onto a natural clayey or silty soil. In this work, we focused on precipitation of sepiolite clay because it is one of the simplest and most robust approaches, but many other possibilities of treatment and operational design could be investigated. The crux of the problem truly lies in cost rather than engineering difficulties.

Possible items for future studies include

- Investigation of minerals other than sepiolite—specifically the most abundant minerals, calcite and gypsum, whose grain size can be engineered through additives. In particular, investigation on how to precipitate calcite in particles as small as possible to reduce porosity and permeability of a clay liner.
- Investigation of the interactions between engineered self-sealing minerals and clay minerals because most evaporation ponds in Texas are lined with clay. Precipitant is mixed with airborne dust, decaying plant matter, and other debris. Physical and chemical interactions at the interface clay liner–bottom sediment may generate under some conditions hydraulic conductivity low enough to apply for an alternative liner waiver under "equivalent containment."
- Investigation of the behavior of the precipitant next to a geomembrane defect/hole: will the precipitant be mechanically entrained into the hole because of increased flux; will precipitation be favored inside and next to a hole because of an increase in chemical action?
- Study of the impact of regulated trace elements (e.g., arsenic) on this report's conclusions.
- A better understanding of evaporation pond processes, especially those with clay liners, in which chemical interactions between liner and concentrated evaporation pond solution are relevant to self-sealing mechanisms and pore plugging. A necessary step of this additional study includes field sampling. Natural saline lakes have been studied and sampled but no equivalent fundamental studies exist on Texas evaporation ponds.
- Study of the impact of temperature on mineral precipitation kinetics and of the impact of seasonal temperature variations.
- Study of the impact of biomass, both at the bottom of the pond, where reducing conditions may exist, and at the surface, where microorganisms such as diatoms may mobilize most of the silica. Evaporation ponds do not seem to reach salinity levels at which life is not sustainable. Such microorganisms may also mediate the precipitation of useful minerals.

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# 7 Appendix List

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# 8 Appendix A: Groundwater and Surface-Water Sample Locations and Piper Plots

This appendix describes in detail the geochemical nature of groundwater and surface-water potential candidates for feedwater of desalination facilities. It should be noted that the geochemical nature of the brackish samples does not necessarily represent that of the fresh-water samples of the same aquifers. One can consult the water quality section of the relevant GAM models for a better picture of the geochemistry of a given aquifer as a whole ([http://www.twdb.state.tx.us/gam/index.htm](http://www.twdb.state.tx.us/gam/index.htm) ). TDS distribution (Figure 8-1) illustrates the preeminence in the sampling of low-TDS brackish waters and does not necessarily give an accurate depiction of the TDS distribution of all brackish water in the 1,000- to 5,000-ppm range. Brackish water is distributed all across the state (Figure 8-2). A previous TWDB-sponsored report investigates the availability of brackish water across the state (LBG-Guyton Associates, 2003). The workers focused on TDS and did not provide a detailed geochemistry analysis.

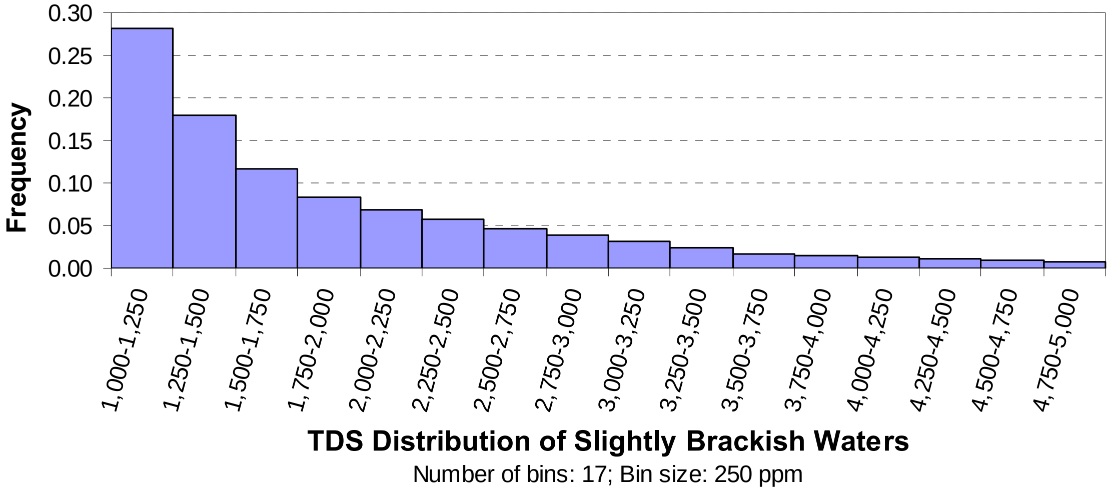


Figure 8-1. TDS distribution of slightly brackish waters

A piper plot provides a visual aid to understanding and comparing different water samples. It consists of two trilinear triangles and a diamond. The triangle on the left shows distribution of the cations (calcium, magnesium, and sodium and potassium). The closer a sample is to an apex, the more prevalent the cation is in the water chemistry. A sample plotting at the exact middle of the triangle will have, on a molar basis, the same amount of calcium, magnesium, and sodium and potassium. A similar explanation holds for the anion triangle of the right-hand side, which maps bicarbonate, sulfate, and chloride. Water samples are sometimes described by how they plot on a Piper plot (e.g., sodium bicarbonate sulfate water). TDS is not captured in a Piper plot; only relative ion abundance is shown. A neutral species of interest to this study (silica - $SiO_2$) is not part of a Piper plot. Also, pH values, that, often times, control precipitation rates and mineral stability domains are not captured by a Piper plot either, although bicarbonate relative abundance may, in some instances, suggest it. The diamond helps in understanding the water sample as a whole and, especially, changes from one sample to the next (e.g., along a flow line from a calcium bicarbonate chemistry at the surface to a sodium chloride chemistry at depth).

Because of the large number of chemical samples to potentially analyze (>13,000), it is important to characterize each of the 20 groups by a small number of samples. The different groups can be, at minimum, characterized by some central values and a measure of the deviation from them. A simplistic approach to obtaining an average sample would be to compute the average of each ion and to assume that the composite sample is representative. However, such a composite sample is unlikely to be charge balanced, nor can it be used in geochemical calculations (e.g., Bethke, 1996, p. 85). A better approach is to determine which actual sample from the data set is the closest in some sense to the composite sample. Such a measure is $MS1_s$, and for any sample s could be defined by

$$MS1_{\mathrm{s}} = \left[ \sum_{i=1}^{n} \alpha_i \left( C_{i,perc} - C_{s,i} \right)^2 \right]^{1/2}$$

where $\alpha_i$ is a weighing factor for each ion *i* (usually taken as equal to 1), *n* is the number of ions considered (generally eight: $SiO_2$, Ca, Mg, Na, K, $HCO_3$, $SO_4$ and Cl), and $C_{s,i}$ is the *molar* concentration of ion *i* for sample *s*. $C_{i,perc}$ represents some chosen *molar* concentration percentile for ion *i*. For example, the sample best representing the central value of a data (sub)set would have the smallest measure $MS_s$ when the percentile is 0.5 (that is, the median) for all ions. A fuller characterization of the data set would also include points located at some distance from the central value in the eight-dimension space of the major ions, for example, with percentile 0.25 and 0.75. In a 3D example with ion A, B, and C, the central value would be the sample closest to the medians of the three ions (A=0.5, B=0.5, C=0.5). A better description of the data set would also include the 25th and 75th percentiles, with the actual samples closest to (A=0.75, B=0.75, C=0.75), (A=0.25, B=0.75, C=0.75), (A=0.75, B=0.25, C=0.75), (A=0.75, B=0.75, C=0.25), (A=0.25, B=0.25, C=0.75), (A=0.25, B=0.75, C=0.25), (A=0.75, B=0.25, C=0.25), (A=0.25, B=0.25, C=0.25), that is a total of eight samples (representing the apexes of a cube in three dimensions). This number also represents the number of permutations with order of three trials with two outcomes or $2^3$. An eight-dimension cube would still be characterized by a large number of samples ($2^8 = 256$ samples). A compromise can be found by using 5 (that is, 32 samples at most) parameters: $SiO_2$, Mg, Ca+Na+K, $HCO_3$, and $SO_4$. Chloride is conservative and is a dependant variable that can be approximately backcalculated using the charge balance equation. Samples best representing the central value of each group are given in Table 8-1.

The measure $MS1_s$ is implicitly weighted by the ion abundance. To give equal weight to all ions, a second measure $MS2_s$ can be defined by

$$MS2_{\mathrm{s}} = \left[ \sum_{i=1}^{n} \left( \frac{C_{i,perc} - C_{s,i}}{C_{i,perc}} \right)^2 \right]^{1/2} \text{, that is, } \alpha_i = \left( \frac{1}{C_{i,perc}} \right)^2$$

The measure $MS_s$ by which each sample is gaged relative to the median sample and other group percentile is

$$MS_{\mathrm{s}} = \mathrm{rank}(MS1_{\mathrm{s}}) + \mathrm{rank}(MS2_{\mathrm{s}})$$

where “rank” represents the rank of the sample when sorted in ascending measure value.

Sepiolite precipitation requires high magnesium and alkaline pH, so samples located near the upper apex of the cation triangle and the lower left-hand side of the anion apex are favored. Figure 8-2 expectedly demonstrates that water chemistry is dominated by sodium and/or calcium, with some magnesium with bicarbonate, sulfate, and chloride present in any proportions.

Table 8-1. Samples best representing the central value of each group (units are ppm)

| Group Name | Figure# | $SiO_2$ | Ca | Mg | Na | K | $HCO_3$ | $SO_4$ | Cl | pH | TDS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mixed Alluvium | Figure 8-3 | 22 | 166 | 64 | 258 | 1.0 | 344 | 353 | 376 | 7.5 | 1,673 |
| Brazos River Alluvium | Figure 8-4 | 20 | 146 | 43 | 133 | N/A | 620 | 122 | 138 | 6.6 | 1,229 |
| Rio Grande Alluvium | Figure 8-4 | 33 | 182 | 37 | 321 | N/A | 410 | 497 | 347 | 7.9 | 1,836 |
| Seymour | Figure 8-5 | 28 | 123 | 51 | 215 | N/A | 389 | 232 | 261 | 7.9 | 1,361 |
| Bolson | Figure 8-6 | 34 | 67.7 | 20.3 | 297 | 10.9 | 137 | 210 | 396 | 7.7 | 1,190 |
| Ogallala | Figure 8-7 | 54 | 89 | 88 | 189 | 14.0 | 245 | 348 | 295 | 8.4 | 1,346 |
| Pecos Valley | Figure 8-8 | 30 | 277 | 86 | 351 | 17 | 220 | 730 | 650 | 7.4 | 2,370 |
| Gulf Coast Sandstone | Figure 8-9 | 22 | 47 | 22 | 383 | 10.8 | 339 | 131 | 431 | 7.2 | 1,423 |
| Eocene All samples | Figure 8-10 | 12 | 24 | 14 | 376 | 5.0 | 264 | 273 | 313 | 8.3 | 1,289 |
| Eocene Mixed | | 34 | 150 | 47 | 290 | 2.9 | 329 | 490 | 330 | 6.5 | 1,680 |
| Eocene Na dominant | | 19 | 4.5 | 1 | 446 | N/A | 444 | 200 | 290 | 8.2 | 1,415 |
| Cretaceous Limestone | Figure 8-11 | 17 | 136 | 60 | 232 | 0.6 | 315 | 493 | 237 | 8.0 | 1,502 |
| Cret. Sandst. All samples | Figure 8-12 | 14 | 74 | 21 | 271 | 4.0 | 371 | 288 | 185 | 8.3 | 1,242 |
| Cret. Sandst. Mixed | | 13 | 167 | 58 | 166 | N/A | 277 | 433 | 208 | 7.3 | 1,369 |
| Cret. Sandst. Na dominant | | 11 | 4.4 | 2.4 | 411 | 2.1 | 510 | 236 | 143 | 7.9 | 1,330 |
| Triassic Sandstone | Figure 8-13 | 12 | 110 | 53 | 281 | 11 | 290 | 410 | 277 | 7.0 | 1,508 |
| Permian Evaporite | Figure 8-14 | 16 | 590 | 127 | 99 | N/A | 196 | 1810 | 92 | 7.4 | 2,940 |
| Permian Limestone | Figure 8-15 | 17 | 159 | 56 | 250 | N/A | 377 | 262 | 324 | 7.4 | 1,623 |
| Permian Sandstone | Figure 8-16 | 21 | 130 | 94 | 227 | N/A | 414 | 391 | 302 | 7.6 | 1,628 |
| Bone Spring – Victorio Peak | Figure 8-17 | 18 | 439 | 171 | 305 | 16.0 | 272 | 1,481 | 519 | 6.8 | 3,250 |
| Capitan Reef | Figure 8-17 | 17 | 152 | 79 | 92 | N/A | 276 | 439 | 133 | 7.4 | 1,198 |
| Pennsylvanian | Figure 8-18 | 11 | 69 | 30 | 348 | N/A | 405 | 181 | 355 | 7.5 | 1,417 |
| Llano Uplift | Figure 8-19 | 11 | 112 | 39 | 190 | 8.0 | 358 | 15 | 388 | 7.7 | 1,130 |
| | | | | | | | | | | | |
| Surface Water | Figure 8-20 | 9.8 | 250 | 86 | 590 | 8.0 | 195 | 800 | 940 | 8.0 | 2,341 |

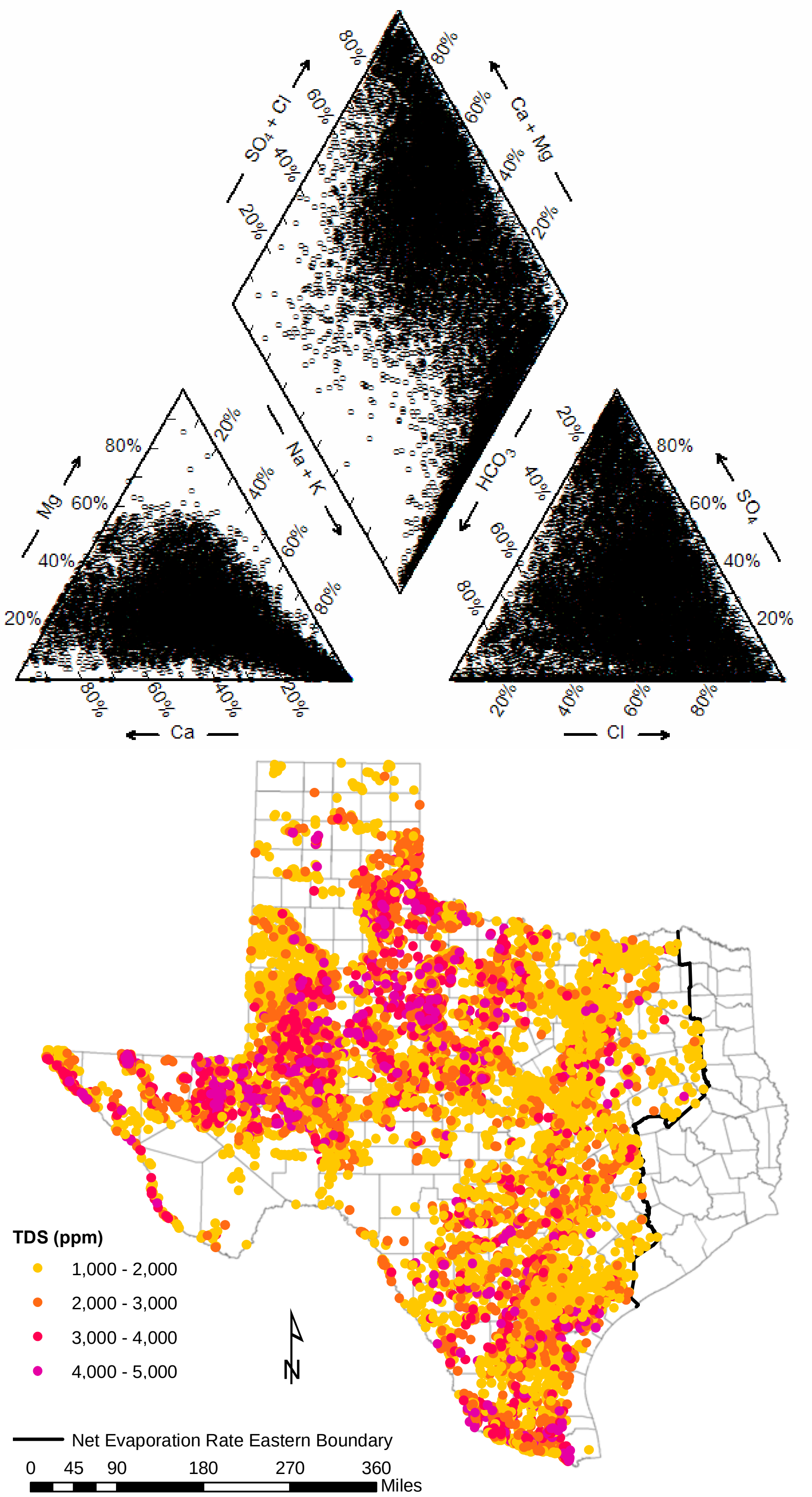


Figure 8-2. Map and Piper plot of all groundwater samples on map of Figure 3-1

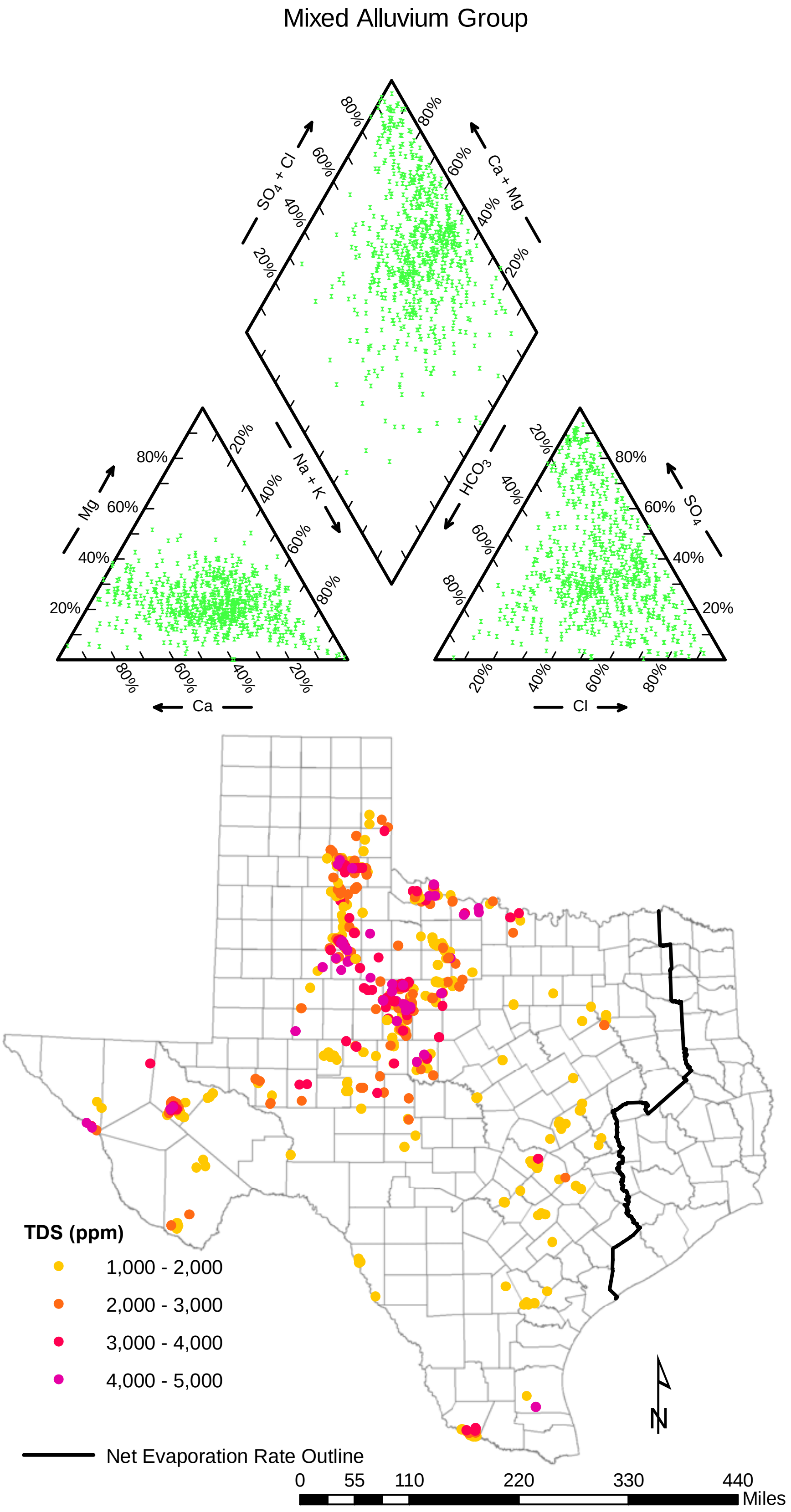
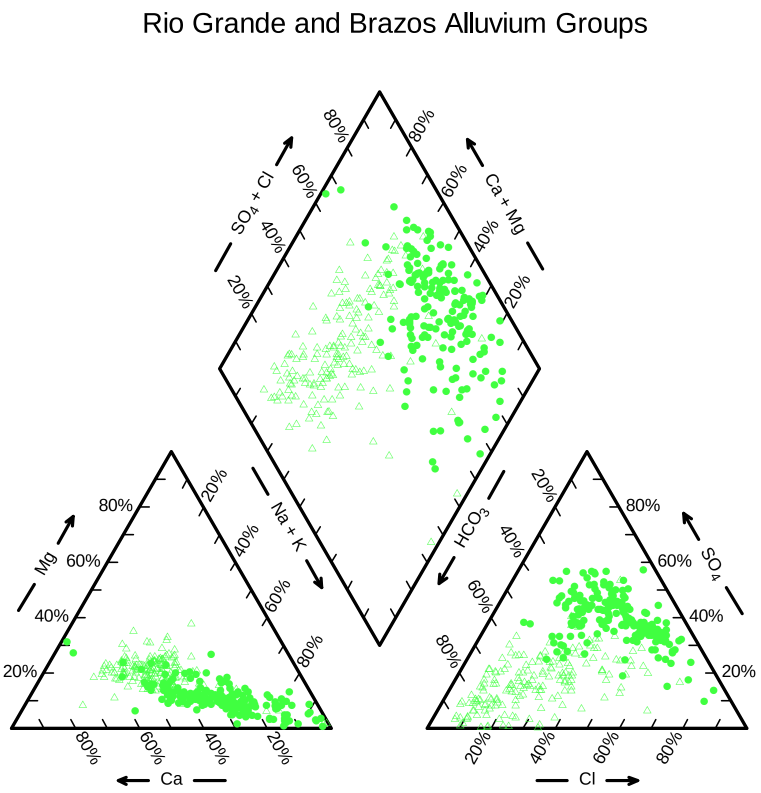


Figure 8-3. Map and Piper plot of Mixed Alluvium group



Note: Empty triangles = Brazos and filled circles = Rio Grande

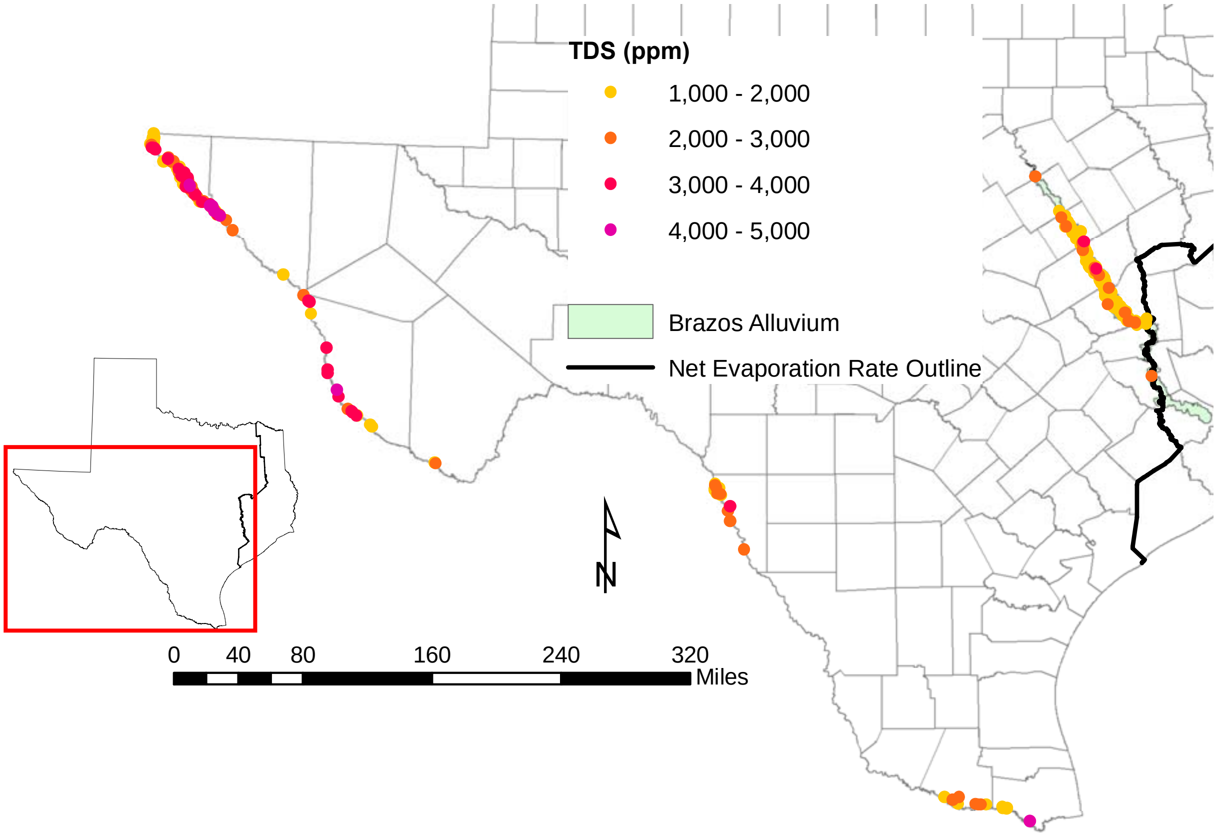


Figure 8-4. Map and Piper plot of Rio Grande and Brazos Alluvium groups

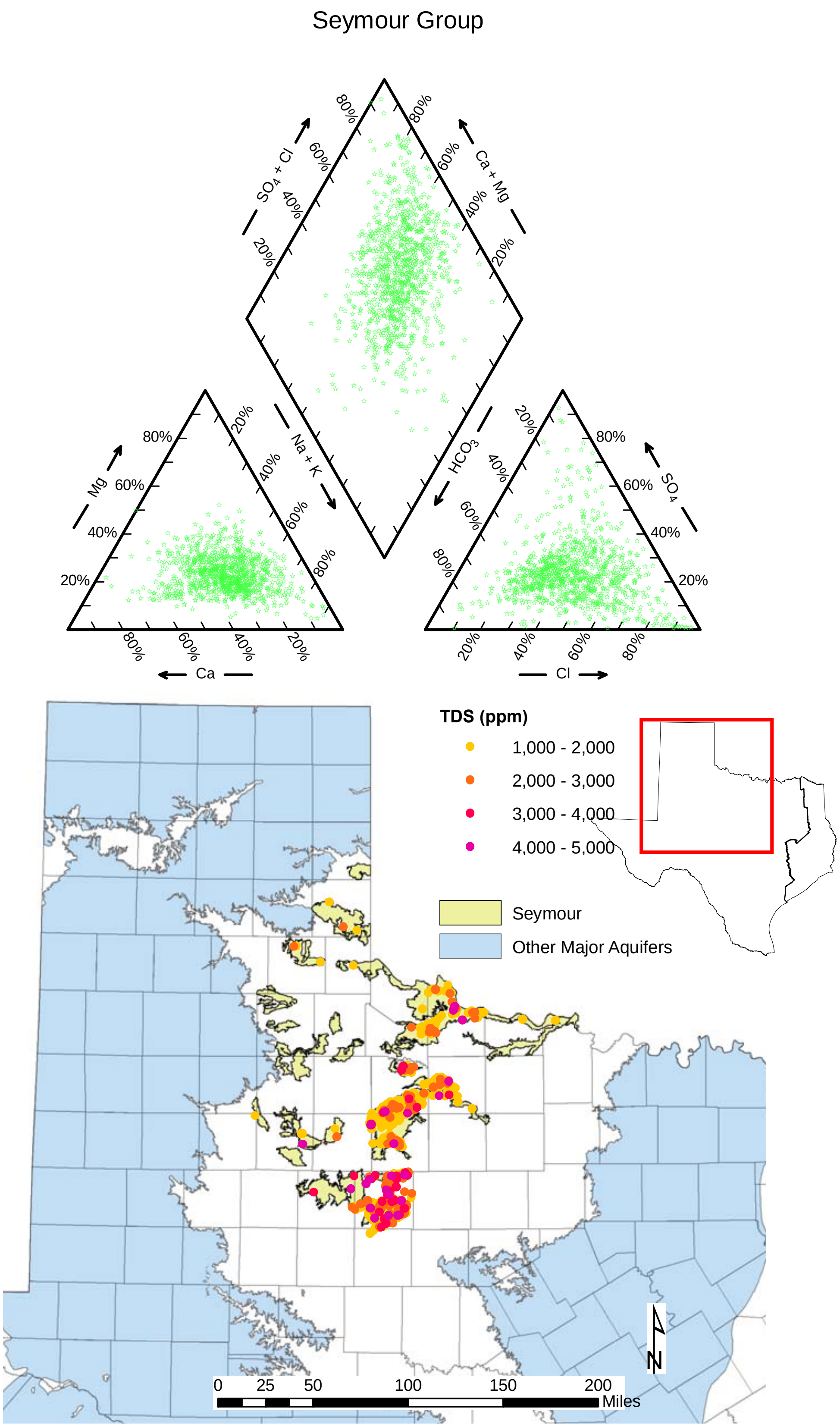


Figure 8-5. Map and Piper plot of Seymour group

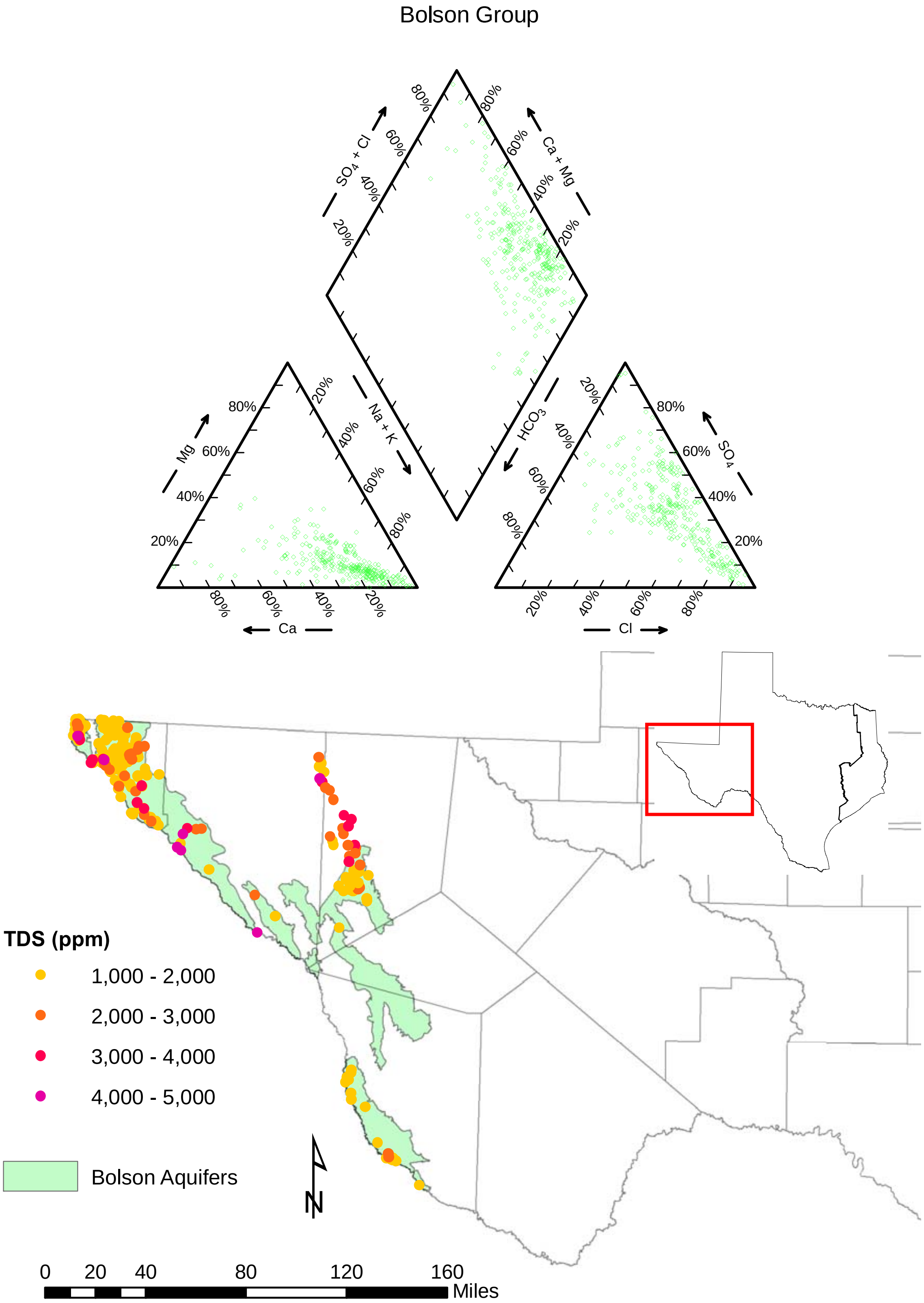


Figure 8-6. Map and Piper plot of Bolson group

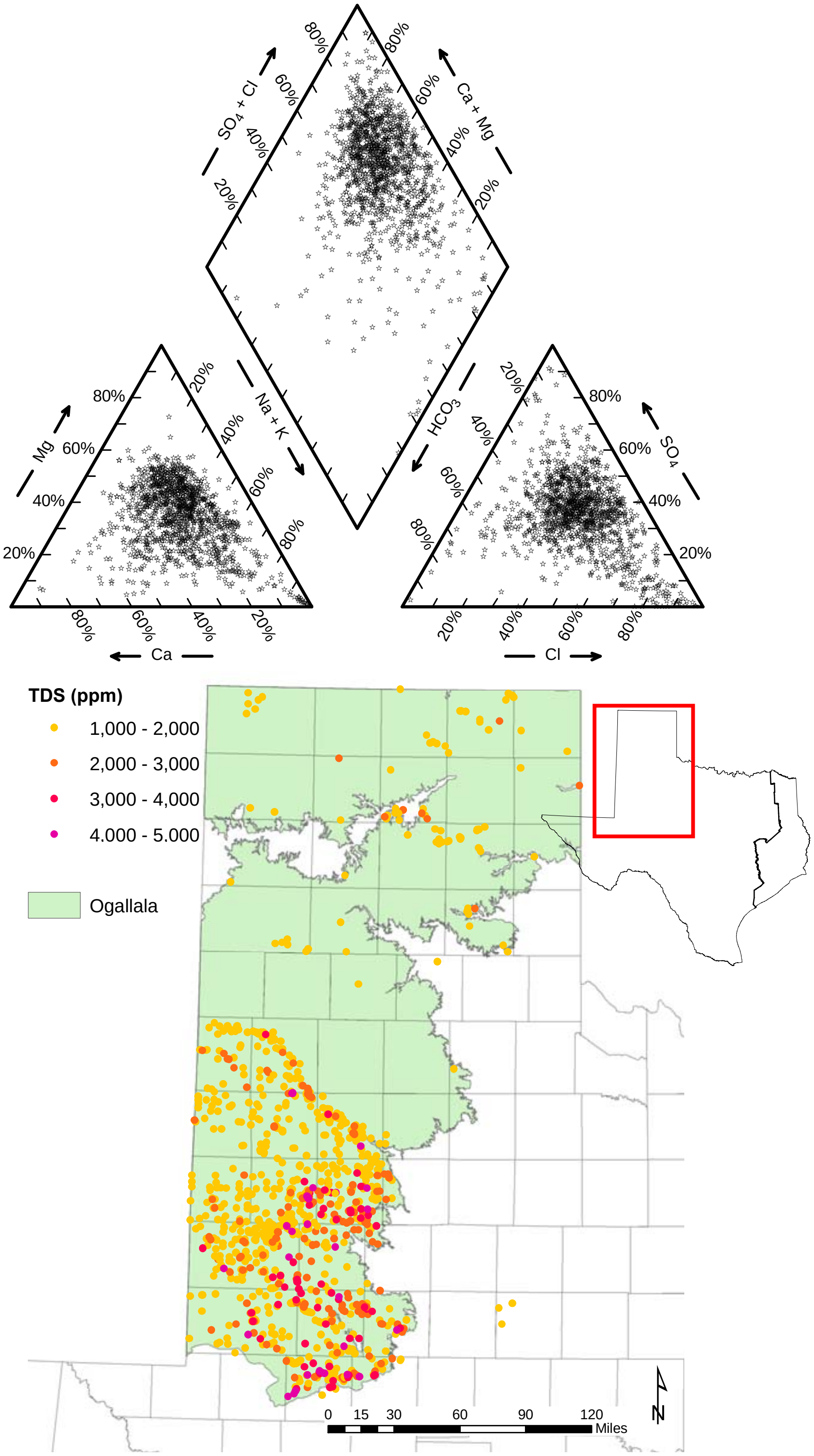


Figure 8-7. Map and Piper plot of Ogallala group

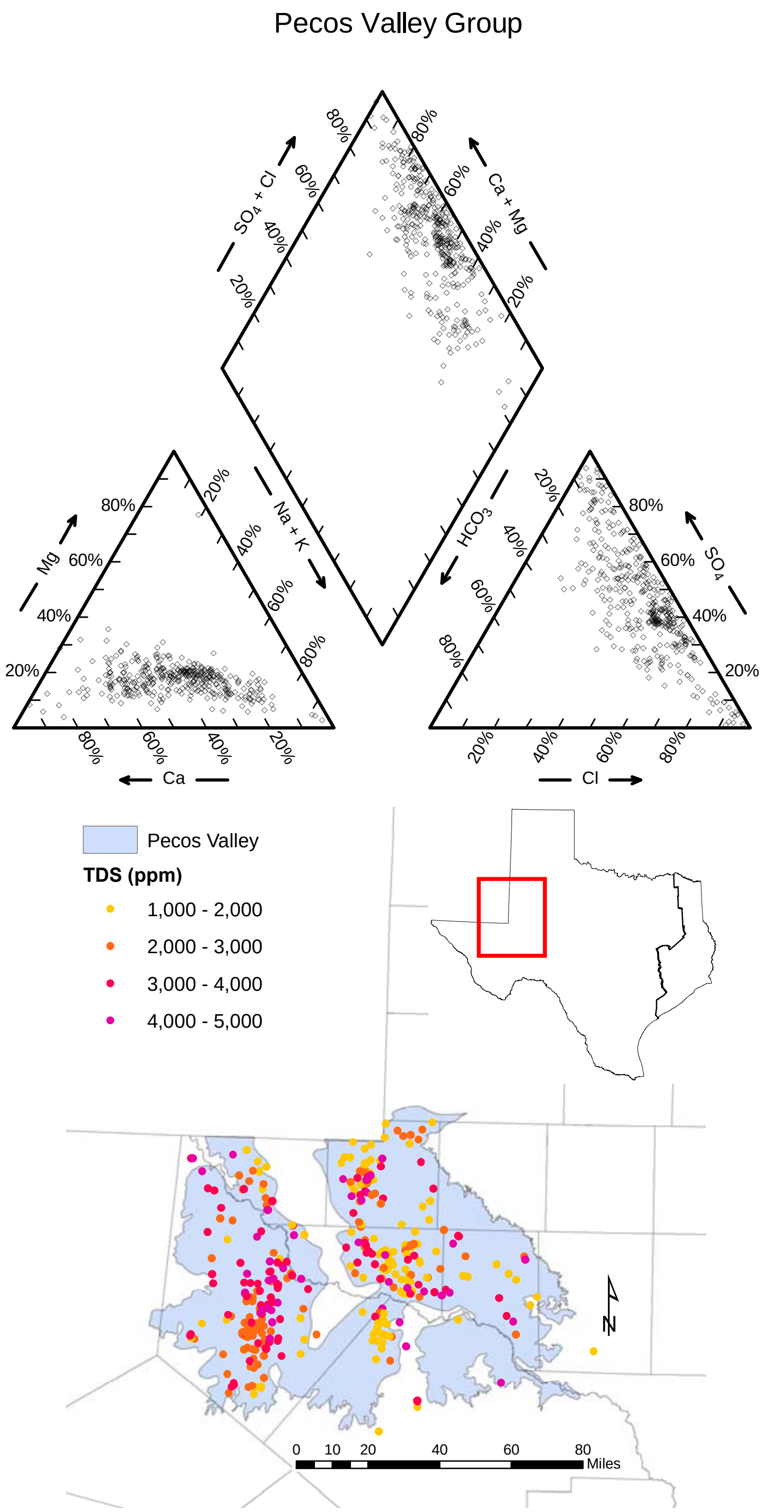


Figure 8-8. Map and Piper plot of Pecos Valley group

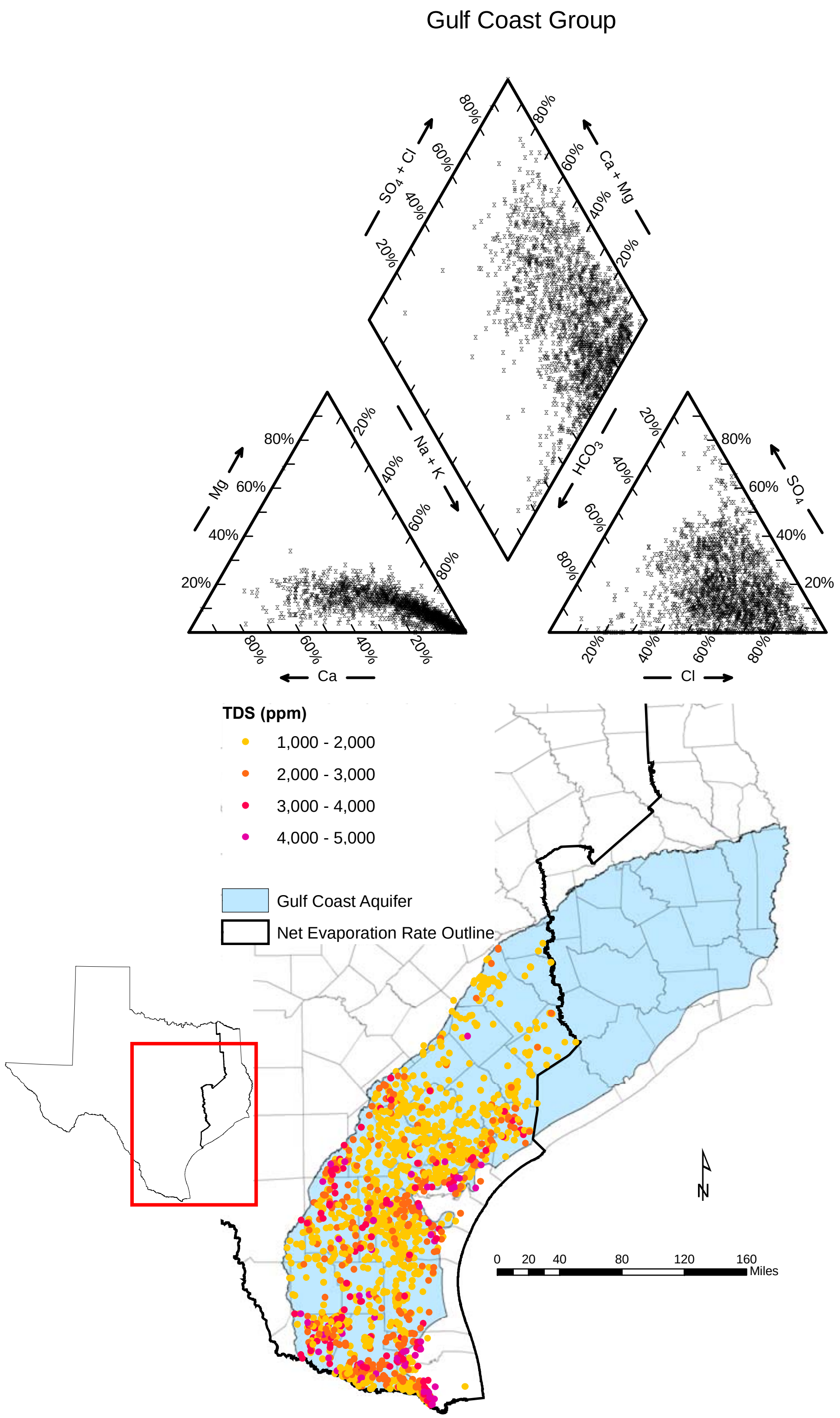

Gulf Coast Group

Figure 8-9. Map and Piper plot of Gulf Coast group

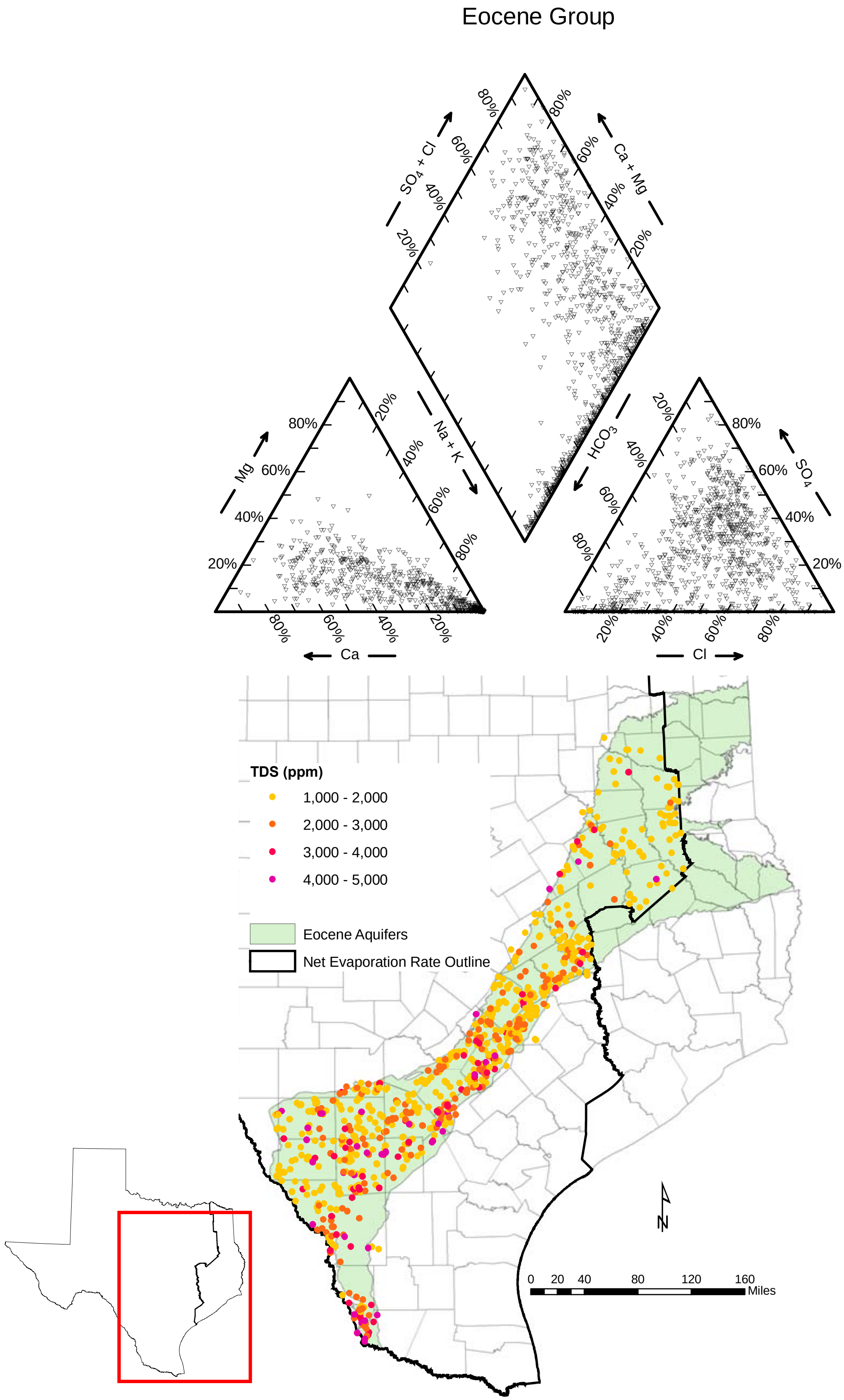


Figure 8-10. Map and Piper plot of Eocene group

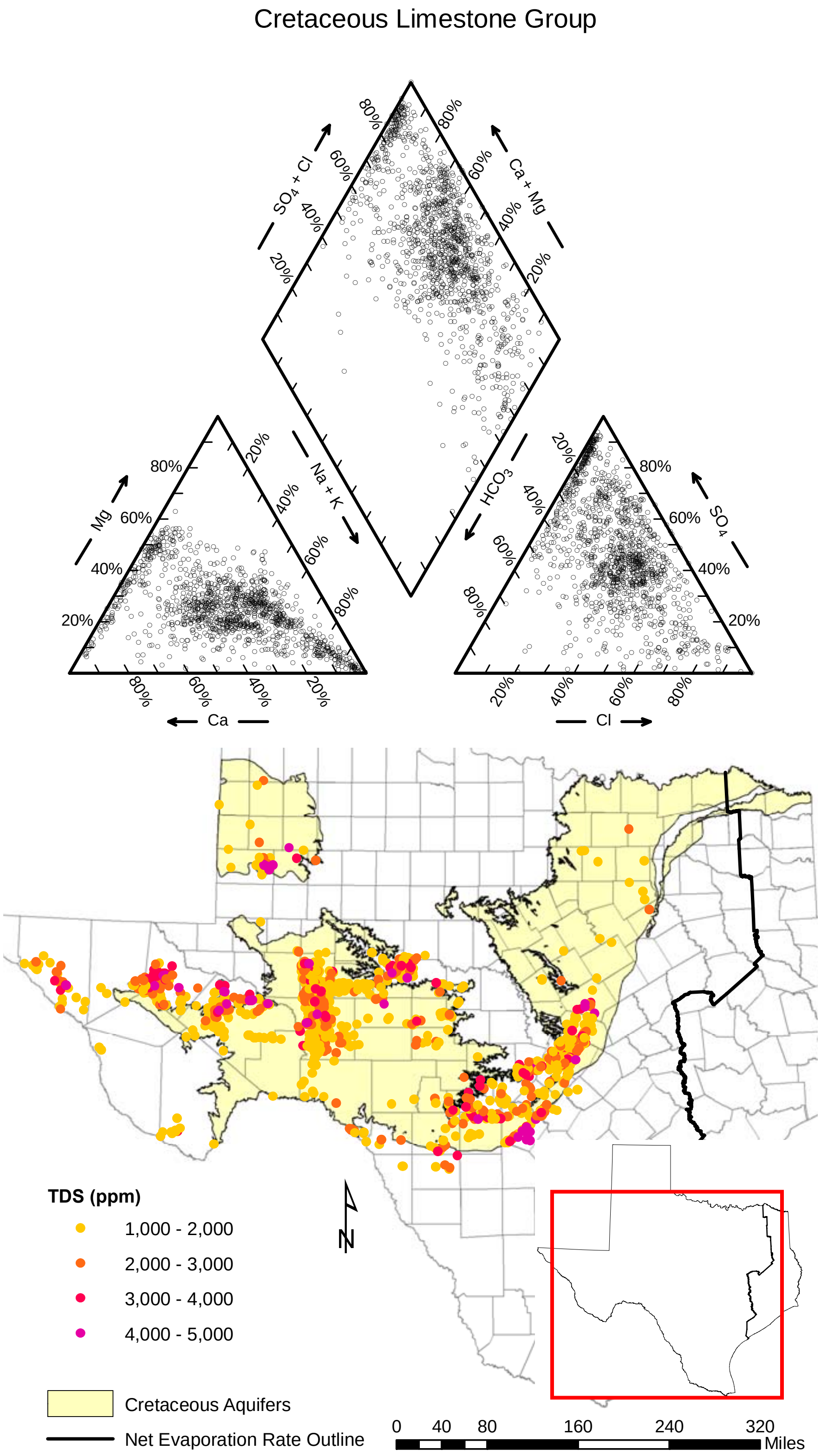


Figure 8-11. Map and Piper plot of Cretaceous Limestone group

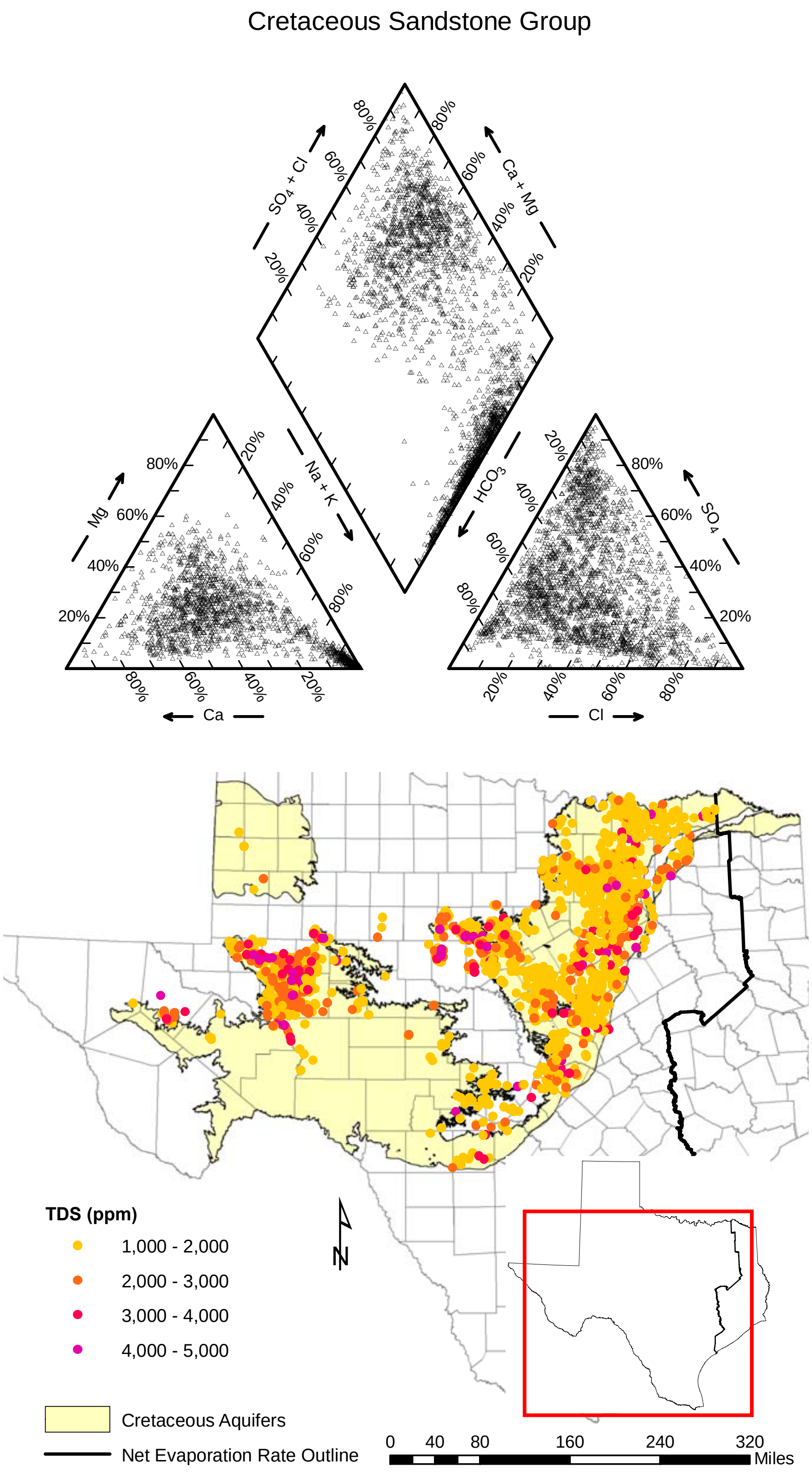


Figure 8-12. Map and Piper plot of Cretaceous Sandstone group

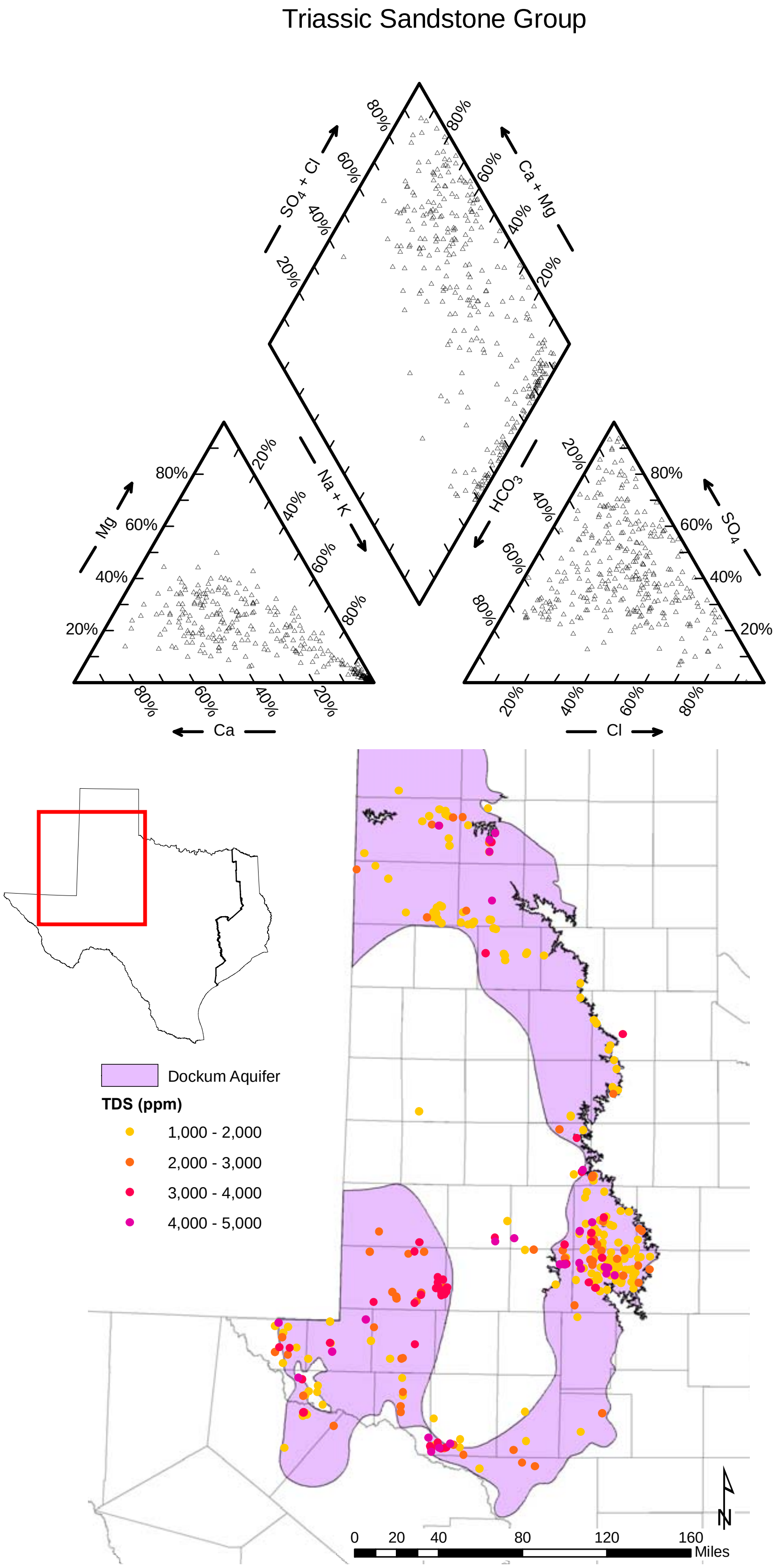


Figure 8-13. Map and Piper plot of Triassic Sandstone group

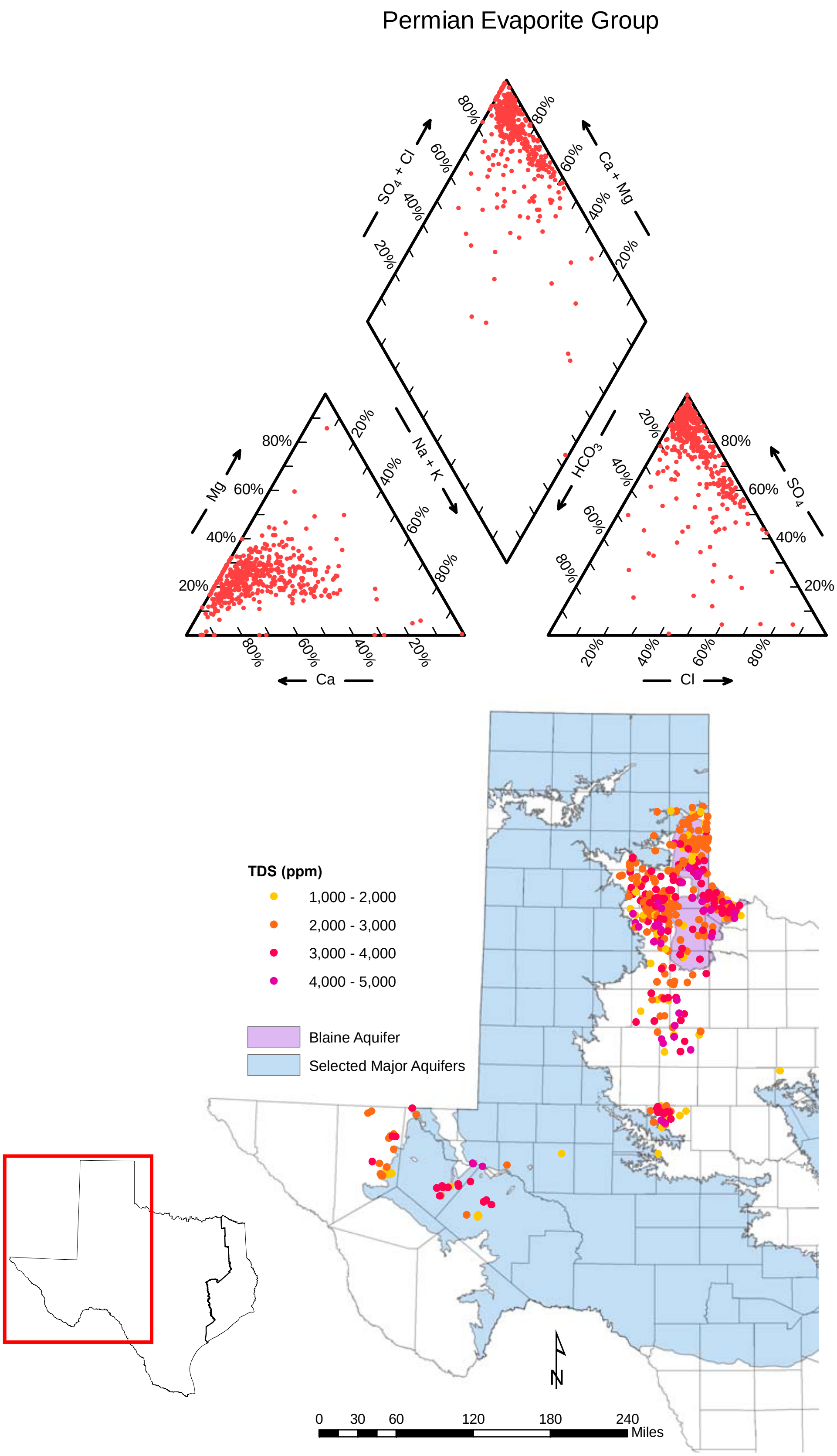


Figure 8-14. Map and Piper plot of Permian Evaporite group

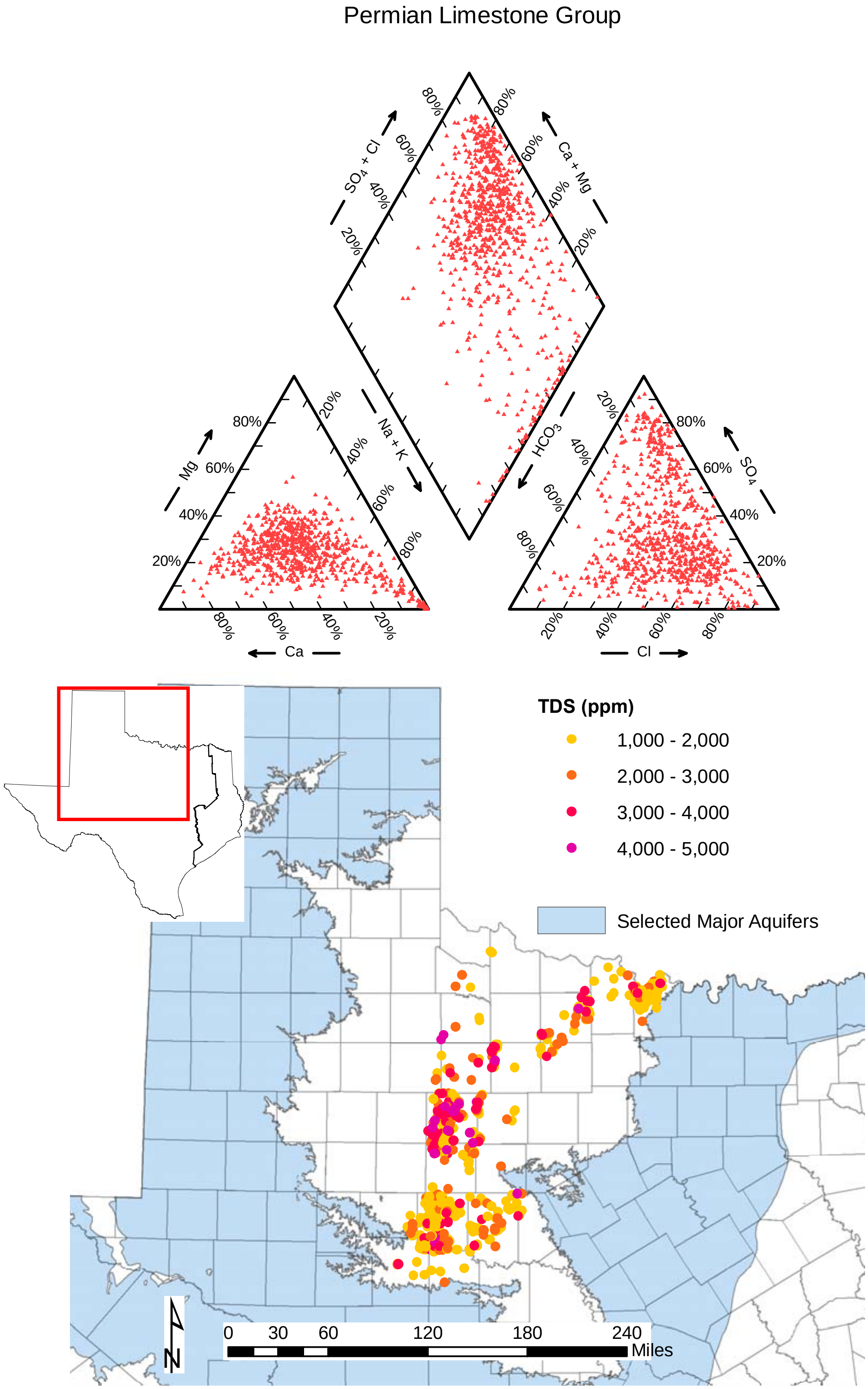


Figure 8-15. Map and Piper plot of Permian Limestone group

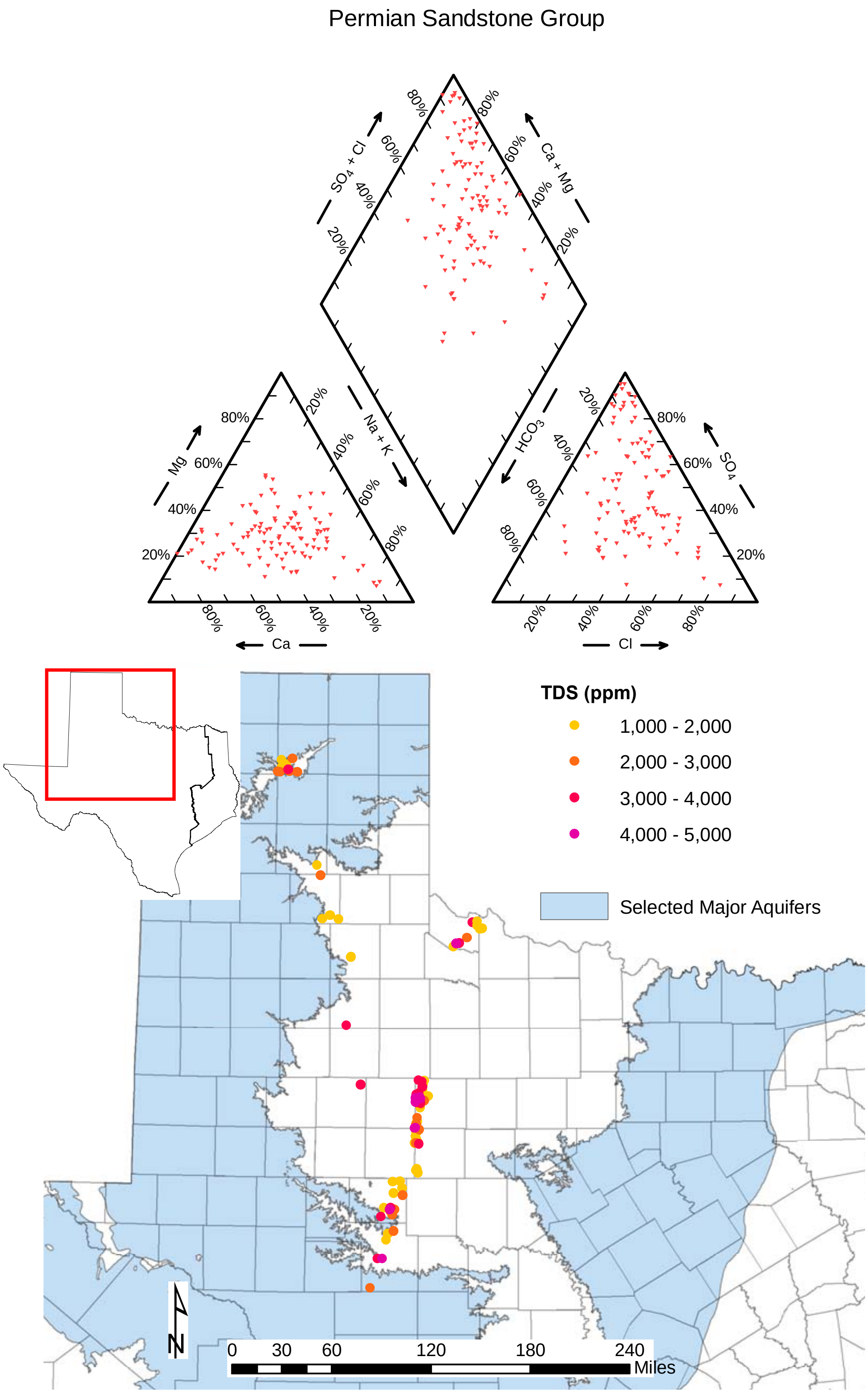
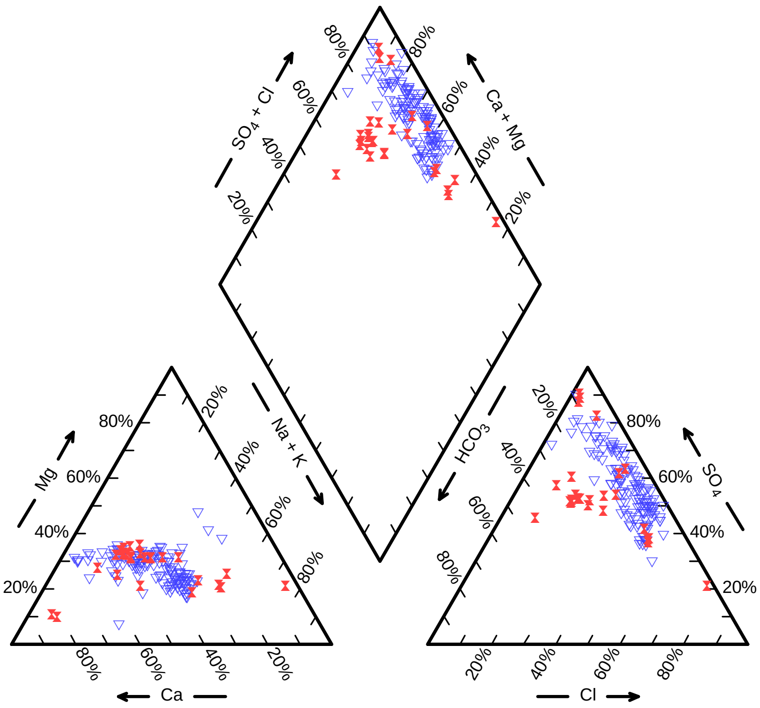


Figure 8-16. Map and Piper plot of Permian Sandstone group

Bone Spring and Capitan Groups



Note: Blue del symbol = Bone Spring and red hourglass symbol = Capitan Reef

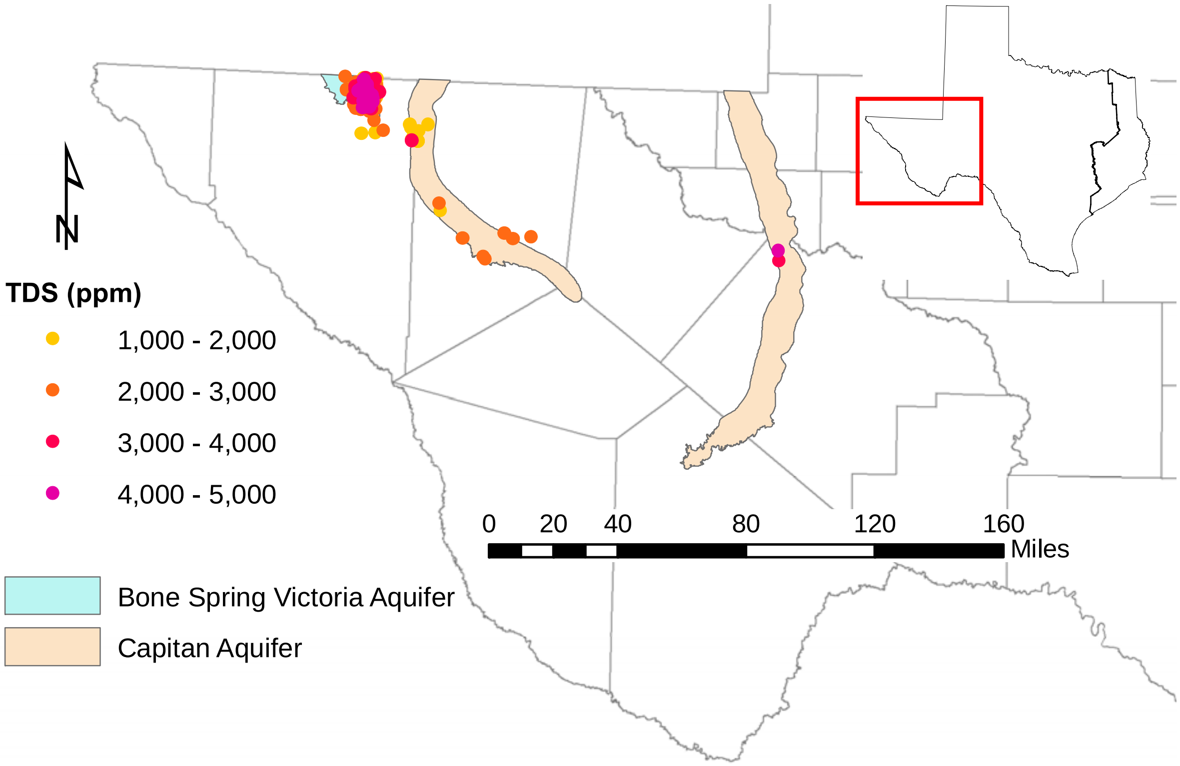


Figure 8-17. Map and Piper plot of Bone Spring – Victorio Peak and Capitan groups

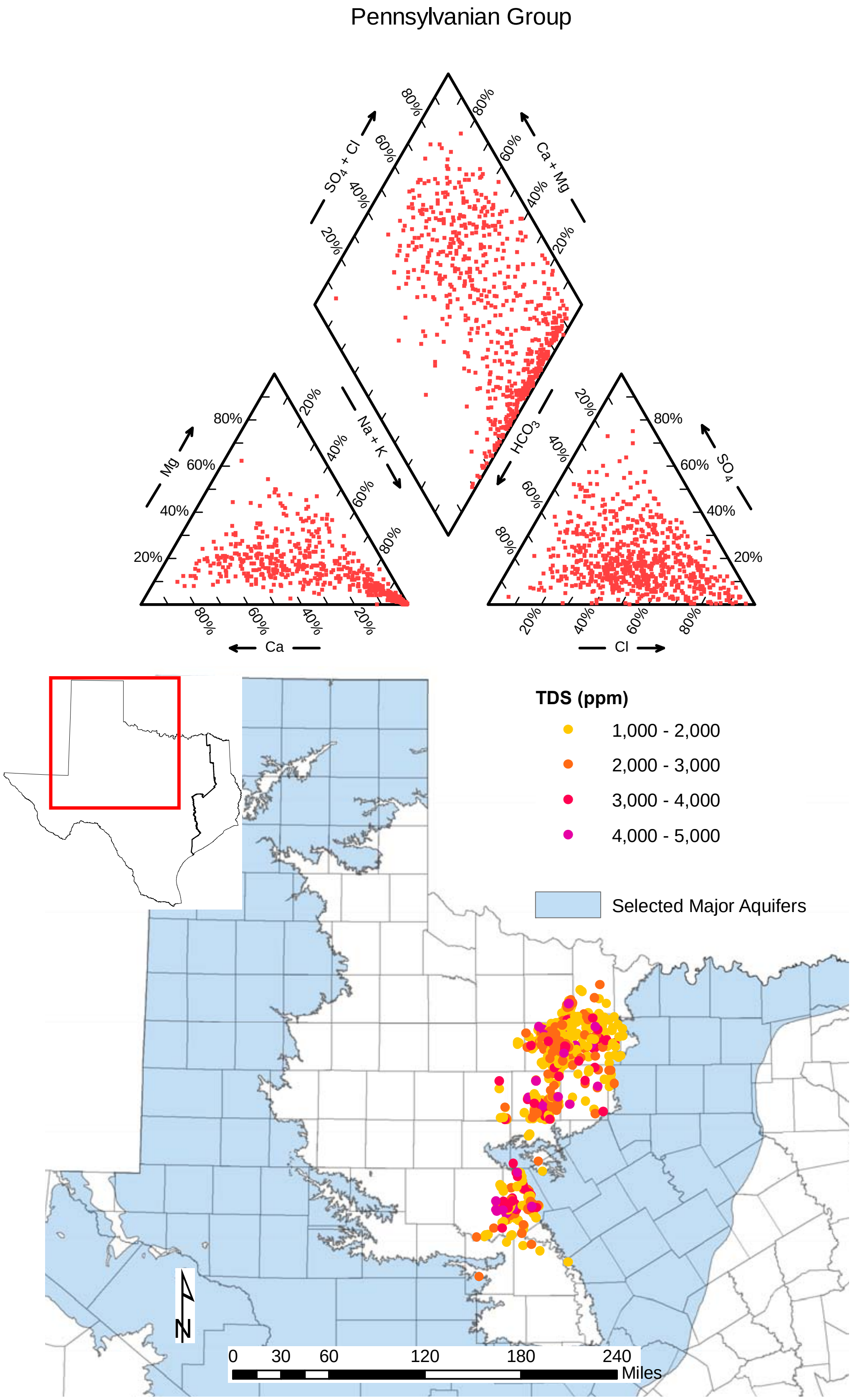
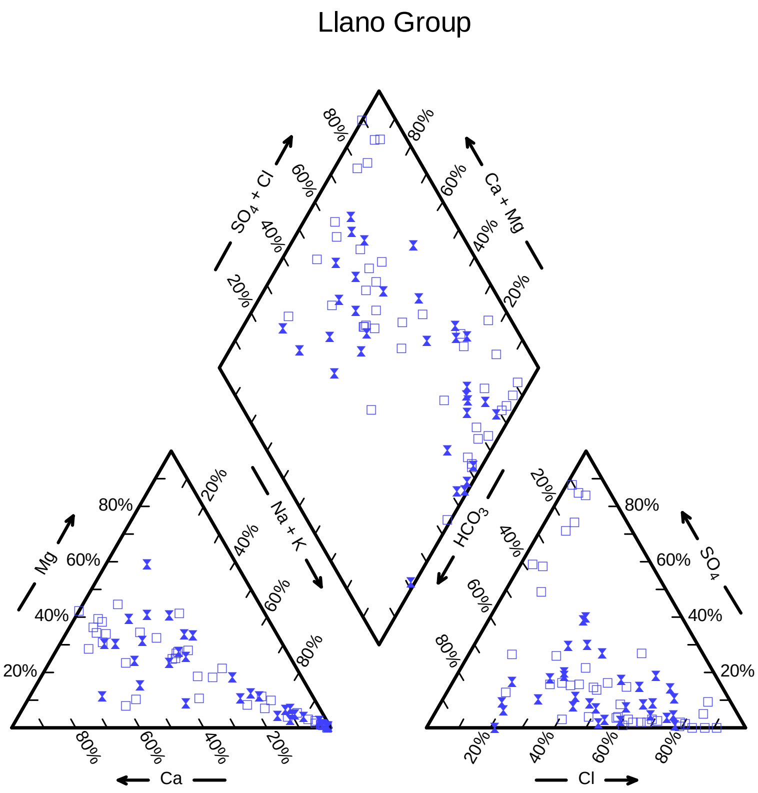


Figure 8-18. Map and Piper plot of Pennsylvanian group



Note: square symbol = limestone and hourglass symbol = sandstone

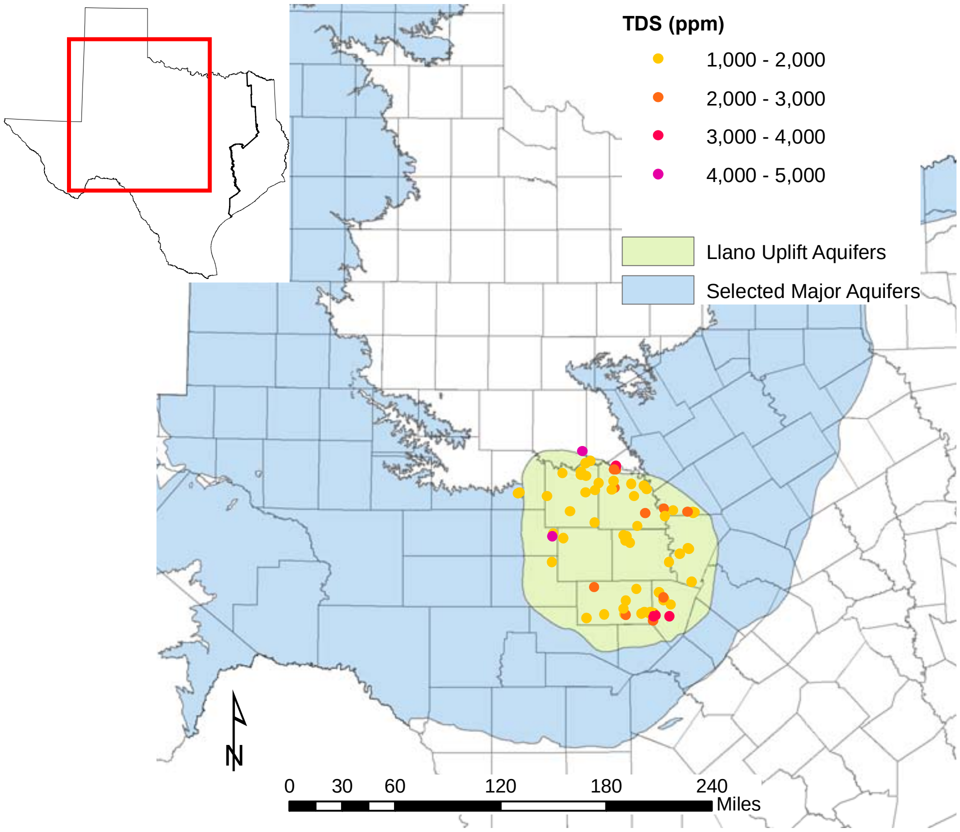
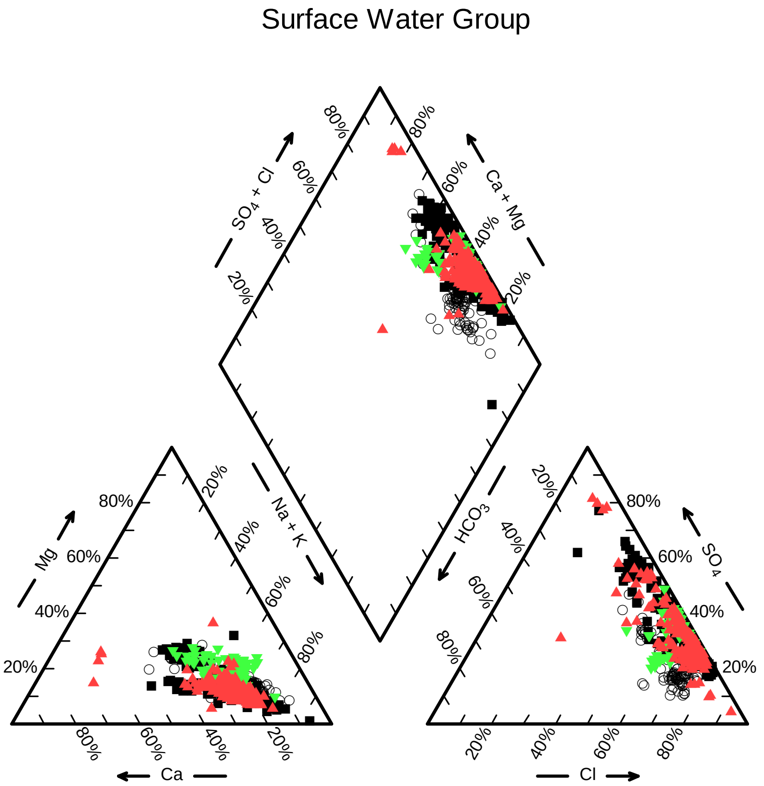


Figure 8-19. Map and Piper plot of Llano Uplift group



Source: TCEQ (2006b)
Note: Data from Red (red triangles), Colorado (green inverted triangles), Canadian (open circles), and Brazos (squares) River basins

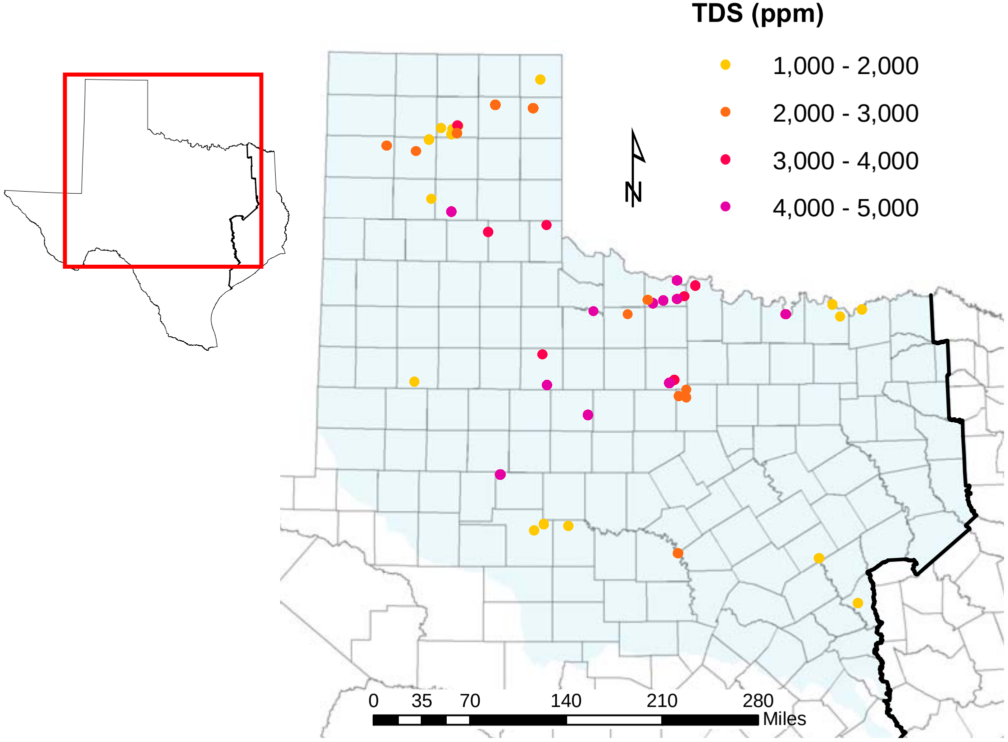


Figure 8-20. Map and Piper plot of surface-water group

# 9 Appendix B:
# Relevant TAC/TCEQ Rules and Excerpts from Form TCEQ 10411/10055-Instructions

Excerpts from TCEQ (2006b, p. 11):

The **owner(s)** of an industrial facility which generates wastewater seeking authorization from the TCEQ to 1) discharge wastewater into water in the state (TPDES) or **2) dispose of wastewater adjacent to waters in the state by irrigation, evaporation, or subsurface disposal (TLAP) must be the applicant for a permit**.

Excerpts from TCEQ (2006b, p. 49):

**INSTRUCTIONS FOR WORKSHEET 3.1 - SURFACE LAND DISPOSAL OF EFFLUENT REQUIRED FOR ALL RENEWAL, AMENDMENT, AND NEW APPLICATIONS FOR A PERMIT TO DISPOSE OF WASTEWATER BY SURFACE LAND DISPOSAL.**

**2. EVAPORATION PONDS**
For evaporation ponds, provide a separate engineering report of evaporation calculations for average long term conditions and worse case conditions (i.e., maximum rainfall and minimum evaporation from the past 25 years of climatological data). The calculations will be used to evaluate the suitability of the disposal volume of the evaporation pond(s). It is necessary to determine the maximum feasible long-term disposal volume under average conditions to prevent effluent accumulation as well as to determine the adequacy of the system under extreme conditions of maximum rainfall and minimum evaporation.

The storage volume calculations consisting of items 12 - 20 of the water balance and storage calculations (See Example 6 ) can be used as one method of demonstrating pond storage capabilities. For column 13, provide the amount of effluent sent to the evaporation pond (normally the permitted flow converted to inches per month per acre of surface area of the evaporation pond(s)).

**Recommended Data Sources:** Data for net evaporation values may be obtained from the Texas Water Development Board's Evaporation/Precipitation Data for Texas, http://hyper20.twdb.state.tx.us/Evaporation/evap.html. Please provide all the appropriate documentation if data utilized in the water balance/storage calculations are from sources other than these.

The following pages contain the rules (valid as of September 2006) pertinent to evaporation ponds: §309.13 (Unsuitable Site Characteristics), §317.1 (General provisions),§317.4 (Wastewater Treatment Facilities), and §317.5 (Sludge Processing).

# Texas Administrative Code

| | |
|---|---|
| **TITLE 30** | ENVIRONMENTAL QUALITY |
| **PART 1** | TEXAS COMMISSION ON ENVIRONMENTAL QUALITY |
| **CHAPTER 309** | DOMESTIC WASTEWATER EFFLUENT LIMITATION AND PLANT SITING |
| **SUBCHAPTER B** | LOCATION STANDARDS |
| **RULE §309.13** | **Unsuitable Site Characteristics** |

(a) A wastewater treatment plant unit may not be located in the 100-year flood plain unless the plant unit is protected from inundation and damage that may occur during that flood event.
(b) A wastewater treatment plant unit may not be located in wetlands. (This prohibition is not applicable to constructed wetlands.)
(c) A wastewater treatment plant unit may not be located closer than 500 feet from a public water well as provided by §290.41(c)(1)(B) of this title (relating to Ground Water Sources and Development) nor 250 feet from a private water well. The following separation distances apply to any facility used for the storage, processing, or disposal of domestic wastewater. Exceptions to these requirements will be considered at the request of a permit applicant on a case-by-case basis, and alternative provisions will be established in a permit if the alternative condition provides adequate protection to potable water sources and supplies:
(1) A wastewater treatment plant unit, land where surface irrigation using wastewater effluent occurs, or soil absorption systems (including low pressure dosing systems, drip irrigation systems, and evapotranspiration beds) must be located a minimum horizontal distance of 150 feet from a private water well;
(2) A wastewater treatment plant unit, or land where surface irrigation using wastewater effluent occurs, must be located a minimum horizontal distance of 500 feet from an elevated or ground potable-water storage tank as provided by §290.43(b)(1) of this title (relating to Location of Clear Wells, Standpipes, and Ground Storage and Elevated Tanks);
(3) A wastewater treatment plant unit, or land where surface irrigation using wastewater effluent occurs, must be located a minimum horizontal distance of 500 feet from a public water well site as provided by §290.41(c)(1)(C) of this title, spring, or other similar sources of public drinking water;
(4) A wet well or pump station at a wastewater treatment facility must be located a minimum horizontal distance of 300 feet from a public water well site, spring, or other similar sources of public drinking water as provided by §290.41(c)(1)(B) of this title; and
(5) A wastewater treatment plant unit, or land where surface irrigation using wastewater effluent occurs must be located a minimum horizontal distance of 500 feet from a surface water treatment plant as provided by §290.41(e)(3)(A) of this title.
(d) A wastewater treatment facility surface impoundment may not be located in areas overlying the recharge zones of major or minor aquifers, as defined by the Texas Water Development Board, unless the aquifer is separated from the base of the containment structure by a minimum of three feet of material with a hydraulic conductivity toward the aquifer not greater than $10^{-7}$ cm/sec or a thicker interval of more permeable material which provides equivalent or greater retardation of pollutant migration. A synthetic membrane liner may be substituted with a minimum of 30 mils thickness and an underground leak detection system with appropriate sampling points.
(e) One of the following alternatives must be met as a compliance requirement to abate and control a nuisance of odor prior to construction of a new wastewater treatment plant unit, or substantial change in the function or use of an existing wastewater treatment unit:
(1) Lagoons with zones of anaerobic activity (e.g., facultative lagoons, un-aerated equalization basins, etc.) may not be located closer than 500 feet to the nearest property line. All other wastewater treatment plant units may not be located closer than 150 feet to the nearest property line. Land used to treat primary effluent is considered a plant unit. Buffer zones for land used to dispose of treated effluent by irrigation shall be evaluated on a case-by-case basis.

The permittee must hold legal title or have other sufficient property interest to a contiguous tract of land necessary to meet the distance requirements specified in this paragraph during the time effluent is disposed by irrigation;

(2) The applicant must submit a nuisance odor prevention request for approval by the executive director. A request for nuisance odor prevention must be in the form of an engineering report, prepared and sealed by a licensed professional engineer in support of the request. At a minimum, the engineering report shall address existing climatological conditions such as wind velocity and atmospheric stability, surrounding land use which exists or which is anticipated in the future, wastewater characteristics in affected units pertaining to the area of the buffer zone, potential odor generating units, and proposed solutions to prevent nuisance conditions at the edge of the buffer zone and beyond. Proposed solutions shall be supported by actual test data or appropriate calculations. The request shall be submitted, prior to construction, either with a permit application and subject to review during the permitting process or submitted for executive director approval after the permitting process is completed; or

(3) The permittee must submit sufficient evidence of legal restrictions prohibiting residential structures within the part of the buffer zone not owned by the applicant. Sufficient evidence of legal restriction may, among others, take the form of a suitable restrictive easement, right-of-way, covenant, deed restriction, deed recorded, or a private agreement provided as a certified copy of the original document. The request shall be submitted, prior to construction, either with a permit application and subject to review during the permitting process or submitted for executive director approval after the permitting process is completed.

(f) For a facility for which a permit application, other than a renewal application, is made after October 8, 1990, if the facility will not meet the buffer zone requirement by one of the alternatives described in subsection (e) of this section, the applicant shall include in the application for the discharge permit a request for a variance. A variance will be considered on a case-by-case basis and, if granted by the commission, shall be included as a condition in the permit. This variance may be granted by the commission, consistent with the policies set out in Texas Water Code, §26.003.

(g) Any approved alternative for achieving the requirements of this subsection must remain in effect as long as the wastewater treatment plant is permitted by the commission. To comply with this requirement, the permittee must carry out the nuisance odor prevention plan at all times, shall ensure sufficient property ownership or interest and shall maintain easements prohibiting residential structures, as appropriate.

(h) For a permitted facility undergoing renewal of an existing permit with plans and specifications approved prior to March 1, 1990, for which no design change is requested, the facility will not be required to comply with the requirements of this subsection.

(i) Facilities for which plans and specifications have been approved prior to March 1, 1990, are not required to resubmit revised plans and specifications to meet changed requirements in this section in obtaining renewal of an existing permit.

## **CHAPTER 317** DESIGN CRITERIA FOR SEWERAGE SYSTEMS

### **RULE §317.1** **General Provisions**

(a) Purpose. These design criteria are minimum guidelines to be used for the comprehensive consideration of domestic sewage collection, treatment, or disposal systems and establish the minimum design criteria pursuant to existing state statutes pertaining to effluent quality necessary to meet state water quality standards. These criteria are intended to promote the design of facilities in accordance with good public health and water quality engineering practices. These criteria include the minimum requirements for a preliminary engineering report which provides the general engineering concepts underlying the proposed project as well as the final engineering report detailing the fully developed project along with related plans and specifications.

(4) Types of approval. Regardless of the type of approval, constructed facilities when in operation are required to produce the quality of effluent specified in their discharge permit(s). The types of approvals described in subparagraphs (A) - (C) of this paragraph will be utilized by the commission or any other review authority.

(A) Standard approval. Plans and specifications found to comply with all applicable parts of these criteria and to conform to commonly accepted sanitary engineering design practices shall be approved for construction.

(B) Approvals of innovative and nonconforming technologies.

(i) Technologies considered to be nonconforming or innovative include ones not conforming to or addressed in the design criteria of this chapter.

(ii) If an approval for nonconforming or innovative technologies is requested, engineering proposals for processes, equipment, or construction materials not covered in these criteria shall be fully described in the submitted planning materials and the reasons for their selection clearly outlined. Processes considered to be nonconforming or innovative should also be supported by results of pilot or demonstration studies. Where similarly designed full scale processes exist and are known to have operated for a reasonable period of time under conditions similar to those suggested for the proposed design, performance data from these existing full scale facilities shall be required to be submitted to the executive director in addition to, or in lieu of, pilot or small scale demonstration studies. Any warranties or performance bond agreements offered by the process, equipment, or material manufacturers shall be fully described in the request.

(iii) Approvals of processes, equipment, or construction materials which are considered to be innovative or nonconforming will be granted only in cases where the commission or review authority determines, after an engineering evaluation of the supporting information provided in the submitting engineer's design report, that the technology will not result in a threat to public health or the environment.

(iv) The executive director or review authority may require the manufacturer or supplier to obtain and furnish evidence of an acceptable two-year performance bond from an approved surety which insures the performance of the innovative or nonconforming technology. The performance bond shall cover the cost of removal or abandonment of the innovative or nonconforming facility and equipment, replacement with previously agreed upon facilities or equipment, and all associated engineering fees necessary for the removal and replacement.

(v) Approval of innovative and nonconforming technologies may include a condition which states that after some predetermined period of time after the installation and startup of the innovative or nonconforming technology, requiring an engineering report to be submitted after start-up, detailing the performance of the nonconforming or innovative technology. The engineering report shall include unbiased calculations and data supporting the technology's performance; and written submittals from the design engineer and permittee which state that the nonconforming or innovative technology has satisfied its manufacturer's claims.

## CHAPTER 317 DESIGN CRITERIA FOR SEWERAGE SYSTEMS
## RULE §317.4 Wastewater Treatment Facilities

(j) Wastewater stabilization ponds (secondary treatment ponds).

(1) Pretreatment. Wastewater stabilization ponds shall be preceded by facilities for primary sedimentation of the raw sewage. Aerated lagoons or facultative lagoons may be utilized in place of conventional primary treatment facilities.

(2) Imperviousness. All earthen structures proposed for use in domestic wastewater treatment or storage shall be constructed to protect groundwater resources. Where linings are necessary, the following methods are acceptable:

(A) in-situ or placed clay soils having the following qualities may be utilized for pond lining:
  (i) more than 30% passing a 200-mesh sieve;
  (ii) liquid limit greater than 30%;
  (iii) plasticity index greater than 15; and
  (iv) a minimum thickness of two feet;
(B) membrane lining with a minimum thickness of 20 mils, and an underdrain leak detection system;
(C) other methods with commission approval.

(3) Distribution of flow. Stabilization ponds shall be of such shape and size to insure even distribution of the wastewater flow throughout the entire pond. While the shapes of ponds may be dictated to some extent by the topography of the location, long narrow ponds are preferable and they should be oriented in the direction of the prevailing wind such that debris is blown toward the inlet. Ponds with narrow inlets or sloughs should be avoided.

(4) Access area. Storm water drainage shall be excluded from all ponds. All vegetation shall be removed from within the pond area during construction. Access areas shall be cleared and maintained for a distance of at least 20 feet from the outside toes of the pond embankment walls.

(5) Multiple ponds. The use of multiple ponds in pond systems is required. The operation of the ponds shall be flexible, enabling one or more ponds to be taken out of service without affecting the operation of the remaining ponds. The ponds shall be operated in series during routine operation periods.

(6) Organic loading. The organic loading on the stabilization ponds, based on the total surface area of the ponds, shall not exceed 35 pounds of $BOD_5$ per acre per day. The loading on the initial stabilization pond shall not exceed 75 pounds of $BOD_5$ per acre per day.

(7) Depth. The stabilization ponds or cells shall have a normal water depth of three to five feet.

(8) Inlets and outlets. Multiple inlets and multiple outlets are required. The inlets and outlets shall be arranged to prevent short circuiting within the pond so that the flow of wastewater is distributed evenly throughout the pond. Multiple inlets and outlets shall be spaced evenly. All outlets shall be baffled with removable baffles to prevent floating material from being discharged, and shall be constructed so that the level of the pond surface may be varied under normal operating conditions. Submerged outlets shall be used to prevent the discharge of algae.

(9) Embankment walls. The embankment walls should be compacted thoroughly and compaction details shall be covered in the specifications. Soil used in the embankment shall be free of foreign material such as paper, brush, and fallen trees. The embankment walls shall have a top width of at least 10 feet. Interior and exterior slope of the embankment wall should be one foot vertical to three feet horizontal. There shall be a freeboard of not less than two feet nor more than three feet based on the normal operating depth. All embankment walls shall be protected by planting grass or riprapping. Where embankment walls are subject to wave action, riprapping should be installed. Erosion stops and water seals shall be installed on all piping penetrating the embankments. Provisions should be made to change the operating level of the pond so the pond surface can be raised or lowered at least six inches.

(10) Partially mixed aerated lagoons.

(A) Horsepower. With partially mixed aerated lagoons, no attempt is made to keep all pond solids in suspension. Mechanical or diffused aeration equipment should be sized to provide a minimum of 1.6 pounds of oxygen per pound of $BOD_5$ applied with the largest unit out of service. Where multiple ponds are used in series, the power input may be reduced as the influent $BOD_5$ to each pond decreases. Proposed oxygen transfer rates in excess of two pounds per horsepower-hour must be justified by actual performance data.

(B) Pond sizing. Partially mixed aerated lagoons should be sized in accordance with the formula in subsection (i)(3) of this section using K-0.28. Pond length to width ratios should be three to one or four to one.

(C) Imperviousness. Requirements for imperviousness, multiple cells, embankment walls, and inlets and outlets shall be the same as for other secondary

## **CHAPTER 317** DESIGN CRITERIA FOR SEWERAGE SYSTEMS

## **RULE §317.5** **Sludge Processing**

(e) Sludge dewatering facilities. Sludge shall be dewatered sufficiently to meet the requirements of the ultimate form of disposal.

(1) Sludge drying beds.

(A) Required area. The area of sludge drying beds to be provided will vary in accordance with the average rainfall, average humidity, and type of treatment process used. The required area for aerobic sludge dewatering shall be determined from §317.12 of this title (relating to Appendix D) (for anaerobic sludge dewatering, the value obtained from §317.12 of this title (relating to Appendix D)) may be reduced 35% to determine the required area) using a waste load based on sewage strength and the daily average flow of the raw sewage. The bed area sizing requirements shown in §317.12 of this title (relating to Appendix D) are for sludge drying beds utilizing a continuous underdrain media as specified in this subsection. Concrete (or similar impervious material) sludge drying beds which do not use an underdrain media may require additional area and will be evaluated on a case-by-case basis; however, in those counties of the state which experience both high rainfall and high relative humidity (Brazoria, Chambers, Fort Bend, Galveston, Hardin, Harris, Jasper, Jefferson, Liberty, Newton, and Orange), other methods of sludge dewatering should be utilized in lieu of sludge drying beds. Where sludge drying beds are used in those counties of high rainfall and humidity, provisions shall be made in the design of these beds for covering the beds, for means of accelerated dewatering, or for extra storage capacity and alternate dewatering methods to effectively dewater the sludge during inclement weather.

(B) General design features. At least two sludge drying beds shall be provided and they shall be constructed at elevations above groundwater level. Construction shall be such as to exclude surface water runoff from the beds and seepage from the beds into the ground. Channels shall be of sufficient grade and size to facilitate the flow of the sludge to the various beds. Runners should be provided to facilitate sludge handling.

(C) Filtrate. The filtrate (or drainage) from the sludge drying beds shall be returned to the head of the treatment works or to the aeration system.

(D) Sludge removal. A splash block or slab shall be provided at the point where digested sludge is discharged onto each of the beds. Appropriate means shall be provided to facilitate the removal of the dried sludge from the beds for disposal without bed damage resulting. Every sludge drying bed should include a removal gate or stop planks in one end to provide access for machinery and trucks to remove and haul away the dried sludge.

(E) Media. A minimum depth of 12 inches of filtering material, of which four to six inches is coarse sand, is required. To exclude surface water and eroded earth, the bed shall be protected by a permanent wall which shall extend at least 12 inches but not more than 24 inches above the finished surface of the beds.

(2) Vacuum filters, belt filters, belt filter presses, and other mechanical dewatering filters.

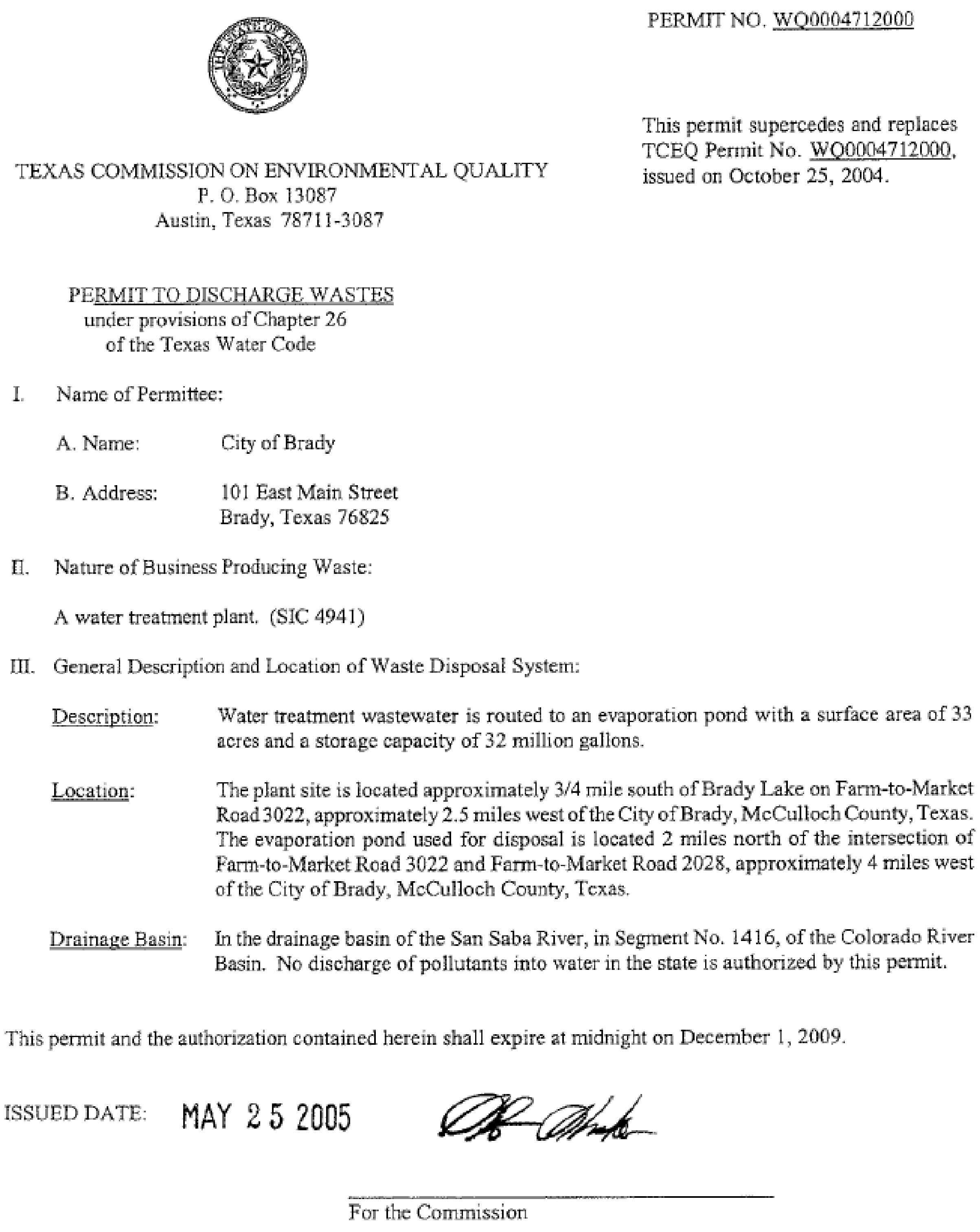
(A) Multiple units. Where dewatering of sludge is proposed, the design engineer shall provide data to document sufficient capacity, alternate disposal means, or storage facilities capable of maintaining normal daily operations during breakdowns, upsets, etc.

(B) Filtrate. The filtrate from the filters shall be returned to the head of the treatment works or to the aeration system. Consideration shall be given to the impact of the returned filtrate on the treatment units and to providing odor and insect control facilities.

(3) Portable dewatering units. If sludge is to be treated using portable mechanical dewatering units, provisions shall be made in the facility plan or preliminary engineering report for the location and connection of the portable dewatering unit(s) during facility operation.

# 10 Appendix C: Example of Permit to Discharge Wastewater to an Evaporation Pond

The following pages show relevant pages extracted from a permit to a recent evaporation pond. In particular it describes the three pond lining options in Section V-3-a, b, and c.



PERMIT NO. WQ0004712000

This permit supercedes and replaces
TCEQ Permit No. WQ0004712000,
issued on October 25, 2004.

TEXAS COMMISSION ON ENVIRONMENTAL QUALITY
P. O. Box 13087
Austin, Texas 78711-3087

## PERMIT TO DISCHARGE WASTES

under provisions of Chapter 26
of the Texas Water Code

I. Name of Permittee:

A. Name: City of Brady

B. Address: 101 East Main Street
Brady, Texas 76825

II. Nature of Business Producing Waste:

A water treatment plant. (SIC 4941)

III. General Description and Location of Waste Disposal System:

Description: Water treatment wastewater is routed to an evaporation pond with a surface area of 33 acres and a storage capacity of 32 million gallons.

Location: The plant site is located approximately 3/4 mile south of Brady Lake on Farm-to-Market Road 3022, approximately 2.5 miles west of the City of Brady, McCulloch County, Texas. The evaporation pond used for disposal is located 2 miles north of the intersection of Farm-to-Market Road 3022 and Farm-to-Market Road 2028, approximately 4 miles west of the City of Brady, McCulloch County, Texas.

Drainage Basin: In the drainage basin of the San Saba River, in Segment No. 1416, of the Colorado River Basin. No discharge of pollutants into water in the state is authorized by this permit.

This permit and the authorization contained herein shall expire at midnight on December 1, 2009.

ISSUED DATE: MAY 25 2005

For the Commission

IV. CONDITIONS OF THE PERMIT:

Character: Water treatment wastewater (*1).

Volume: At a daily average flow not to exceed 0.075 million gallons per day and a daily maximum flow of 0.15 million gallons per day.

Quality: All wastewater shall be routed to the evaporation pond. Effluent quality routed to the pond shall meet the following limitations:

| Parameter | Daily Avg | Daily Max | Frequency | Sample Type |
|---|---|---|---|---|
| Flow (MGD) | (0.075) | (0.15) | 1/week | Estimate |
| Total Dissolved Solids | N/A | Report, mg/l | 1/month | Grab |
| pH (Standard Units) | (6.0 minimum) | (9.0 maximum) | 1/month | Grab |

(*1) See Special Provision No. 8.

Results from the analyses shall be retained on site for five years and available for inspection by authorized representatives of the TCEQ. This data shall be submitted to the Enforcement Division (MC 224), Industrial Permits Team (MC-148) of the Water Quality Division, and the Regional Office of the Texas Commission on Environmental Quality (TCEQ) during the month of September of each calendar year.

V. SPECIAL PROVISIONS:

1. For the effluent testing/monitoring requirements of this permit, the following definitions shall apply:

   a. A grab sample means an individual sample collected in less than 15 minutes.

   b. Grab sample quality means the quality determined by measuring the concentration in milligrams per liter, parts per million or other appropriate units of measurement in a single grab sample of the defined waste.

   c. Annual average flow means the arithmetic average of all daily flow determinations taken within the preceding 12 consecutive calendar months. The annual average flow determination shall consist of daily flow volume determinations made by a totalizing meter, charted on a chart recorder and limited to major domestic wastewater discharge facilities with a 1 million gallons per day or greater permitted flow.

   d. Daily maximum flow means the highest total flow for any 24-hour period in a calendar month.

2. All wastewater evaporation and backwash water ponds shall be operated in such a manner as to maintain a minimum freeboard of two feet.

3. All wastewater evaporation and backwash water ponds shall be lined in compliance with one of the following requirements.

   a. Soil Liner: The soil liner shall contain at least 3 feet of clay-rich (liquid limit greater than or equal to 30 and plasticity index greater than or equal to 15) soil material along the sides and bottom of the pond compacted in lifts of no more than 9 inches, to 95% standard proctor density at the optimum moisture content to achieve a permeability equal to or less than $1 \times 10^{-7}$ cm/sec.

b. Plastic/Rubber Liner: The liner shall be either a plastic or rubber membrane liner at least 30 mils in thickness which completely covers the sides and the bottom of the pond and which is not subject to degradation due to reaction with wastewater with which it will come into contact. If this lining material is vulnerable to ozone or ultraviolet deterioration it should be covered with a protective layer of soil of at least 6 inches. A leak detection system is also required.

c. Alternative Liner: The permittee shall submit plans for any other pond lining method. Pond liner plans must be approved in writing by the Executive Director of the Texas Commission on Environmental Quality prior to pond construction.

Certification of the lining specifications shall be provided by a Texas licensed professional engineer and shall be submitted to the Water Quality Assessment Team (MC - 150) and available for inspection by TCEQ personnel upon request. In lieu of the above specified liner requirements, liner certification may be demonstrated according to one of the following options:

i. Option 1

The permittee shall submit water quality data outlining the useable groundwater quality produced in the area from referenced literature or from sampling the first occurrence of groundwater. The industrial wastewater liner requirements will be exempted if the water chemistry and water quality of the wastestream entering the wastewater holding ponds is equal in water chemistry or possesses a higher water quality than the first occurrence of groundwater and/or useable groundwater produced in the area. Appropriate water quality components should at a minimum include total dissolved solids (TDS), chloride, sulfate, pH, fecal coliform and any additional parameter considered to be characteristic of the facilities operation.

ii. Option 2

The permittee shall demonstrate equivalent protective measures. Soil core engineering criteria, defined by a soils laboratory, may show thicker intervals of more permeable soil and/or lithology provides a downward pollution migration velocity equivalent or greater than protective measures outlined above. A licensed engineer may then certify the pond liner as meeting or exceeding the liner requirements. Option 2, Equivalent protective measures, are conditional upon the absence of an apparent high water table or shallow groundwater encountered during the soil coring and sampling event. If groundwater is encountered during the soil core extraction, then option 1, liner certification, or option 3 will be considered.

iii. Option 3

The permittee shall monitor the groundwater beneath the wastewater holding structure for changes in water chemistry and water quality for at least the lifetime of the wastewater holding structure's use. A Groundwater Monitoring Plan shall be submitted to the Groundwater Protection Team for review and approval.

If the permittee chooses to demonstrate compliance with the specified liner requirements in accordance with one of the above liner exemption options, the permittee shall submit the required information to the TCEQ Water Quality Assessment Team (MC - 150), the Wastewater Permitting Section (MC - 148) and Regional Office for review within 180 days of permit issuance. Based on a technical review of the submitted analytical results, an amendment may be initiated by TCEQ staff to include effluent limitations and/or monitoring requirements.

4. The permittee shall provide readily accessible sampling points for determining both the quality of the water entering and contained in the evaporation pond.

5. This permit does not authorize the discharge of any pollutant from the evaporation pond. The wastewater disposal system shall be designed and operated to prevent:

    1. Discharges or overflows from the evaporation pond.

    2. Recharge of groundwater resources which supply or may potentially supply domestic raw water.

    3. The occurrence of nuisance conditions.

6. The permittee shall notify the TCEQ Region 8 Office upon completion of construction of any pond and at least a week prior to its use.

7. The permittee shall notify the Executive Director in writing, at least 90 days prior to discontinuing use of any surface impoundment, pit, or basin authorized by this permit. The permittee shall, at the request of the Executive Director, submit such information as is necessary to evaluate closure of the waste management unit(s) including, but not limited to, chemical analyses of bottom sediments, soils, and groundwater samples.

8. The term 'water treatment wastewater' shall mean reject water from a reverse osmosis system and backwash water from a microfiltration system.

9. Within 60 days from the date this facility begins routing water to the evaporation pond, wastewater discharged via Outfall 001 shall be sampled and tested for those parameters listed on Table 1 of this permit for a minimum of four (4) separate sampling events which are a minimum of one (1) week apart. Table 1 shall be completed with the analytical results for Outfall 001 and sent to the TCEQ, Wastewater Permitting Section (MC-148), Industrial Team. Based on a technical review of the submitted analytical results, an amendment may be initiated by TCEQ staff to include additional effluent limitations and/or monitoring requirement. Failure to submit data within specified timeframes is a violation of this permit.

# 11 Appendix D: Panhandle Saline Lake Sampling

A few of the High Plains saline lakes were sampled for water chemical analyses (Table 11-1) and bottom sediment mineralogical analyses (fine-grained fraction, Table 11-2). A location map is given in Figure 11-1. Because of recent precipitation events at the time of the sampling, samples were taken on the edges of lakes where detrital input is likely important.

Table 11-1. Chemical analysis results of Panhandle saline lake, summer 2006 field sampling

| **Sampling Location** | **Si*** | **Ca** | **Mg** | **Na** | **K** | **Sr** | **Fe** | **Cl** | **$SO_4$** |
|---|---|---|---|---|---|---|---|---|---|
| **Baileyboro Lake** | 6.7 | 1,435 | 3,503 | 9,022 | 232 | 105.1 |  | 15,633 | 13,975 |
| **Goose Lake** | 48.1 | 121 | 85 | 263 | 45 | 4.9 |  | 186 | 163 |
| **Pauls Lake** | 2.9 | 342 | 1,314 | 8,257 | 245 | 8.5 | 3.5 | 10,400 | 9,410 |
| **White Lake** |  | 852 | 1,232 | 11,029 | 414 | 21.4 |  | 9,468 | 17,404 |
| **Double Lake** | 8.8 | 65 | 321 | 2,954 | 143 | 7.7 | 20.1 | 1,799 | 3,227 |
| **Tahoka Lake** | 0.3 | 156 | 882 | 3,991 | 572 | 26.5 |  | 4,034 | 6,002 |
| **Guthrie Lake** | 12.0 | 107 | 72 | 2,551 | 33 | 4.2 |  | 3,099 | 1,067 |
| **Cedar Lake** | 7.0 | 216 | 12,876 | 73,434 | 11,747 | 11.0 |  | 154,916 | 18,294 |

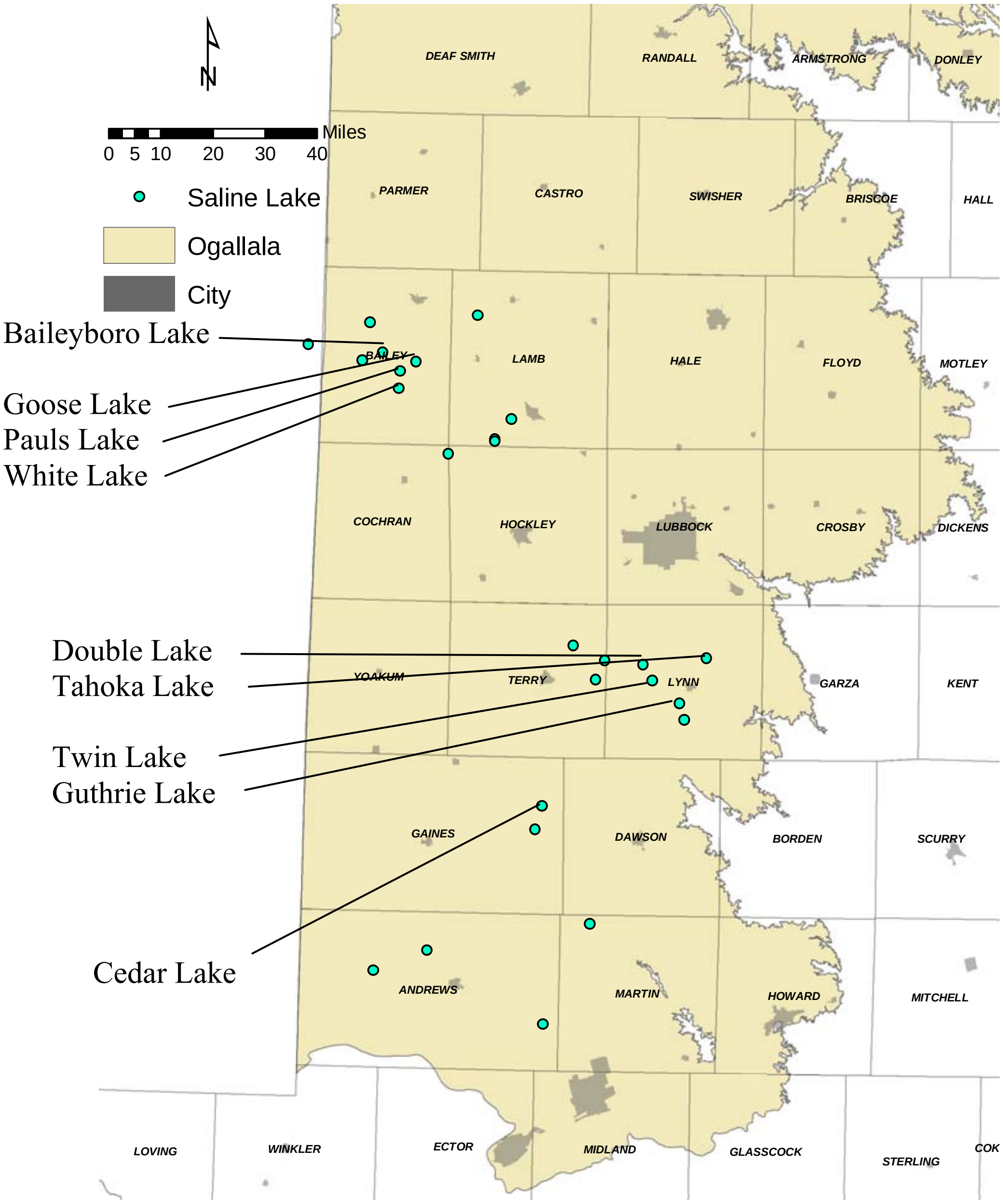
Note: Units are ppm

*Silicon (Si) is reported, not silica ($SiO_2$); there are no chemical analysis results for Twin Lakes because they were dry at the time of sampling.

Table 11-2. X-ray analyses of saline lake sediments (fine-grained fraction)

| **Sampling Location** | **Mineral Abundance** |
|---|---|
| **Baileyboro Lake** | Quartz > calcite; trace of illite and kaolinite, and even less sepiolite or smectite |
| **Goose Lake** | Quartz>> calcite, dolomite, trace kaolinite<br>Quartz>> calcite>K-feldspar, trace illite |
| **Pauls Lake** | Quartz>> calcite, trace feldspar, kaolinite, very small amount of illite and other clays |
| **White Lake** | Quartz>> calcite, trace of dolomite and kaolinite<br>Calcite>quartz, trace kaolinite and illite |
| **Double Lake** | Quartz >> calcite and gypsum, trace of illite<br>Quartz >> calcite, dolomite trace of feldspar and kaolinite.<br>Halite, quartz>dolomite>calcite, trace illite |
| **Tahoka Lake** | Quartz>> calcite, trace of feldspar, illite and kaolinite |
| **Guthrie Lake** | Quartz>> calcite, trace feldspar and kaolinite, ± gypsum |
| **Cedar Lake** | Quartz > calcite; trace of illite, kaolinite and dolomite, and even less sepiolite or smectite |
| **Twin Lakes** | Quartz>> calcite, trace of feldspar, dolomite, illite and Kaolinite |

Note: X-Ray analyses performed by J. Krumhansl at Sandia National Laboratories; multiple lines correspond to multiple samples in the same saline lake; ">" = more abundant than; ">>" = vastly more abundant than.



Note: Only sampled lakes are named on the map

Figure 11-1. Locations of Panhandle saline lakes

# 12 Appendix E:
# Evaporation Pond Sampling

In the summer/fall 2006, four evaporation ponds across Texas were sampled (Figure 12-1): River Oaks Ranch, near Austin; Horizon Regional MUD, near El Paso; and the Abilene and Brady facilities. At each location, pond bottom sediment and crust (Table 12-1), as well as well water, desalination concentrate, and pond water, were sampled (Table 12-2 and Figure 12-2) and X-ray diffraction analyses performed (Figure 12-3). Each sample contained approximately 50 to 100 cm$^3$ of water. This observation is particularly important for pond samples because they represent an average over some depth and do not fully characterize the vertical gradient obvious in some ponds. Conductivity, temperature, dissolved oxygen, and pH were collected directly in the field using a Quanta model from Hydrolab Corporation. The water samples were stored in an ice chest for transport and then in a cold room until chemical analyses. Anion analyses were performed at BEG using ion chromatography. Cation analyses were performed by the Lower Colorado River Authority (LCRA) Environmental Laboratory Services (ELS) using the ICP method. Samples sent to the LCRA-ELS were already filtered and x100-diluted, explaining a few missing sodium analyses when sodium concentrations were low. Silica analyses were performed at BEG on an LED photometer using a Vacu-vials® kit for silica.

The theoretical precipitation sequence (Figure 12-4), obtained by running PHREEQC, is consistent with observations. Pond salinity is low in all cases, and only the initial section of the sequence is applicable. Modeling of the River Oaks Ranch facility shows that little else than gypsum will precipitate, with very minor calcite and other clays. This finding is in agreement with the observations presented in Table 12-1. Modeling of the three horizon MUD samples shows not only gypsum precipitation, which has not been observed in the samples, but also calcite and a trace of clays, consistent with observations. The Abilene and Brady samples show mostly calcite with minor clay, as expected by results of evaporation first stages that were indicated by geochemical modeling.

Table 12-1. X-ray analyses of pond bottom sediments and crusts

| Facility | Sample | Mineral Abundance |
|---|---|---|
| **Bottom Sediments** | | |
| **ROR** | 1 | Mostly gypsum with some calcite and no clays or quartz |
| | 2 | |
| **Hor. MUD** | 1 | Calcite>quartz, trace kaolinite, illite, trace smectite/sepiolite? |
| | 2 | |
| | 3 | |
| **Abilene** | 1 | Quartz>calcite, trace illite and kaolinite-like clay |
| | 2 | |
| | 3 | |
| **Brady** | | Mostly calcite, a very small addition of quartz and traces of illite and kaolinite |
| **Crust/efflorescence** | | |
| **ROR** | | Gypsum and some calcite and no clays and quartz |
| **Hor. MUD** | | Gypsum and quartz |

Note: X-Ray analyses performed by J. Krumhansl at Sandia National Laboratories; multiple lines correspond to multiple samples in the same pond

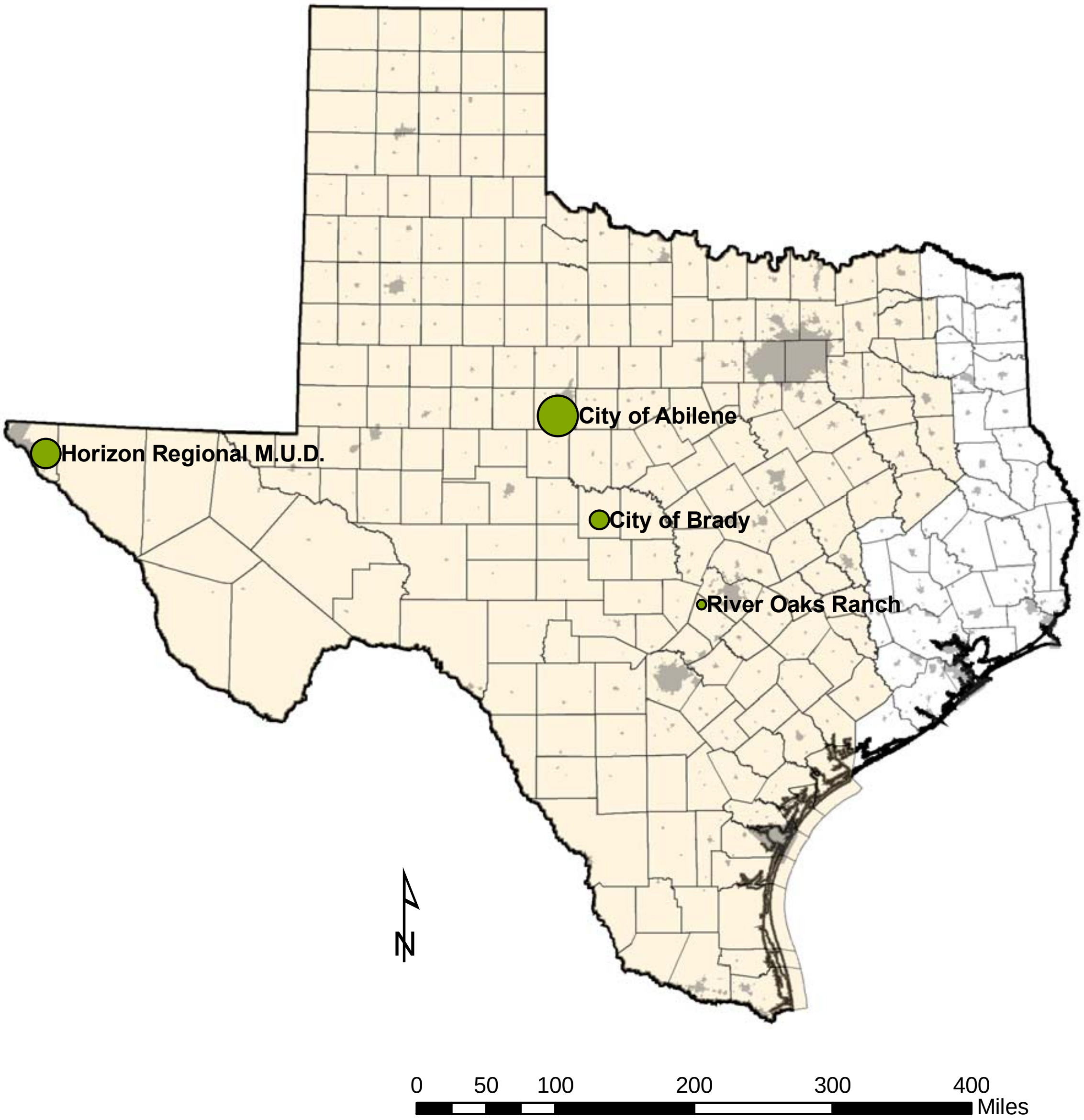
X-ray diffraction analysis is an instrumental technique for identifying minerals and estimating their degree of crystallinity. An X-ray beam is generated and hits the sample. The beam is then diffracted according to the unique structure of each mineral in the sample, producing a distinctive pattern or fingerprint on what is generally called the 2-theta scale (Figure 12-3). The size of the peak is related to the abundance of the mineral in the sample and its sharpness to the crystallinity of the mineral.

Table 12-2. Evaporation pond sampling results

| Facility | Sampling Location | Ture (°C) | pH | $SiO_2$ (mg/L) | Ca (mg/L) | Mg (mg/L) | Na (mg/L) | K (mg/L) | Cl (mg/L) | $SO_4$ (mg/L) | $HCO_3$ (mg/L) | TDS (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **ROR** | Well Water | NM | NM | 12.3 | 318.1 | 227.4 | 77.8 | 23.7 | 67.3 | 1,598.4 | *23.8* | 2,356 |
| | Concentrate | NM | NM | 34.7 | 1401.3 | 923.6 | 312.0 | 74.9 | 203.7 | 6,832.0 | *14.2* | 9,799 |
| | Pond sample 3 | NM | NM | 4.1 | 697.9 | 1662.1 | 615.3 | 147.6 | 441.9 | 9,651.6 | *10.2* | 13,277 |
| | Pond sample 4 | NM | NM | 4.1 | 695.4 | 1770.7 | 653.2 | 154.1 | 439.9 | 9,509.9 | *10.3* | 13,240 |
| | Pond sample 5 | NM | NM | 4.3 | 746.7 | 1782.7 | 661.3 | 156.9 | 441.5 | 9,643.5 | *9.6* | 13,463 |
| | Pond sample 6 | NM | NM | 4.9 | 754.7 | 1758.8 | 650.5 | 153.5 | 435.3 | 9,547.7 | *9.5* | 13,317 |
| | | | | | | | | | | | | |
| **Hor. MUD** | Well Water | 24.5 | 7.94 | 23.5 | 94.9 | 24.7 | 483.7 | *10.6* | 419.0 | 595.3 | *76.4* | 1,736 |
| | Well Water | 25.3 | 7.94 | 31.6 | 98.0 | 22.3 | 493.1 | *10.6* | 415.0 | 593.1 | *72.3* | 1,775 |
| | Concentrate | 24.3 | 8.03 | 70.3 | 256.5 | 63.5 | 1259.7 | 28.4 | 997.2 | 1,519.5 | *35.1* | 4,230 |
| | Concentrate | 24.7 | 7.96 | 66.3 | 189.7 | 47.2 | 928.3 | 22.2 | 958.9 | 1,461.2 | *52.0* | 3,731 |
| | Concentrate | 26.0 | 7.89 | 106.8 | 301.5 | 75.0 | 1436.3 | 35.1 | 1485.9 | 2,344.5 | *46.0* | 5,831 |
| | Pond sample 1 | 21.4 | 8.57 | 65.7 | 257.0 | 62.1 | 1280.2 | 32.1 | 1169.0 | 1,753.8 | *12.0* | 4,664 |
| | Pond sample 2 | 22.4 | 8.53 | 66.5 | 322.8 | 81.6 | 1603.9 | 42.1 | 1023.3 | 1,517.6 | *10.2* | 4,668 |
| | Pond sample 3 | 21.3 | 8.65 | 47.8 | 319.3 | 80.9 | 1587.0 | 44.4 | 1376.6 | 1,990.7 | *8.9* | 5,504 |
| | | | | | | | | | | | | |
| **Abilene** | Well Water | 23.9 | 7.88 | 5.2 | 82.8 | 60.6 | 192.6 | *10.9* | 381.9 | 311.1 | *84.4* | 1,130 |
| | Concentrate | 24.5 | 7.36 | 16.0 | 311.7 | 229.8 | 712.0 | 39.1 | 1,232.2 | 1,098.1 | *122.9* | 3,772 |
| | Pond sample 2 | 20.3 | 8.80 | 2.8 | 0.0 | 48.7 | 1762.2 | 28.6 | 2,717.3 | 2,127.2 | *0.0* | 3,683 |
| | Pond sample 3 | 20.8 | 8.41 | 0.2 | 278.4 | 318.4 | 1843.6 | 24.5 | 2,743.6 | 2,125.3 | *8.5* | 7,318 |
| | Pond sample 4 | 20.1 | 8.31 | 0.7 | 292.3 | 328.0 | 1895.0 | 23.2 | 1,785.0 | 1,419.7 | *18.0* | 7,441 |
| | | | | | | | | | | | | |
| **Brady**[A] | Well Water | 25.9 | 8.40 | 10.8 | 44.5 | 47.6 | 315.1 | 17.4 | 590.1 | 139.0 | *42.5* | 1,245 |
| | Concentrate | 24.4 | 8.32 | 26.6 | 114.5 | 130.0 | 855.4 | 48.0 | 1,596.9 | 364.6 | *29.9* | 3,180 |
| | Pond sample | 27.5 | 8.68 | 12.4 | 73.8 | 118.4 | 810.8 | 42.5 | 1,641.6 | 375.3 | *19.0* | 3,108 |

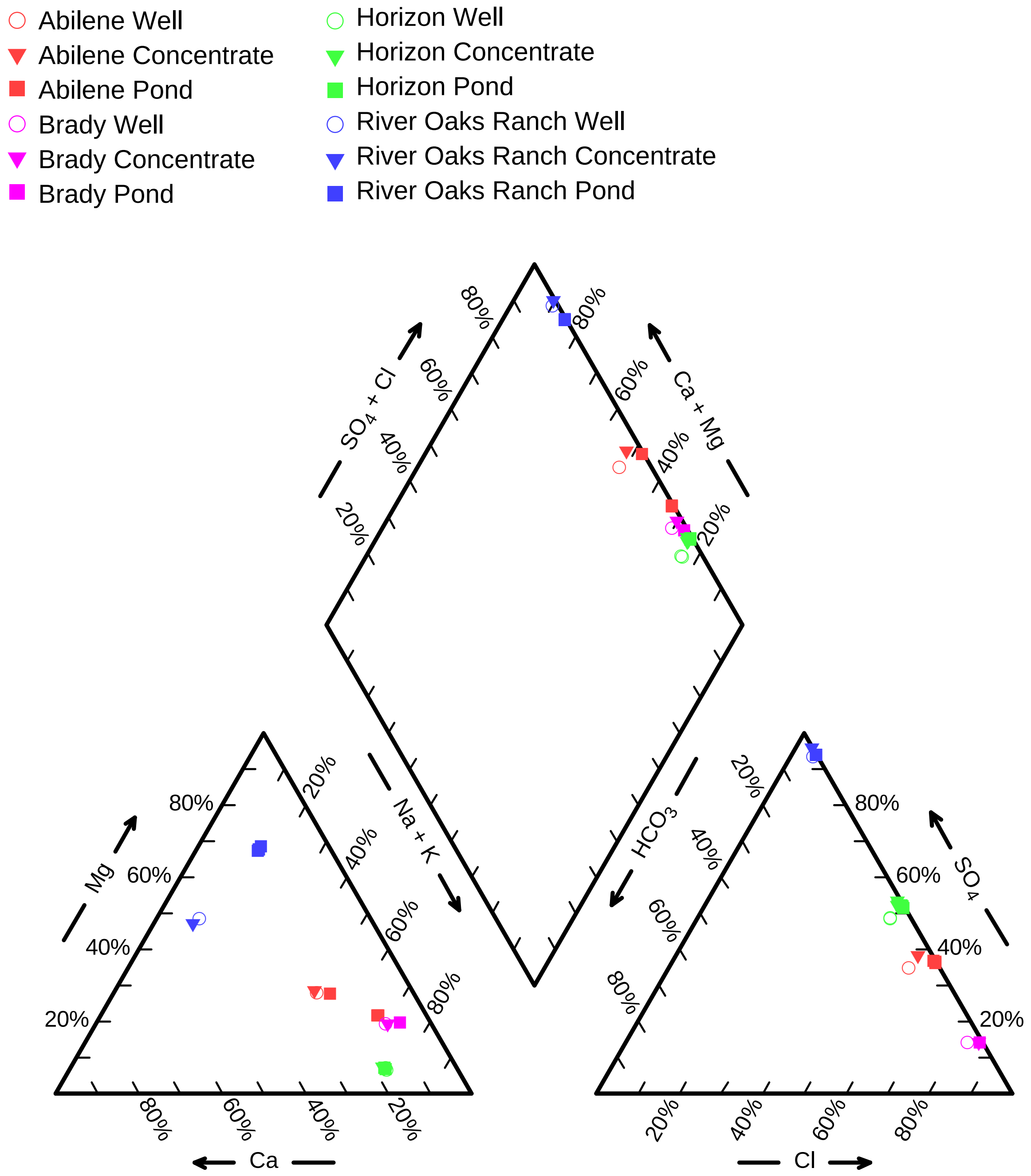
Note: NM= not measured; italic (and blue) cells contain data not provided in the source but calculated to approximately match TDS and electrical balance– Feedwater K computed from concentrate K by assuming average concentrate/feed ratio; bicarbonate computed with PHREEQC assuming equilibrium with calcite

[A] Concentrate obtained at the Brady facility does not represent the ultimate concentrate but its composition after one pass



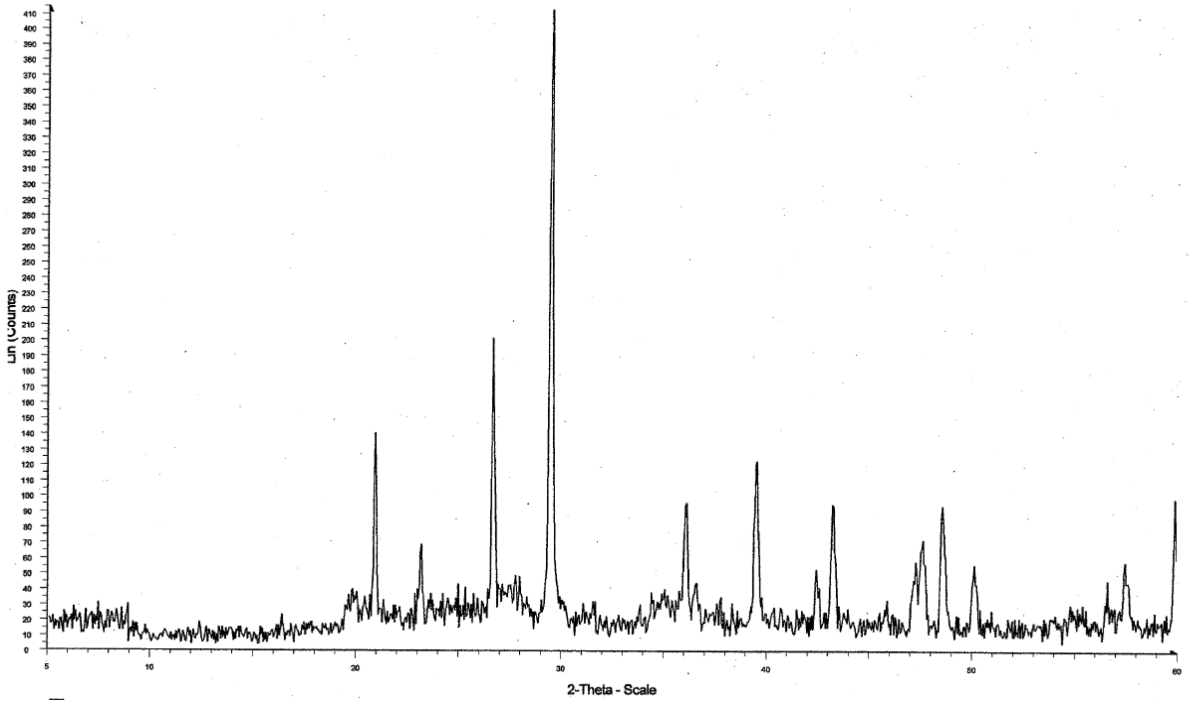
Note: Symbols are proportional to facility size; area with positive net evaporation rate also shown

Figure 12-1. Location map of the four sampled evaporation ponds

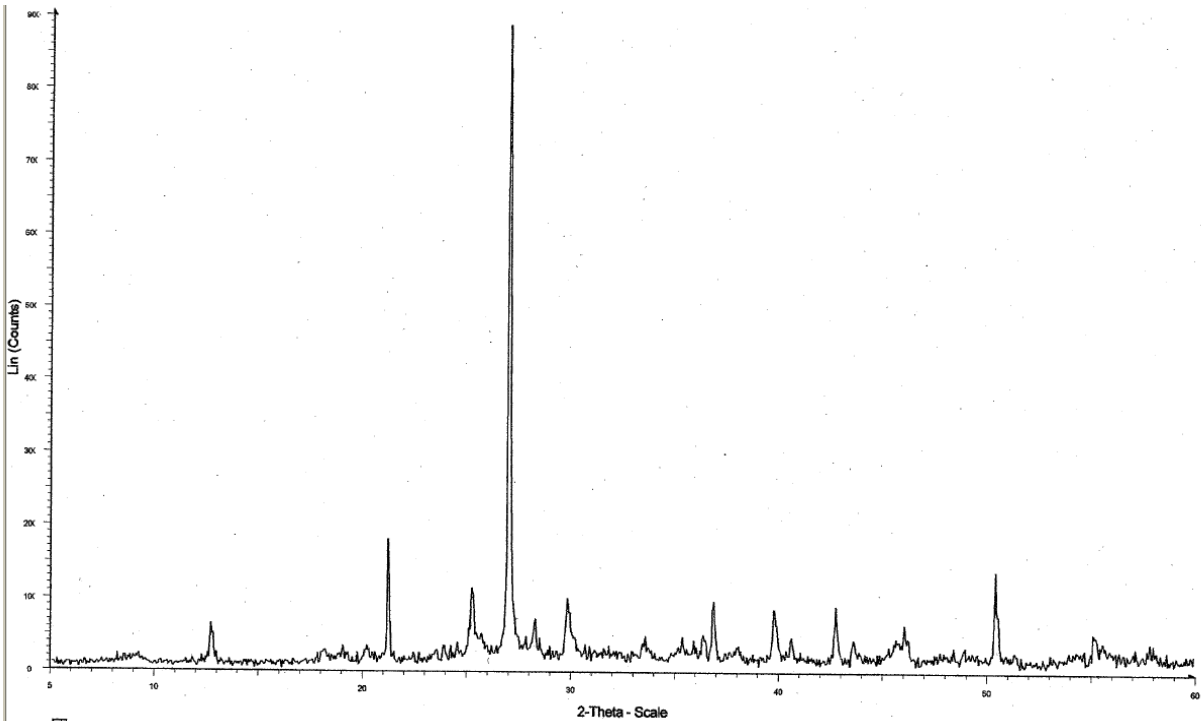


Note: Circle = feedwater; inverted delta = concentrate; square = pond water

Figure 12-2. Piper plots of samples from selected Texas desalination facilities



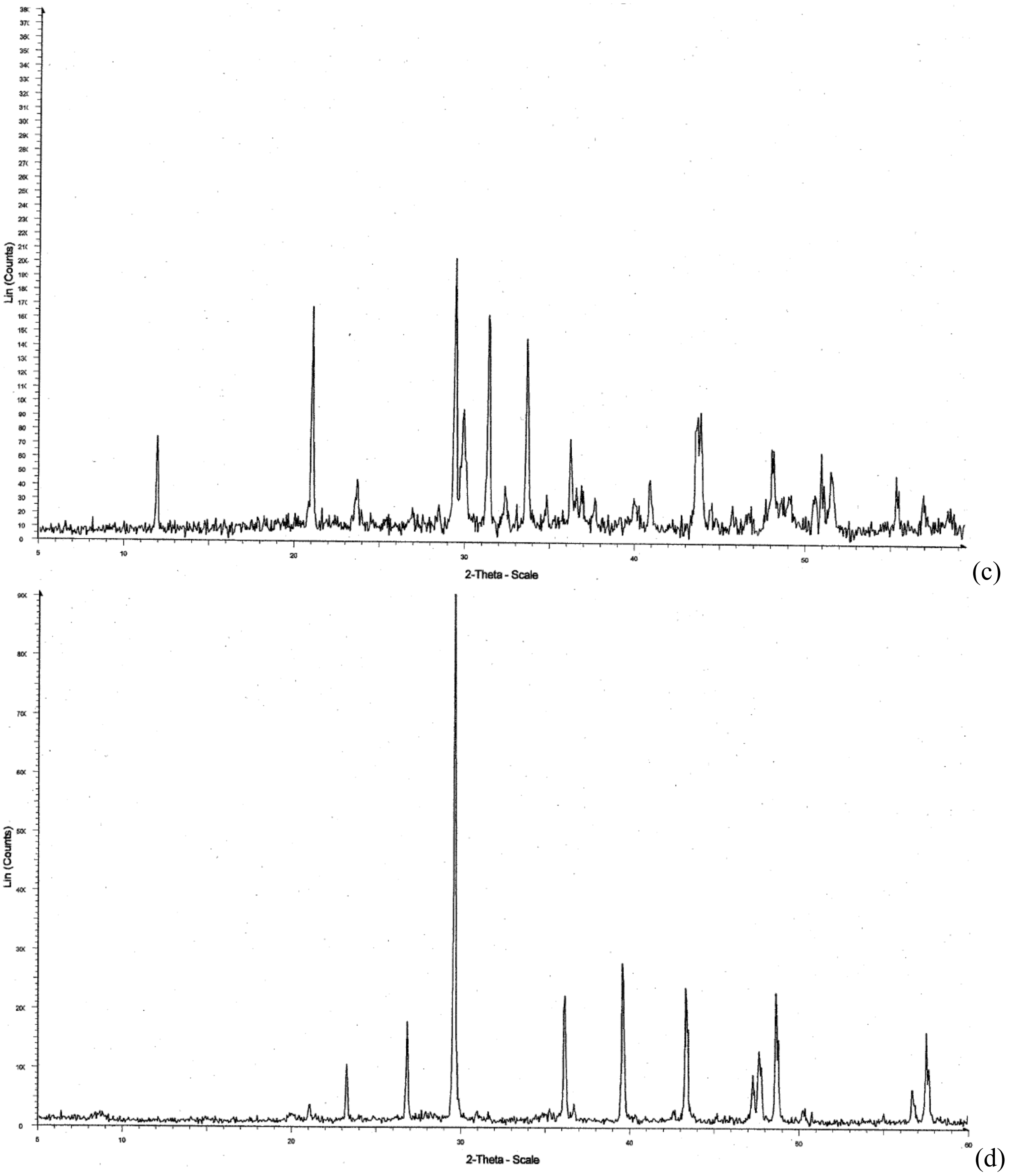
(a)



(b)

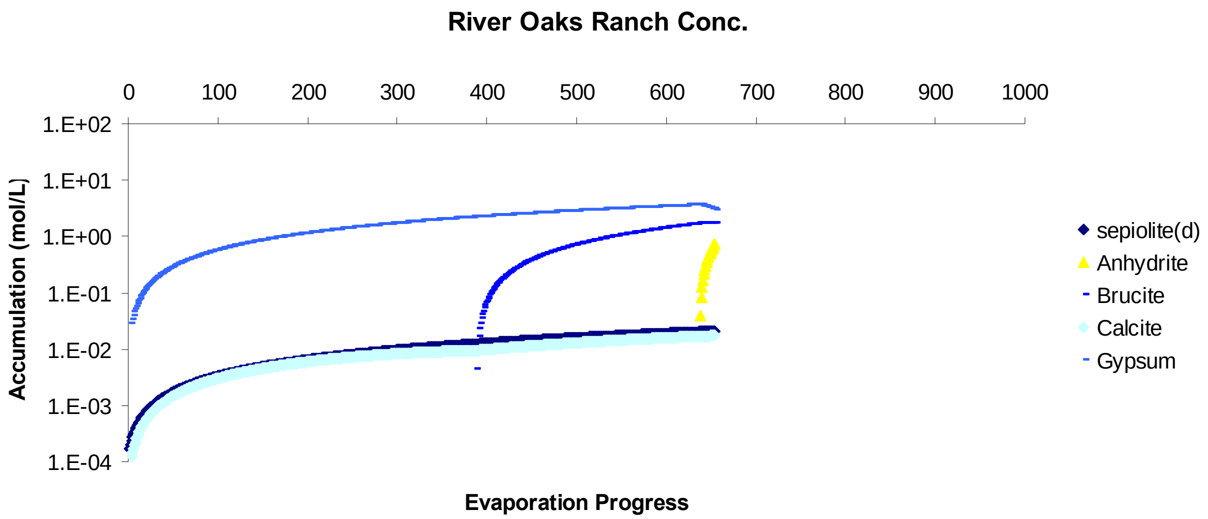
Note: Both samples show the presence of calcite (strong peak at 2$\theta$≈29.5 and secondary peaks at ~39.5 and 43, as well as multiple peaks between 47 and 49) and quartz (strong peak at 2$\theta$≈26.7 and secondary peak at ~21). Sample (a) is dominated by calcite whereas sample (b) contains mostly quartz. There are traces of clay minerals as well but no significant amount of sepiolite (no peak at 2$\theta$≈7.4)

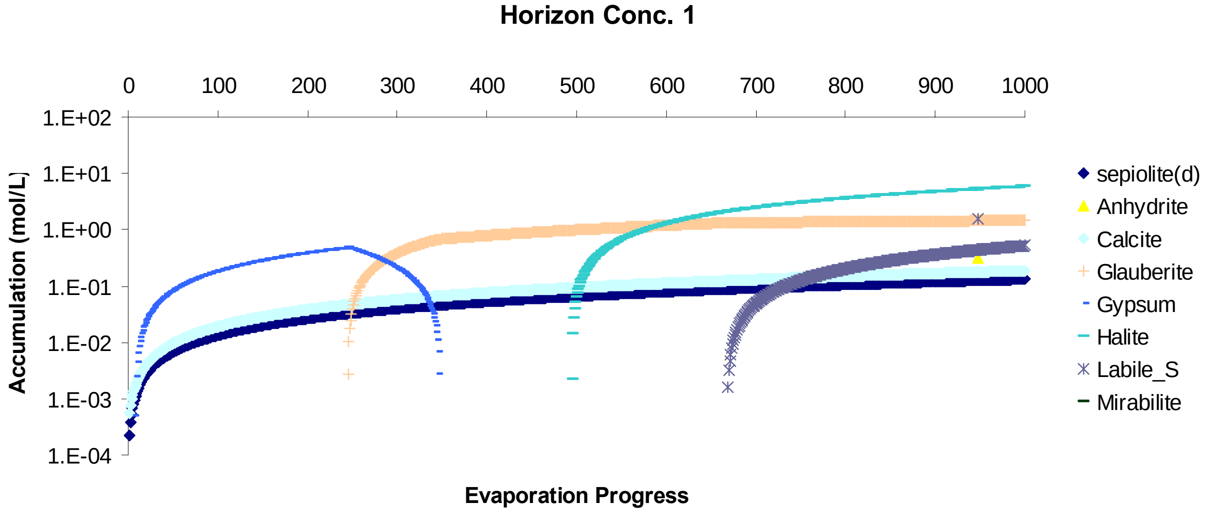
Figure 12-3. Examples of X-ray diffraction patterns of bottom pond sediments: Horizon MUD sample 3 (a), Abilene sample 1 (b), River Oaks Ranch sample 1 (c) and Brady sample 1 (d)

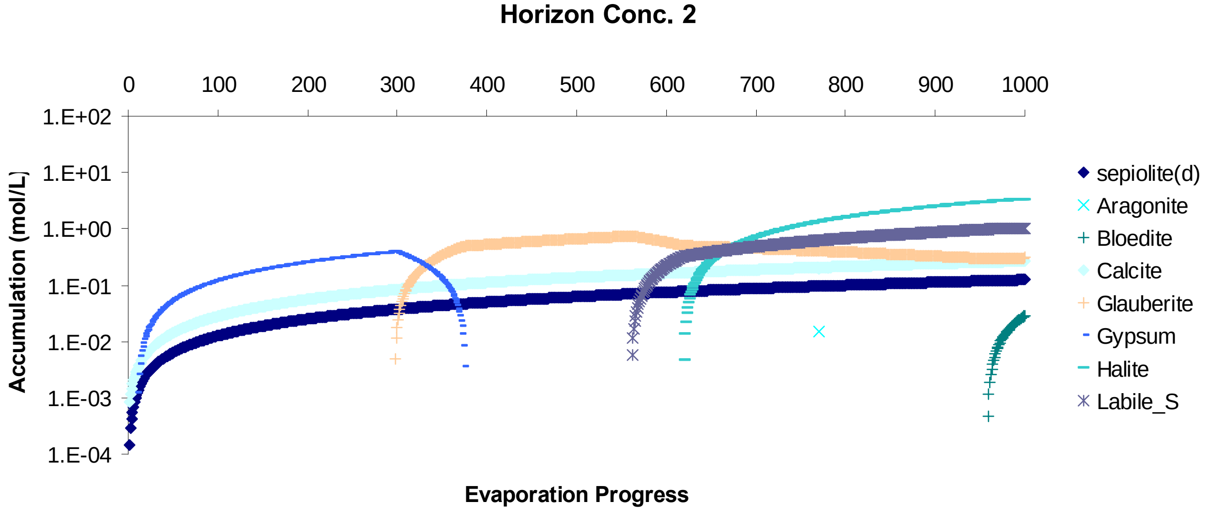


Note: Sample (c) from River Oaks Ranch is dominated by gypsum (strong peaks at ~12, ~21, and strong double peak ~30), with some calcite. Sample (d) is dominated by calcite (strong peak at $2\theta\approx29.5$), with some quartz (strong peak at $2\theta\approx26.7$). There are traces of clay minerals as well but no significant amount of sepiolite (no peak at $2\theta\approx7.4$)

Figure 12-3. Examples of X-ray diffraction patterns of bottom pond sediments (continued): River Oaks Ranch sample 1 (c) and Brady sample 1 (d)



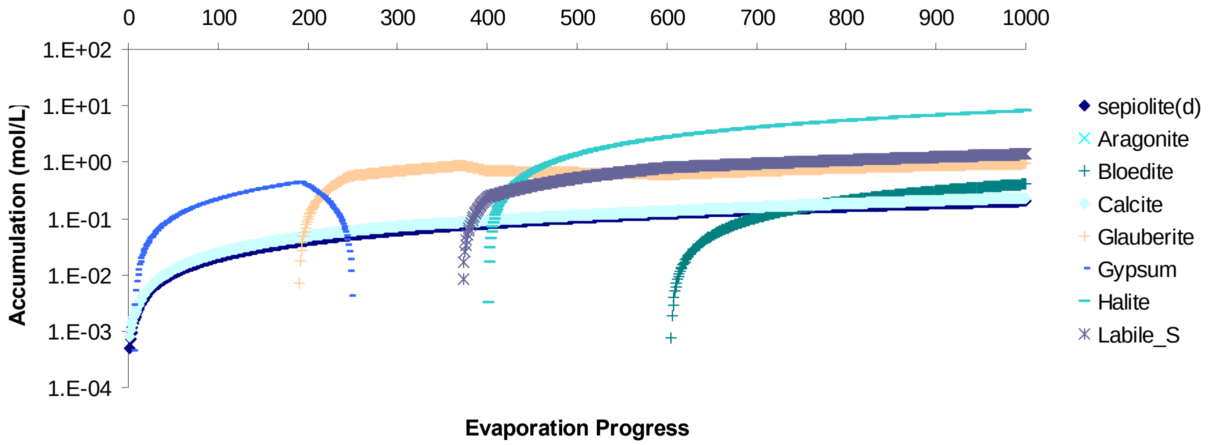




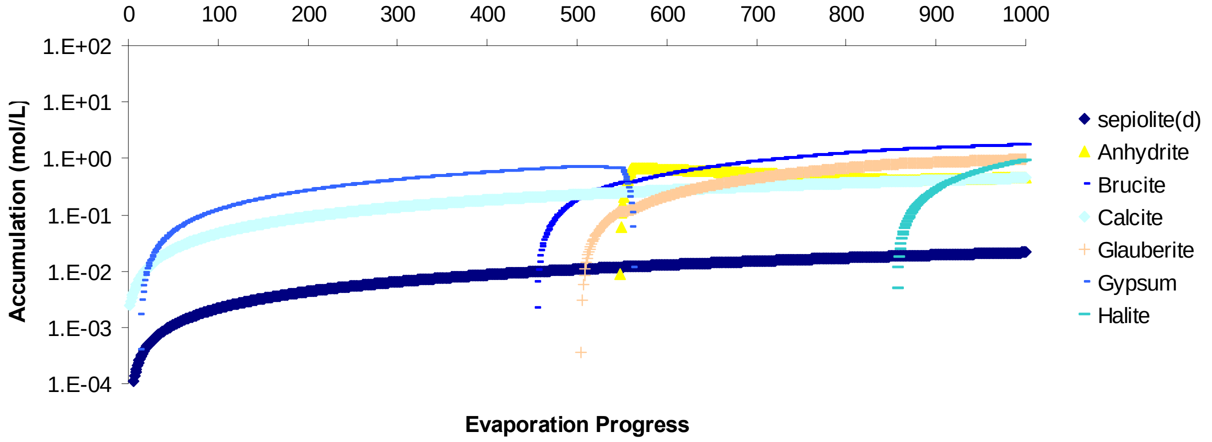
Note: Brady run had convergence issues

Figure 12-4. Mineral precipitation sequence as evaporation progresses using sampled concentrate as the source.

Horizon Conc. 3



Abilene Conc. 1



Brady Conc.

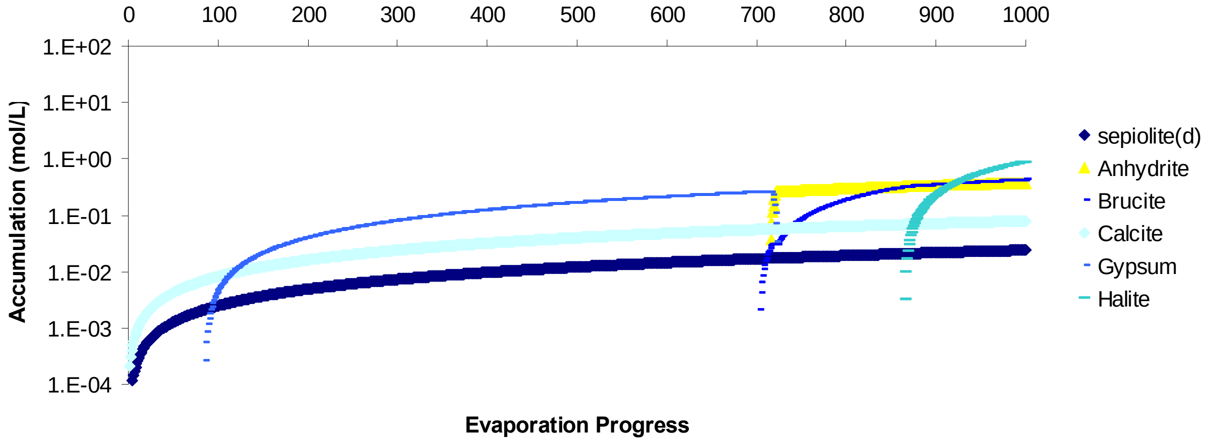


Figure 12-4. Mineral precipitation sequence as evaporation progresses using sampled concentrate as the source. (continued)

## River Oaks Ranch Facility

We visited the River Oaks Ranch PWS facility (#ID 1050099) on August 29, 2006, at the end of a summer with no significant precipitation. Sample locations are shown in Figure 12-5. The evaporation pond area is approximately 2 acres. Two groundwater wells (G1050099A and B) tap the Glenrose–Trinity aquifer at an approximate depth of 650 to 700 ft. The pond has a liner with a leak-detection system through sumps located on its northeast side. Figure 12-6 shows a white gypsum crust. Whitish sediments can also be seen at the bottom of the pond, most of which appears to be windblown dust. The cover photo of this report shows a large area with no vegetative covers and supports this possibility. Figure 12-7 suggests that the pond water depth is more than 1 ft. It was noted that the well water is high in dissolved iron and is treated with a green sand filter before it enters the RO system.

Note: Yellow line across the pond is ~180 m long

Figure 12-5. Aerial view of River Oaks Ranch evaporation pond showing sampling location (courtesy of Google Earth)

Figure 12-6. View of River Oaks Ranch evaporation pond from sampling point #4 showing the gypsum crust

Figure 12-7. View of River Oaks Ranch evaporation pond showing concentrate outfall and water-level gage

## Horizon Regional MUD Facility

The feedwater of this facility (PWS#0710005) comes from multiple wells drilled into the Rio Grande River Alluvium located about 6 miles away. The concentrate stream of the plant receives no treatment but the initial filtration of the well water. Sampling was done on October 10, 2006, 1 day after a precipitation event of about ¼ inch and a rainy summer. Concentrate is disposed of alternatively into two large 20-acre holding ponds (Figure 12-8). Alternatively and every 6 months, the pond bottoms are scraped to get rid of vegetation. None of the ponds was ever observed full, and they are typically partly filled to a depth of a few inches (Figure 12-9 and Figure 12-10). Sediments are locally reduced, as evidenced by the dark coloration and strong odor of the pond-bottom sediment samples. The pond bottoms are composed of a clay liner made up of a mixture of local clay and bentonite.

Note: Yellow line along the ponds is ~380 m long; blue outline shows water body at time of sampling; red outline represents approximate location of pond samples.

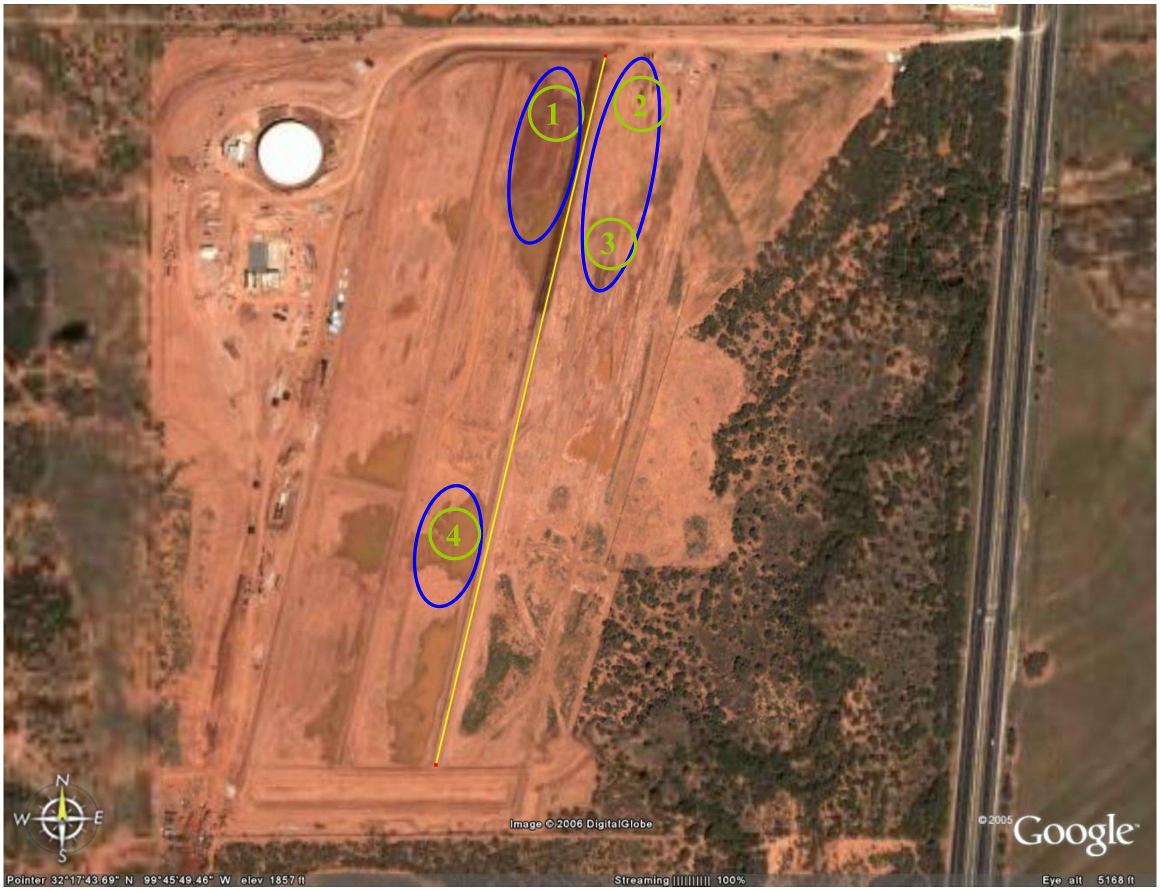
Figure 12-8. Aerial view of Horizon MUD evaporation ponds showing approximate water limits at time of sampling and sampling locations (courtesy of Google Earth)

Figure 12-9. Horizon City MUD north evaporation pond showing the sampled water; outfall is on the far left-hand side of the picture behind the trees.

Figure 12-10. Horizon MUD south pond (not active) being scraped

## Abilene Facility

We visited the recent (2004) facility (PWS#2210001) on October 12, 2006. Figure 12-11 shows it still under construction. Its feedwater comes from nearby Lake Ivie. The evaporation ponds are used only intermittently because the city sewer system is used preferentially to dispose of the desalination concentrate. Pond samples (Figure 12-12 and Figure 12-13) had been diluted by recent rainwater. Operators noted some barium in the water. Pond bottoms are made of compacted local clay.



Note: Yellow line along the ponds is ~732 m (2,402 ft) long; blue outline shows water body at time of sampling; when picture was taken, the site was still apparently under construction

Figure 12-11. Aerial view of evaporation pond of City of Abilene desalination facility showing sampling location (courtesy of Google Earth)

Figure 12-12. City of Abilene east pond showing some of the sampled water (“2” and “3”)

Figure 12-13. City of Abilene west pond showing the liners emplaced to control wave action

## Brady Facility

This facility (PWS#1540001) has a dual feedwater system. Water from the Brady reservoir is desalted and blended with well water from the Hickory aquifer (where radium concentrations are high). The blend has a higher proportion of lake water and meets all new radionuclide regulations. The facility is quite recent (2005), as can be seen in Figure 12-14. The pond bottom is composed of an in-situ liner made up of local clay/silt material (Figure 12-15 and Figure 12-16).

Note: Yellow line along the pond is ~582 m (1,911 ft) long; blue outline shows water body at time of sampling

Figure 12-14. Aerial view of the evaporation pond of City of Brady desalination facility showing sampling location (courtesy of Google Earth)

Figure 12-15. City of Brady evaporation pond showing the sampled water

Figure 12-16. City of Brady evaporation pond seen from the western berm. The pond water is visible under the line of vegetation on the right-hand side of the picture.

# 13 Appendix F:
# A Few Words about Clay Minerals

Minerals of the clay family can be categorized into five main groups (Table 13-1): smectites, vermiculites, chlorites, illites, and kaolinites (e.g., Brady, 1990). They all share a sheetlike crystallographic structure. An elementary layer of a clay mineral is made of either silicon tetrahedrons or aluminum octahedrons with oxygen atoms at the angles. A separate group containing sepiolite, palygorskite, and related minerals can be added. They also contain octahedral and tetrahedral sheets, but they are arranged in a more complex pattern that translates into a needlelike morphology instead of the typical flat crystallographic structure of most clay minerals. In all groups, because of electrical imbalances, cations ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $H^{+}$) are attached to the silicon (Si) or aluminum (Al) elementary layers. Substitution of Si or Al by Mg or other cations is possible. The way Si-Al layers are organized, whatever substitutions are made and whatever cations charge-balance the elementary layers determine the clay group. The elementary pattern (called 1:1) of kaolinites is a stack of single Si and Al layers; there is no associated cation. Neither water nor cations can penetrate the interlayer space. In illite clays, two elementary Si layers sandwich an elementary Al layer (pattern 2:1); some Al is substituted for Si, and K ions glue the multiple Si-Al-Si sheets together. Smectites also have a 2:1 pattern but with some substitution of $Mg^{++}$ for $Al^{3+}$ and/or $Al^{3+}$ for $Si^{4+}$. The stacked sheets are held together by weakly adsorbed $Ca^{2+}$, $Mg^{2+}$, or $Na^{+}$ cations. The peculiarity of smectites (whose group includes montmorillonites as the most common member) is their ability to absorb water between the sheets, the molecular origin of the so-called swelling. Vermiculites have a crystallographic structure similar to that of smectites, although it does not allow as much swelling. Chlorites have an extra sheet of Mg octahedrons (pattern 2:1:1) that, in essence, locked the structure. Chlorites cannot undergo layer expansion. Mixed-layer clay minerals are materials in which different kinds of clay layers alternate with one another. The mixing in vertical stacking can be regular or random. Commonly described mixed-layer clays include illite-vermiculite, illite-smectite, chlorite-vermiculite, chlorite-smectite, and kaolinite-smectite. If not all clays can undergo swelling, all can be subject to flocculation/deflocculation, although at a much smaller scale for sepiolite/palygorskite. Relevant to sealing of evaporation ponds, de-/flocculation impacts permeability of the bottom sediments. When solution salinity decreases, the exchange cations have a tendency to diffuse into the bulk solution. Below some salinity thresholds, diffuse forces overcome attractive Van derWaals forces, and clay particles disperse (Scheuerman and Bergersen, 1990). At a given molar concentration, potassium cations are more effective than sodium cations at holding clay particles together, and calcium cations even more so ($Ca^{2+} >> K^{+} > Na^{+}$).

Kaolinite is formed by degradation of feldspars, especially K-feldspars, particularly at low pHs. Illite also results from the degradation of K-feldspar and other K-rich alumino-silicates, but at higher pHs. Smectites commonly result from the alteration of silicates rich in Ca and Mg. Smectite and vermiculite clays can exchange those adsorbed cations with their environment, typically, $H^{+}$, $Na^{+}$, $K^{+}$, $Ca^{2+}$, and $Mg^{2+}$. Their ability to do so—*reactivity*—is measured by cation exchange capacity (CEC). Smectites have a CEC one order of magnitude higher than that of illites (~1 and 0.1-0.2 moles/kg, respectively) and up to one order of magnitude higher than that of kaolinites (0.01-0.1 moles/kg). There are several general rules to determine the cation most likely to be accepted in the interlayers: the highest charge density wins but only if has not been overwhelmed by a higher concentration of an ion with a smaller charge density. For example, $Na^{+}$ will be the most frequent cation in the interlayers if the smectite is in equilibrium with an NaCl solution with minor $CaCl_2$. The percentage of exchange sites occupied by divalent ions increases with decreasing salinity. The exchange reaction can be written

$$2\text{Na-Clay} + \text{Ca}^{++} = \text{Ca-Clay} + 2\text{Na}^{+}$$

The equilibrium reaction constant can be written as

$$K=(\text{Na}^{+})^{2}(\text{Ca-Clay})/(\text{Ca}^{++})(\text{Na-Clay})^{2}$$

where ( ) represents activity of the reactants. In general, high salinity, high charge density, and low pH (specific case of high charge density) favor clay flocculation, whereas low salinity and low charge density, including high pH, favor deflocculation. Because divalent cations are much more effective at keeping clays flocculated, increasing $\text{Ca}^{++}$ sharply reduces flocculation salinity (also called the critical salt concentration), that is, the salinity at which a given type of clay stays flocculated.

Table 13-1. Physical characteristics of clay minerals

| **Clay Type** | **CEC**[1] | **Expansion**[2] | **Reactivity**[3] | **Formation** |
|---|---|---|---|---|
| Kaolinite | Very Low | None | Low | Degradation of other silicates (K-feldspar, muscovite), precipitate from solution |
| Illite | Low | None | Low | Degradation of other silicates (micas, feldspars) |
| Chlorite | Low | None | Low | Higher temperature clay |
| Vermiculite | Very High | High | High | Degradation of other silicates (micas and Fe-Mg silicates) |
| Smectite | High | High | High | Degradation of other silicates |
| Sepiolite/Palygorskite (group sometimes called hormites) | Low | None | Low | Degradation of other silicates, precipitate from solution |

[1] Cation Exchange Capacity
[2] Expansion of mixed layer clays
[3] Reaction of solution ions with the clay minerals

## Kaolinite Group

Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) has a relatively simple structure, 1:1 of alternating octahedral and tetrahedral sheets. A hydrated version of kaolinite, called halloysite, also exists ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4.2\text{H}_2\text{O}$). Kaolinite derives mainly from the degradation of crystalline rocks such as granites but has been observed to precipitate directly from solution in the laboratory (e.g., Iriarte et al., 2005), and by mixing Na metasilicate and Al chloride in adequate proportions at pH~6, a kaolinitic gel is obtained. The reaction rate to obtain well-crystallized kaolinite can be slow (years) unless appropriate organics are added (Hem and Lind, 1974) or the experiment temperature is raised (Dixon, 1989, p. 481). An overview of precipitation kinetics was given by Nagy (1995, p. 219).

## Illite Group

Low-temperature illite and higher-temperature muscovite have the same ideal chemical formula: $\text{KAl}_2\text{SiAlO}_{10}(\text{OH})_2$, with considerably more substitutions possible for illite. Illite is generally the result of high-temperature silicate degradation, but it can also be neoformed. Its formation is favored by moderate silica concentrations and high potassium concentrations (Langmuir, 1997, p.319).

Other minerals of interest from the illite group include celadonite and glauconite. They have a general chemical formula $K(Mg,Fe^{2+})(Fe^{3+},Al)(Si_4O_{10})(OH)_2$, where an octahedral Al site is substituted for an Mg ion, K being the interlayer cation. A substantial amount of ferrous and ferric iron is also generally present. Minerals of similar composition, generally described as celadonite, have been observed to precipitate in playa/evaporation-pond conditions.

### Smectite Group

Smectites are classified according to the substitution for Al and Si in the octahedral (Al) and tetrahedral (Si) sheets and to the presence of empty sites (e.g., Güven, 1988). In dioctahedral clays two of the three sites are occupied by $Me^{+++}$, where Me is a trivalent cation. While in trioctahedral clays, the three sites are occupied by $Me^{++}$, a divalent cation. Their formation is favored by alkaline pH, high concentrations in silica and divalent cations, and low concentrations in potassium (Langmuir, 1997, p.319).

*Dioctahedral Smectites*

The most common dioctahedral smectite clay minerals are from the montmorillonite–beidellite series of general formula: $E_{x+y}(Al_{2-y}Mg_y)(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$, where E represents interlayer cations needed to charge balance the substitution of $Mg^{2+}$ for $Al^{3+}$ and/or $Al^{3+}$ for $Si^{4+}$. $Fe^{3+}$ can also be present in significant amounts in the octahedral sites. If y>x, the clay is a montmorillonite, if x>y, the clay is a beidellite. In the PHREEQC thermodynamic database, montmorillonites are represented by x=0 and y=0.33—for example, $Ca_{0.165}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$ for calcium montmorillonite. The substitution of Mg for Al creates a deficit of charge in the octahedral sheet that must be balanced by an interlayer cation. A sodium montmorillonite would have an end-member composition of $Na_{0.33}(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$. Similarly, magnesium and potassium montmorillonite can be defined.

Bentonite is a rock composed of a large fraction of montmorillonite, especially Na-montmorillonite (Na-bentonite or swelling bentonite) or Ca-montmorillonite (Ca-bentonite or nonswelling bentonite). Only Na-bentonite expands greatly when wet. Na-bentonites are often used as a barrier to transport. They are also called swelling bentonites because they can absorb (and lose) a lot of water. They occur naturally in the U.S. in Wyoming and other northwestern states, deriving mostly from the degradation of volcanic ash layers. Ca-bentonites do not swell as much and are sometimes called "nonswelling" bentonites, and they have a higher Mg/Al ratio. Commercial Na-bentonites have a low Mg/Al ratio. Ca-bentonites are more common worldwide and occur in the U.S. in the Gulf Coast area, also deriving from material of volcanic origin. Monovalent ions ($Na^+$) are generally less strongly attracted to the surface of clays, allowing more water to slip in and yielding a higher swelling capacity. High-salinity solutions, especially those rich in divalent ions, lead to a compression of the double layer of smectites and an increase in permeability. Sepiolite is not subject to this effect.

At the other end of the dioctahedral smectite series is beidellite, a common example of which is the case with x=0.33 and y=0. The chemical formula of Ca-beidellite is $Ca_{0.165}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$, that is, $Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$. In the beidellite case, substitution occurs in the tetrahedrons ($Al^{3+}$ for $Si^{4+}$), as opposed to the montmorillonite case, where substitution occurs in the octahedrons ($Mg^{2+}$ for $Al^{3+}$). However, similar to montmorillonite, the interlayer cations can be $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $H^+$, $NH_4^+$, $Fe^{2+}$, or another trace element. Nontronite is equivalent to a Fe-rich beidellite. It is clear that beidellites have a higher Al/Si ratio (e.g., 2.33/3.67=0.64) than that of montmorillonites (e.g., 1.67/4=0.42).

### *Trioctahedral Smectites*

Magnesium and ferrous ions are common trioctahedral substitution cations. A general formula for those Fe-Mg trioctahedral smectites is $E_x(Fe^{2+}, Mg)_3(Si_{4-x}Al_x)O_{10}(OH)_2$ with $x<0.6$. They are termed saponite and iron-saponite. A typical formula for Ca-saponite is $Ca_{0.165}Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2$, and similar formulas can be written for Mg-, K-, Na-, or H-saponite. Iron saponite is much less common because ferrous ion is not stable in surface conditions, as in most evaporation ponds. Stevensite is equivalent to nonaluminous saponite (no Al in the tetrahedral sheet): $E_xMg_3(Si_4O_{10}(OH)_2$.

Trioctahedral smectites can precipitate directly from solution, as demonstrated by Decarreau (1985) and Vogels et al. (2005). A specific clay mineral, closely related to stevensite (hectorite) and of beneficial properties, has been synthesized in large quantities for the oil industry.

## Sepiolite—Palygorskite Group

This group is also called the hormite group, although usage of this term is not widespread. Similar to the situation in the smectite group, trioctahedral (sepiolite) and dioctahedral (palygorskite) structures in this group can be defined. Although aluminum sepiolite exists, there is a compositional gap between them and palygorskites (Jones and Galan, 1988).

## Other Phyllosilicates of Interest

Talc ($Mg_3Si_4O_{10}(OH)_2$), like sepiolite, is an Mg-Si silicate. It is the trioctahedral form of the simplest 2:1 phyllosilicates. Talc has been reported in evaporites and thus could directly precipitate from solutions (Evans and Guggenheim, 1985, p. 265) at high pH (Zelazny and White, 1989, p. 541).

## Stability Fields

Table 13-2 is extracted from Jones and Galan (1988) and shows the environmental conditions in which magnesian clays predominate.

Table 13-2. Environmental conditions for magnesian clay associations

| Condition | Range | Palygorskite | Sepiolite | Trioct. Smectites |
|---|---|---|---|---|
| pH and alkalinity | pH<8.5 (moderate) | ++ | + | - |
| | pH=8-9.5 (intermediate) | + | ++ | + |
| | pH>9.5 (high) | - | - | ++ |
| Major constituent ratios | High (Mg+Si)/Al | + | ++ | - |
| | High (Mg+Fe)/Si | - | - | ++ |
| Sediment/water $P_{CO2}$ | High | - | - | ++ |
| | Low | ++ | ++ | - |
| Alkali salinity | High | - | - | ++ |
| | Intermediate | + | ++ | + |
| | Moderate | ++ | + | - |

# 14 Appendix G:
# Commented Geochemical Input Files

The following pages present one of the PHREEQC input files. Input file statements are in Arial 10, whereas comments are in Time New Roman 12. The expressions @text@ are placeholders for actual values read from a central manager routine that allows many cases to run automatically and processes them with limited effort.

All items in "SOLUTION_MASTER_SPECIES," "SOLUTION_SPECIES," and "PHASES" were added to complement the Pitzer database, which is lacking data on Si and Al and their associated aqueous species and minerals. Results of such a hybrid database are not as accurate as those from a stand-alone Pitzer database, but they give semiquantitative information

```
DATABASE  pitzer.dat

SOLUTION_MASTER_SPECIES
#add those elements not present in pitzer.dat
Al      Al+3          0.0     Al            26.9815
Si      H4SiO4        0.0     SiO2          28.0843
#use same molecular weight as in llnl.dat for easier handling of templates
H       H+            -1.     H             1.0079
H(1)    H+            -1.     0.0
E       e-            0.0     0.0           0.0
O       H2O           0.0     O             15.994
O(-2)   H2O           0.0     0.0
#to compute how much caustic/acid is added
Nx      Nx+           0.0     Nx            22.9898
Cx      Cx-           0.0     Cx            35.453

SOLUTION_SPECIES
Nx+ =  Nx+
          -llnl_gamma     4.0000
          log_k 0
Cx- =  Cx-
          -llnl_gamma     4.0000
          log_k 0
Al+3 = Al+3
      log_k         0.000
      -gamma   9.0000   0.0000
H4SiO4 = H4SiO4
      log_k         0.000
Al+3 + H2O = AlOH+2 + H+
      log_k         -5.00
      delta_h 11.49   kcal
      -analytic     -38.253      0.0        -656.27      14.327
Al+3 + 2 H2O = Al(OH)2+ + 2 H+
      log_k         -10.1
      delta_h 26.90         kcal
      -analytic     88.500       0.0        -9391.6      -27.121
Al+3 + 3 H2O = Al(OH)3 + 3 H+
      log_k         -16.9
      delta_h 39.89         kcal
      -analytic     226.374      0.0        -18247.8     -73.597
Al+3 + 4 H2O = Al(OH)4- + 4 H+
      log_k         -22.7
      delta_h 42.30         kcal
      -analytic     51.578       0.0        -11168.9     -14.865
Al+3 + SO4-2 = AlSO4+
```

```
        log_k           3.5
        delta_h 2.29 kcal
Al+3 + 2SO4-2 = Al(SO4)2-
        log_k           5.0
        delta_h 3.11 kcal
Al+3 + HSO4- = AlHSO4+2
        log_k           0.46
H4SiO4 = H3SiO4- + H+
        log_k           -9.83
        delta_h 6.12            kcal
        -analytic       -302.3724     -0.050698      15669.69      108.18466    -1119669.0
H4SiO4 = H2SiO4-2 + 2 H+
        log_k           -23.0
        delta_h 17.6            kcal
        -analytic       -294.0184     -0.072650      11204.49      108.18466    -1119669.0

PHASES
Gibbsite
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           8.110
        delta_h -22.800 kcal
Al(OH)3(a)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           10.800
        delta_h -26.500 kcal
Kaolinite
        Al2Si2O5(OH)4 + 6 H+ = H2O + 2 H4SiO4 + 2 Al+3
        log_k           7.435
        delta_h -35.300 kcal
Albite
        NaAlSi3O8 + 8 H2O = Na+ + Al(OH)4- + 3 H4SiO4
        log_k           -18.002
        delta_h 25.896 kcal
Anorthite
        CaAl2Si2O8 + 8 H2O = Ca+2 + 2 Al(OH)4- + 2 H4SiO4
        log_k           -19.714
        delta_h 11.580 kcal
K-feldspar
        KAlSi3O8 + 8 H2O = K+ + Al(OH)4- + 3 H4SiO4
        log_k           -20.573
        delta_h 30.820  kcal
K-mica
        KAl3Si3O10(OH)2 + 10 H+ = K+ + 3 Al+3 + 3 H4SiO4
        log_k           12.703
        delta_h -59.376 kcal
Chlorite(14A)
        Mg5Al2Si3O10(OH)8 + 16H+ = 5Mg+2 + 2Al+3 + 3H4SiO4 + 6H2O
        log_k           68.38
        delta_h -151.494 kcal
Ca-Montmorillonite
        Ca0.165Al2.33Si3.67O10(OH)2 + 12 H2O = 0.165Ca+2 + 2.33 Al(OH)4- + 3.67 H4SiO4 + 2 H+
        log_k           -45.027
        delta_h 58.373  kcal
Talc
        Mg3Si4O10(OH)2 + 4 H2O + 6 H+ = 3 Mg+2 + 4 H4SiO4
        log_k           21.399
```

```
        delta_h -46.352 kcal
Illite
        K0.6Mg0.25Al2.3Si3.5O10(OH)2 + 11.2H2O = 0.6K+ + 0.25Mg+2 + 2.3Al(OH)4- + 3.5H4SiO4 +
1.2H+
        log_k           -40.267
        delta_h 54.684 kcal
Sepiolite
        Mg2Si3O7.5OH:3H2O + 4 H+ + 0.5H2O = 2 Mg+2 + 3 H4SiO4
        log_k           15.760
        delta_h -10.700 kcal
Sepiolite(d)
        Mg2Si3O7.5OH:3H2O + 4 H+ + 0.5H2O = 2 Mg+2 + 3 H4SiO4
        log_k           18.660
Alunite
        KAl3(SO4)2(OH)6 + 6 H+ = K+ + 3 Al+3 + 2 SO4-2 + 6H2O
        log_k           -1.400
        delta_h -50.250 kcal
        log_k           -0.1
        delta_h -14.74  kcal
SiO2(a)
        SiO2 + 2 H2O = H4SiO4
        log_k           -2.710
        delta_h 3.340 kcal
        -analytic       -0.26           0.0          -731.0
Chalcedony
        SiO2 + 2 H2O = H4SiO4
        log_k           -3.550
        delta_h 4.720 kcal
        -analytic       -0.09           0.0          -1032.0
Quartz
        SiO2 + 2 H2O = H4SiO4
        log_k           -3.980
        delta_h 5.990 kcal
        -analytic       0.41           0.0          -1309.0
Diaspore  #translated from llnl.dat (provided with PHREEQC download)
 AlHO2 + 3. H+1 =  Al+3 + 2. H2O
       log_k      7.757000
```

The following fictitious species allow keeping pH at the chosen value by adding either acid if the pH is too high, or caustic if the pH is too low.

```
###Fictituous phases for constant pH
Fix_H+
H+ = H+
log_k 0.0
BaseNa
NxOH = Nx+ + OH-
log_k 0.0
AcidHCl
#HCx = H+ + Cx-
HCl = H+ + Cl-
log_k 0.0
```

This is the beginning of the simulations. “SOLUTION 0” is the concentrate water set at equilibrium with $CO_2$ and, depending on the run, with diaspore (AlOOH). In addition, sepiolite precursors are also added at this stage when warranted. In the following simulations, the amount of water treated by PHREEQC will remain constant as some “SOLUTION 0” (that is, concentrate) is added to replenish the water lost through evaporation. As pure water is lost and replaced by an aqueous solution, the salinity in the pond (“SOLUTION 1”) will progressively increase.

```
SOLUTION 0  Outfall Water
-units ppm
pH @pH@
#pe @pe@
temp @T_C@
Ca @Ca@
Mg @Mg@
Na @Na@
K  @K@
Si @Si@
Cl @Cl@
Alkalinity @HCO3@ as HCO3
S(6) @SO4@
Nx 1.e-16
Cx 1.e-16

REACTION 0
MgCl2   @MgReact@
Na2SiO3          @SiReact@
@MoleReact@ moles

SOLUTION_SPECIES
H2O + 0.01e- = H2O-0.01 # helps convergence
          log_k    -9.

EQUILIBRIUM_PHASES  0
CO2(g)             @CO2@          99
#diaspore 0 99

SAVE SOLUTION 0
END
```

“SOLUTION 1” is the pond water whose salinity slowly increases as pure water is removed and replaced by concentrate water and its companion ions. This section of the input file dictates what information to send to the output file and how often and in what format (“USER_PUNCH” and “SELECTED_OUTPUT”) to facilitate the user’s interpretation of the results. The “EQUILIBRIUM_PHASES” field lists the species allowed to precipitate or to have the solution equilibrated with.

```
SOLUTION 1   Pond Water (initially same as outfall water)
-units ppm
pH @pH@
#pe @pe@
temp @T_C@
Ca @Ca@
Mg @Mg@
Na @Na@
K  @K@
Si @Si@
```

```
Cl @Cl@
Alkalinity @HCO3@ as HCO3
S(6) @SO4@

USER_PUNCH
    -headings AcidAdded(moles) BaseAdded(moles) TDS(g.L-1) Time(yr) Vol.Min.(cm3.L-1)
Prec.Height(inch) Sepiol.Vol.frac%
    -start
#10 REM convert to ppm
20 PUNCH TOT("Cx")
25 PUNCH TOT("Nx")
# TDS in mg/L
60 TDS=40.08*TOT("Ca")+24.305*TOT("Mg")+22.9898*TOT("Na")+22.9898*TOT("Nx")+39.0983*TOT(
"K")+35.453*TOT("Cl")+96.064*TOT("S")+61.0111*TOT("C")+60.0843*TOT("Si")+26.9815*TOT("Al")
70 PUNCH TDS
# time in years
80 MYTIME=(SIM_NO-1)*@height@/(@evap@/12)/12
90 PUNCH MYTIME
# precipitate volume in cm3
100 VOLUME=142.8*EQUI("sepiolite(d)")+150*EQUI("Ca-
Montmorillonite")+45.94*EQUI("Anhydrite")+34.15*EQUI("Aragonite")+65.5*EQUI("Arcanite")+129.57*EQ
UI("Bischofite")+149.98*EQUI("Bloedite")+24.63*EQUI("Brucite")+151.19*EQUI("Burkeite")+36.934*EQUI
("Calcite")+172.58*EQUI("Carnallite")+64.365*EQUI("Dolomite")+146.8*EQUI("Epsomite")+148.15*EQUI(
"Gaylussite")+246.23*EQUI("Glaserite")+101.12*EQUI("Glauberite")+74.69*EQUI("Gypsum")+27.015*EQ
UI("Halite")+132.58*EQUI("Hexahydrite")+115.3*EQUI("Kainite")+46.14*EQUI("Kalicinite")+56.6*EQUI("Ki
eserite")+182.504*EQUI("Labile_S")+95.74*EQUI("Leonhardite")+166.3*EQUI("Leonite")+28.018*EQUI("
Magnesite")+219.8*EQUI("Mirabilite")+427.275862068966*EQUI("Misenite")+38.62*EQUI("Nahcolite")+1
95.99*EQUI("Natron")+74.79*EQUI("Nesquehonite")+110.76*EQUI("Pentahydrite")+102.3*EQUI("Pirsson
ite")+218.1*EQUI("Polyhalite")+33.056*EQUI("Portlandite")+197.5*EQUI("Schoenite")+37.524*EQUI("Syl
vite")+124.2*EQUI("Syngenite")+29*EQUI("SiO2(a)")
105 IF (VOLUME>0) THEN sepiolvolume =142.8*EQUI("sepiolite(d)")/VOLUME*100 ELSE
sepiolvolume=-99
110 VOLUME=VOLUME/((1+(SIM_NO-1)*@mixkw@)/SIM_NO)
120 PUNCH VOLUME
130 VOLUME=VOLUME/1000*@height@
140 PUNCH VOLUME
150 PUNCH sepiolvolume
    -end

SELECTED_OUTPUT
        -file       @file.xls@
        -totals Ca Mg Na Nx K Cl Cx S C Si Al
        -equilibrium_phases sepiolite(d) Ca-Montmorillonite Anhydrite Aragonite Arcanite Bischofite
Bloedite Brucite Burkeite Calcite Carnallite Dolomite Epsomite Gaylussite Glaserite Glauberite Gypsum
Halite Hexahydrite Kainite Kalicinite Kieserite Labile_S Leonhardite Leonite Magnesite Mirabilite Misenite
Nahcolite Natron Nesquehonite Pentahydrite Pirssonite Polyhalite Portlandite Schoenite Sylvite
Syngenite SiO2(a)
        -saturation_indices CO2(g) sepiolite(d) Ca-Montmorillonite Anhydrite Aragonite Arcanite
Bischofite Bloedite Brucite Burkeite Calcite Carnallite Dolomite Epsomite Gaylussite Glaserite Glauberite
Gypsum Halite Hexahydrite Kainite Kalicinite Kieserite Labile_S Leonhardite Leonite Magnesite Mirabilite
Misenite Nahcolite Natron Nesquehonite Pentahydrite Pirssonite Polyhalite Portlandite Schoenite Sylvite
Syngenite SiO2(a)
        -time     true
        -step     true
        -ionic_strength true
        _charge_balance true
```

```
        _percent_error true
        -water true

PRINT
        -saturation_indices        true
        -species            true
KNOBS
        -logfile            false
        -diagonal_scale true

MIX   1
1   1
0   @mixkw@

REACTION 1
H2O -1.0
@reactkw@ moles #mix=@mixkw@

EQUILIBRIUM_PHASES 1
sepiolite(d) 0 0                 Glaserite  0 0                  Nahcolite  0 0
Ca-Montmorillonite 0 0           Glauberite  0 0                 Natron  0 0
Anhydrite  0 0                   Gypsum  0 0                     Nesquehonite  0 0
Aragonite  0 0                   Halite  0 0                     Pentahydrite  0 0
Arcanite  0 0                    Hexahydrite  0 0                Pirssonite  0 0
Bischofite  0 0                  Kainite  0 0                    Polyhalite  0 0
Bloedite  0 0                    Kalicinite  0 0                 Portlandite  0 0
#Brucite  0 0                    Kieserite  0 0                  Schoenite  0 0
Burkeite  0 0                    Labile_S  0 0                   Sylvite  0 0
Calcite  0 0                     Leonhardite  0 0                Syngenite  0 0
Carnallite  0 0                  Leonite  0 0                    #Trona  0 0
#Dolomite  0 0                   #Magnesite  0 0                 SiO2(a) 0 0
Epsomite  0 0                    Mirabilite  0 0
Gaylussite  0 0                  Misenite  0 0
#CO2(g)                 @CO2@       99
#diaspore 0 99
#Fix_H+ -@fixph@ BaseNa 99
Fix_H+ -@fixph@ AcidHCl 99
SAVE SOLUTION 1
SAVE EQUILIBRIUM_PHASES 1
END
```

Hundreds of the following simulations are added to the input file, each corresponding to a single point along the evaporation progress line.

```
USE SOLUTION 1
USE EQUILIBRIUM_PHASES 1
MIX   1
1   1
0   @mixkw@
REACTION 1
H2O -1.0
@reactkw@ moles #mix=@mixkw@

SAVE SOLUTION 1
SAVE EQUILIBRIUM_PHASES 1
END
```

# 15 Appendix H:
# Results of Some Geochemical Runs

Precipitation sequence is a function of the ratio *e*/*h*, where *e* is the net evaporation rate (in inches/month) and *h* is the pond depth. For easy scaling, results are presented in terms of evaporation progress (Figure 15-1). As an example, if a pond depth of 3 inches is assumed, an evaporation progress of 500 corresponds to duration values shown in Table 15-1, according to the formula: $e/h=(CF-1)/t$, where *CF* is the concentration factor (equivalent to the more descriptive term of evaporation progress) and *t* is time.

Table 15-1. Correspondence table between evaporation progress as given in plot abscissa and duration (calendar years)

| **Group** | **Pond Depth (inches)** | **Annual Evaporation Rate (inches/yr)** | **Duration (years) Corresponding to Evaporation Progress = 500** | **Evaporation Progress Value Corresponding to Duration = 30 years** |
|---|---|---|---|---|
| Mixed Alluvium | 3 | 32.2 | 47 | 322 |
| Brazos River Alluvium | 3 | 8.9 | 169 | 89 |
| Rio Grande Alluvium | 3 | 45.4 | 33 | 454 |
| Seymour | 3 | 30.8 | 49 | 308 |
| Bolson | 3 | 48.6 | 31 | 486 |
| Ogallala | 3 | 41.7 | 36 | 417 |
| Pecos Valley | 3 | 50.3 | 30 | 503 |
| Gulf Coast Sandstone | 3 | 22.7 | 66 | 227 |
| Eocene All Samples | 3 | 19.2 | 78 | 192 |
| Eocene Mixed | 3 | 19.2 | 78 | 192 |
| Eocene Na Dominant | 3 | 19.2 | 78 | 192 |
| Cretaceous Limestone | 3 | 33.8 | 44 | 339 |
| Cret. Sandst. All Samples | 3 | 23.9 | 63 | 240 |
| Cret. Sandst. Mixed | 3 | 23.9 | 63 | 240 |
| Cret. Sandst. Na Dominant | 3 | 23.9 | 63 | 240 |
| Triassic Sandstone | 3 | 40.6 | 37 | 406 |
| Permian Evaporite | 3 | 36.1 | 42 | 361 |
| Permian Limestone | 3 | 30.0 | 50 | 300 |
| Permian Sandstone | 3 | 34.5 | 43 | 345 |
| Bone Spring – Victorio Peak | 3 | 46.2 | 32 | 462 |
| Capitan Reef | 3 | 42.4 | 35 | 424 |
| Pennsylvanian | 3 | 25.0 | 60 | 250 |
| Llano Uplift | 3 | 23.3 | 64 | 233 |
| Surface Water | 3 | 30.3 | 49 | 303 |

Because runs for two groups (Permian Limestone and Permian Sandstone) did not converge properly with the Pitzer database, we used the less appropriate LLNL database as a substitute. To assess the importance of the exchange, comparison of results from two groups (Mixed Alluvium and Surface Water) with similar evaporation rates were run successively with the Pitzer and LLNL databases, as presented in Figure 15-2. Differences, although not negligible, are minor, most likely because ionic strength has not built up too high yet. Figure 15-3 displays the mineral volume accumulation for two pond depths (3 and 12 inches). Figure 15-4 presents a set of results similar to that in Figure 15-1. Runs were done by adding 0.01 mol/L of sepiolite precursor (2 moles of Mg and 3 moles of Si /mol of precursor). Figure 15-5 is equivalent to Figure 15-3 for runs with the addition of the sepiolite precursor. The impact of adding Ca-montmorillonite to the mineral list is displayed in Figure 15-6. In some instances, sepiolite is still the major clay to precipitate; in others, only Ca-montmorillonite is. In most cases when Ca-montmorillonite is allowed to precipitate, it precipitates in the early stages of evaporation, and sepiolite precipitates later than in the no Ca-montmorillonite case.

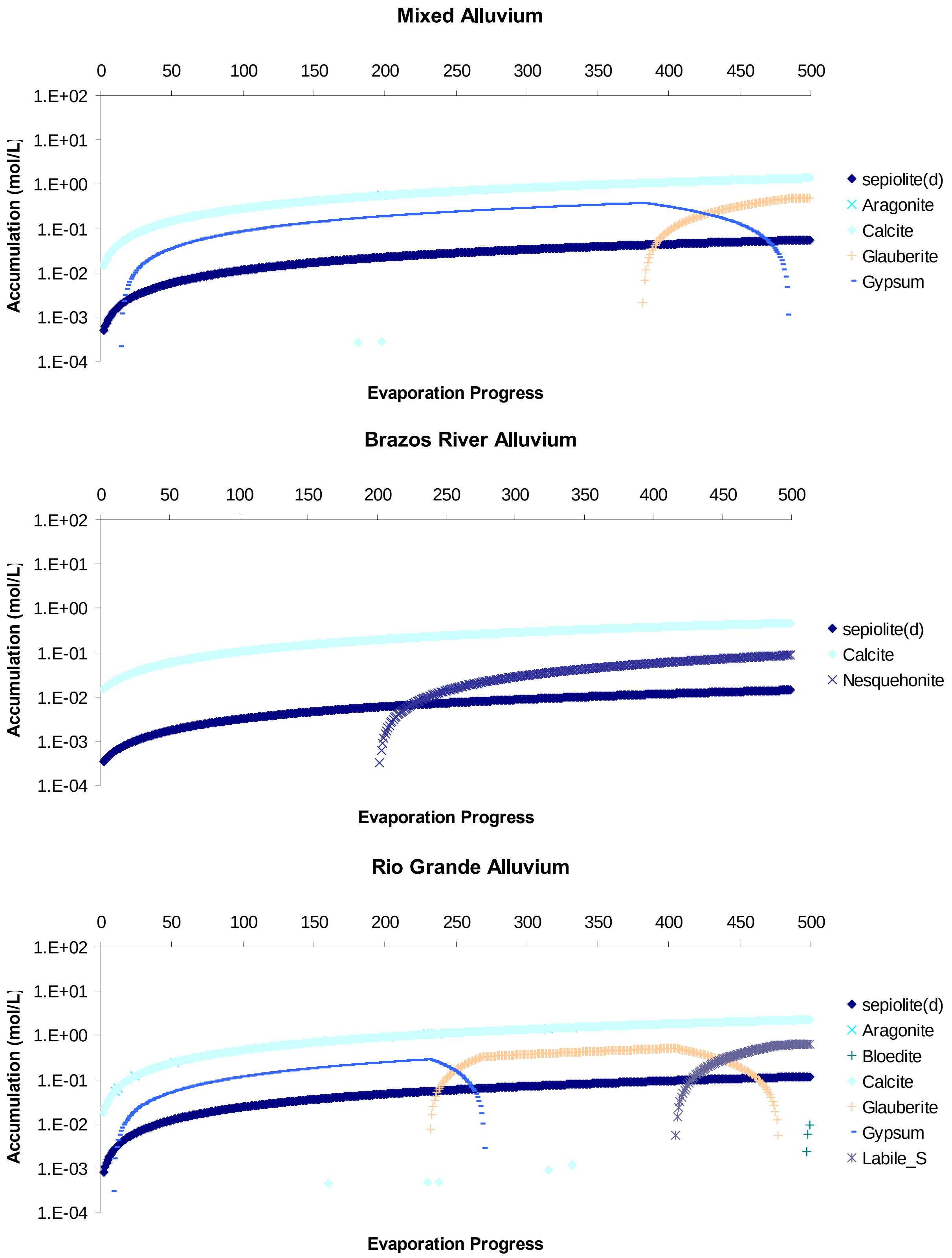
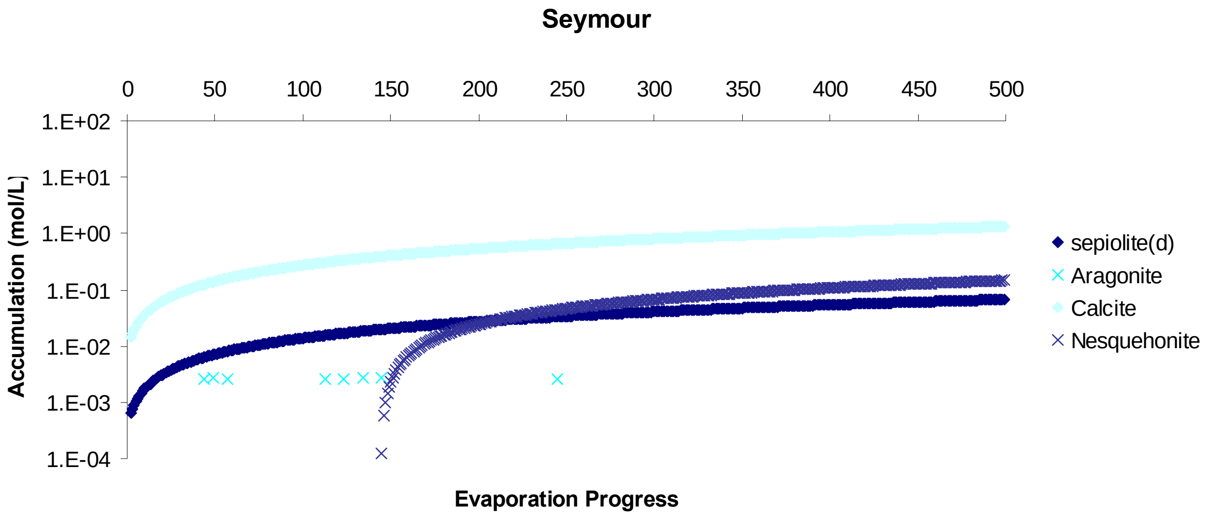
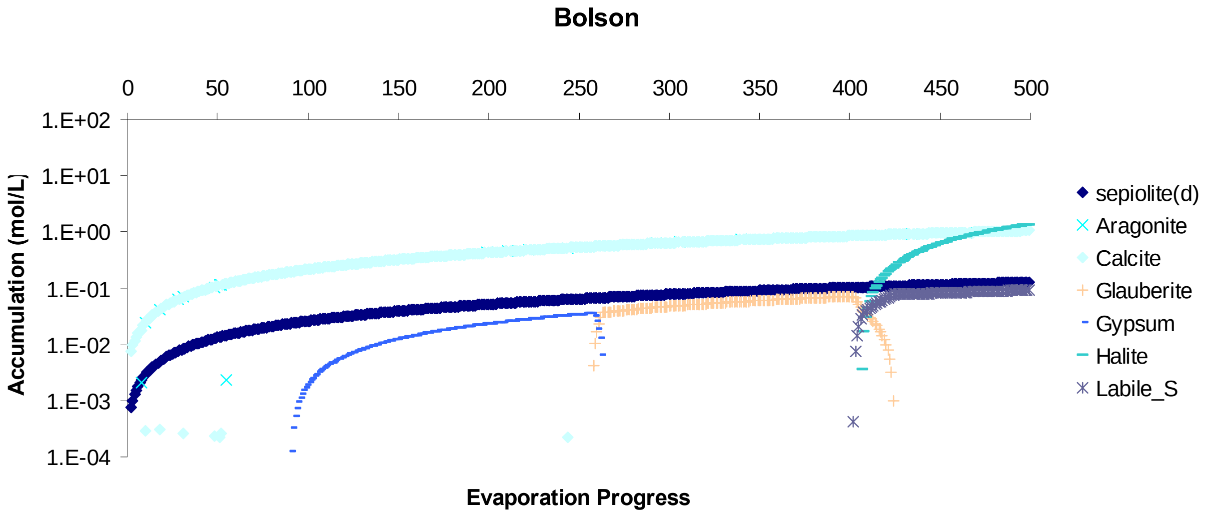


Figure 15-1. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions





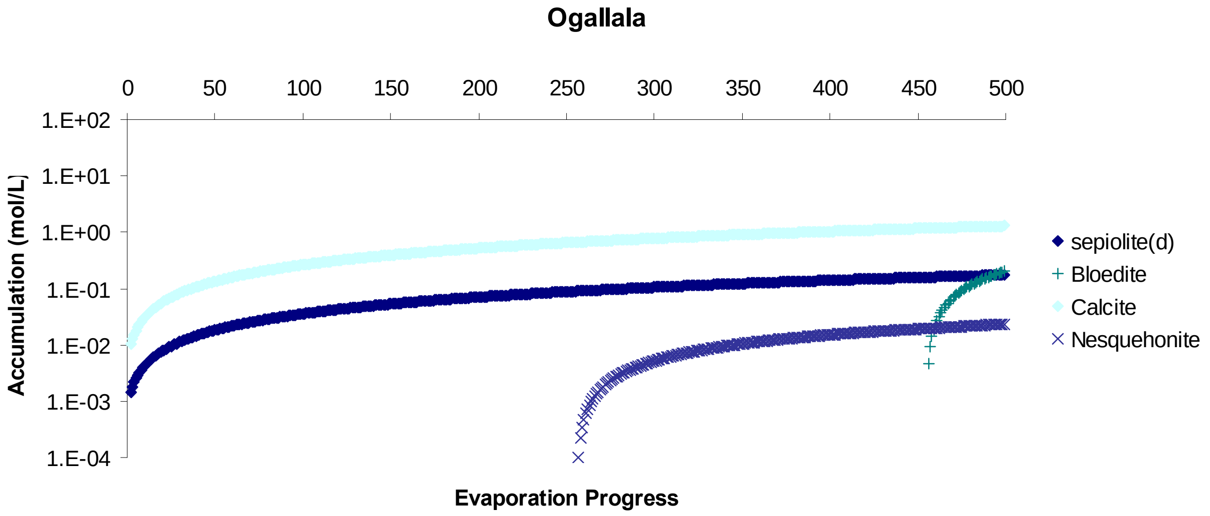


Figure 15-1. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions (continued)

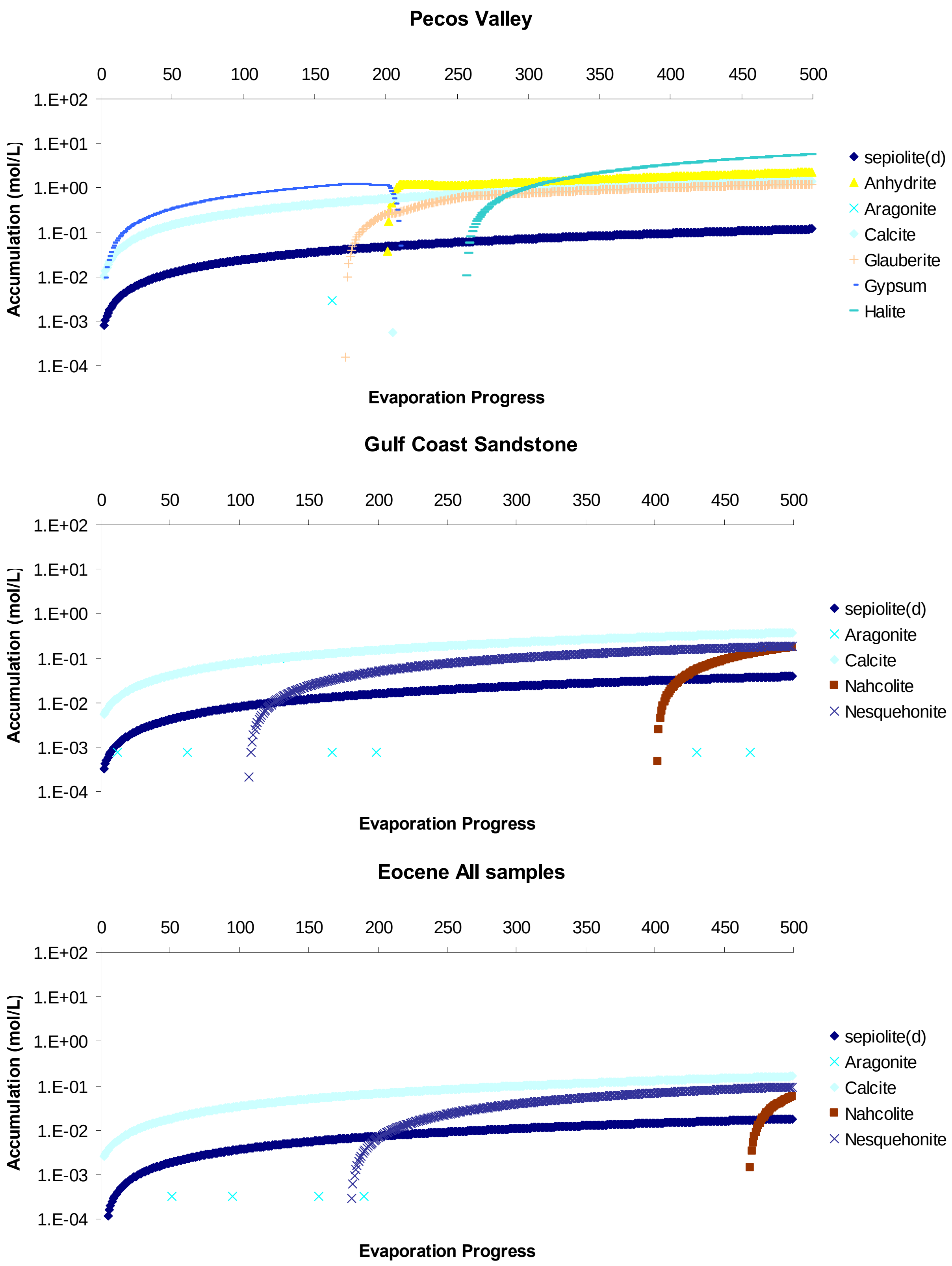
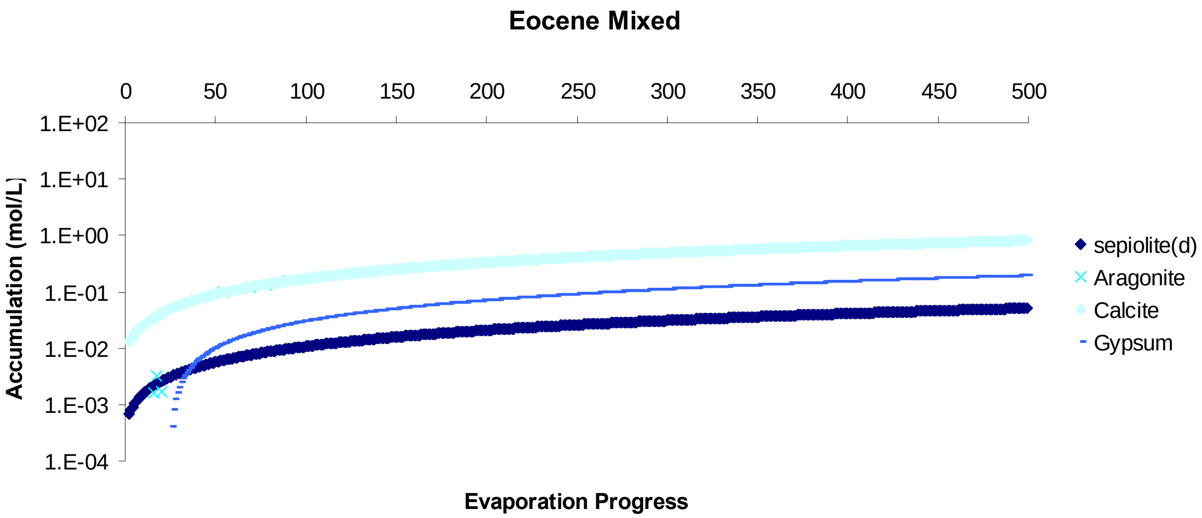
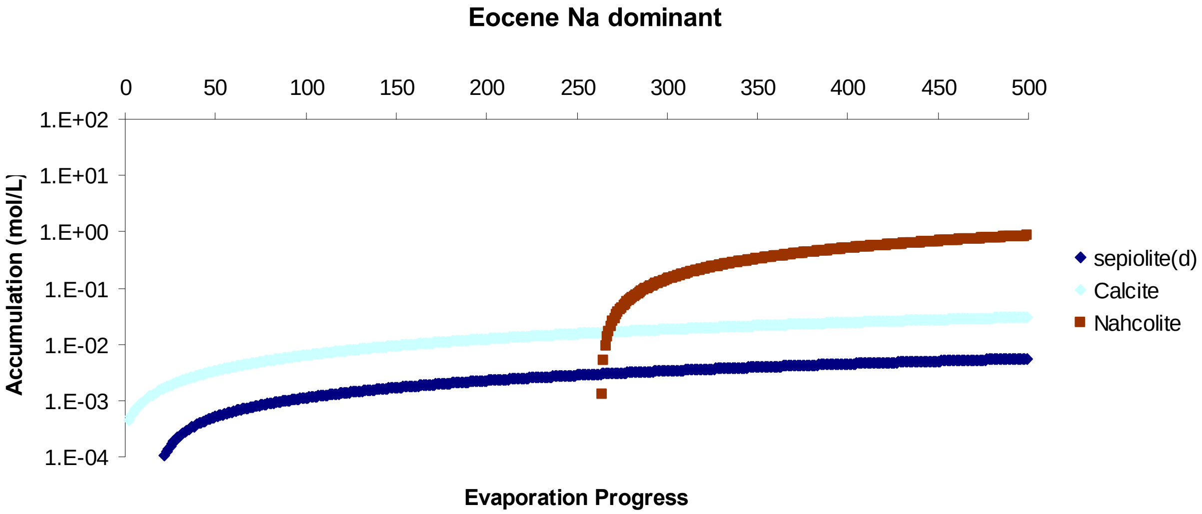


Figure 15-1. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions (continued)


Eocene Mixed


Eocene Na dominant

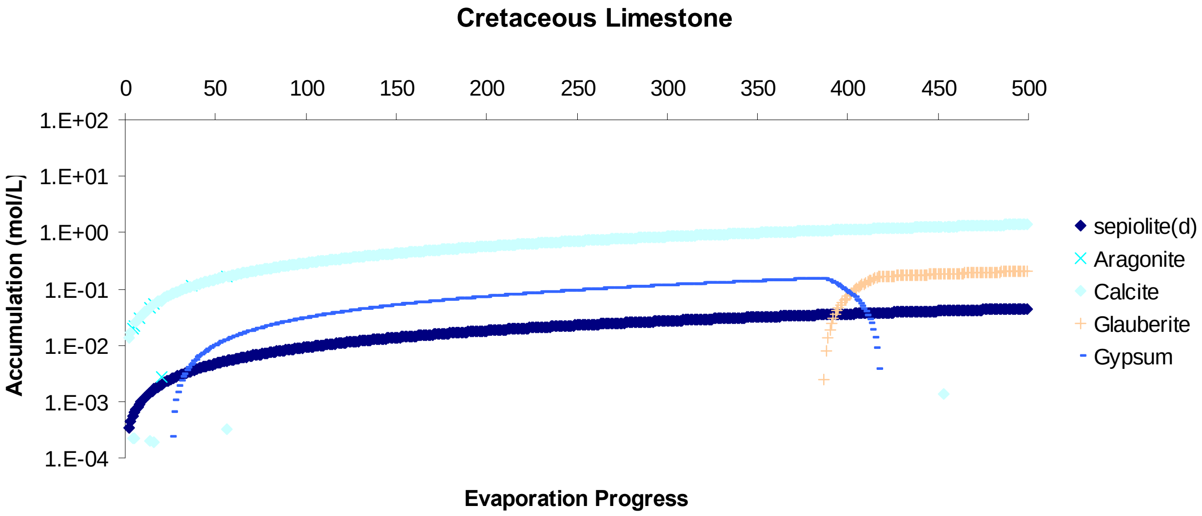

Cretaceous Limestone

Figure 15-1. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions (continued)

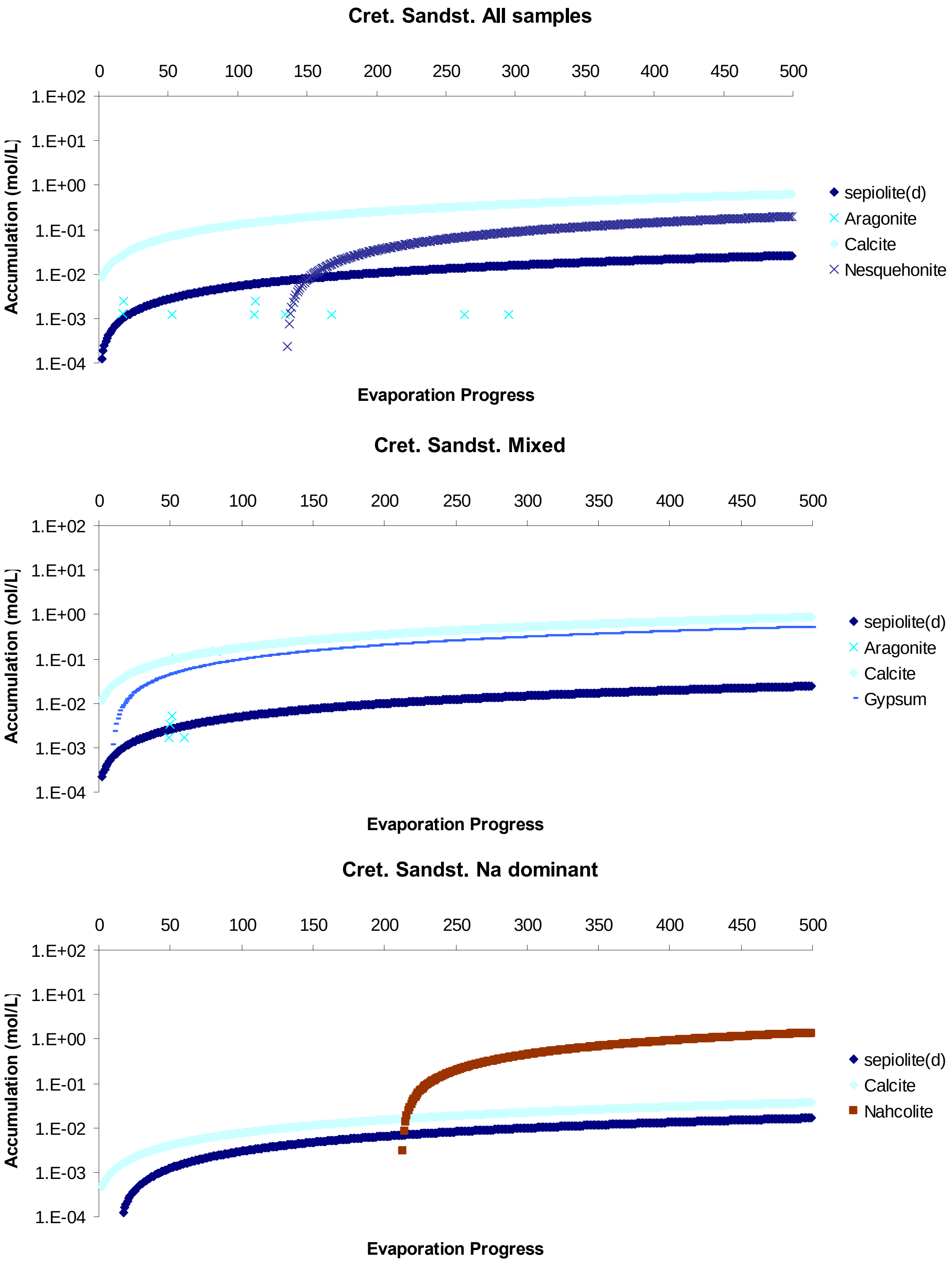
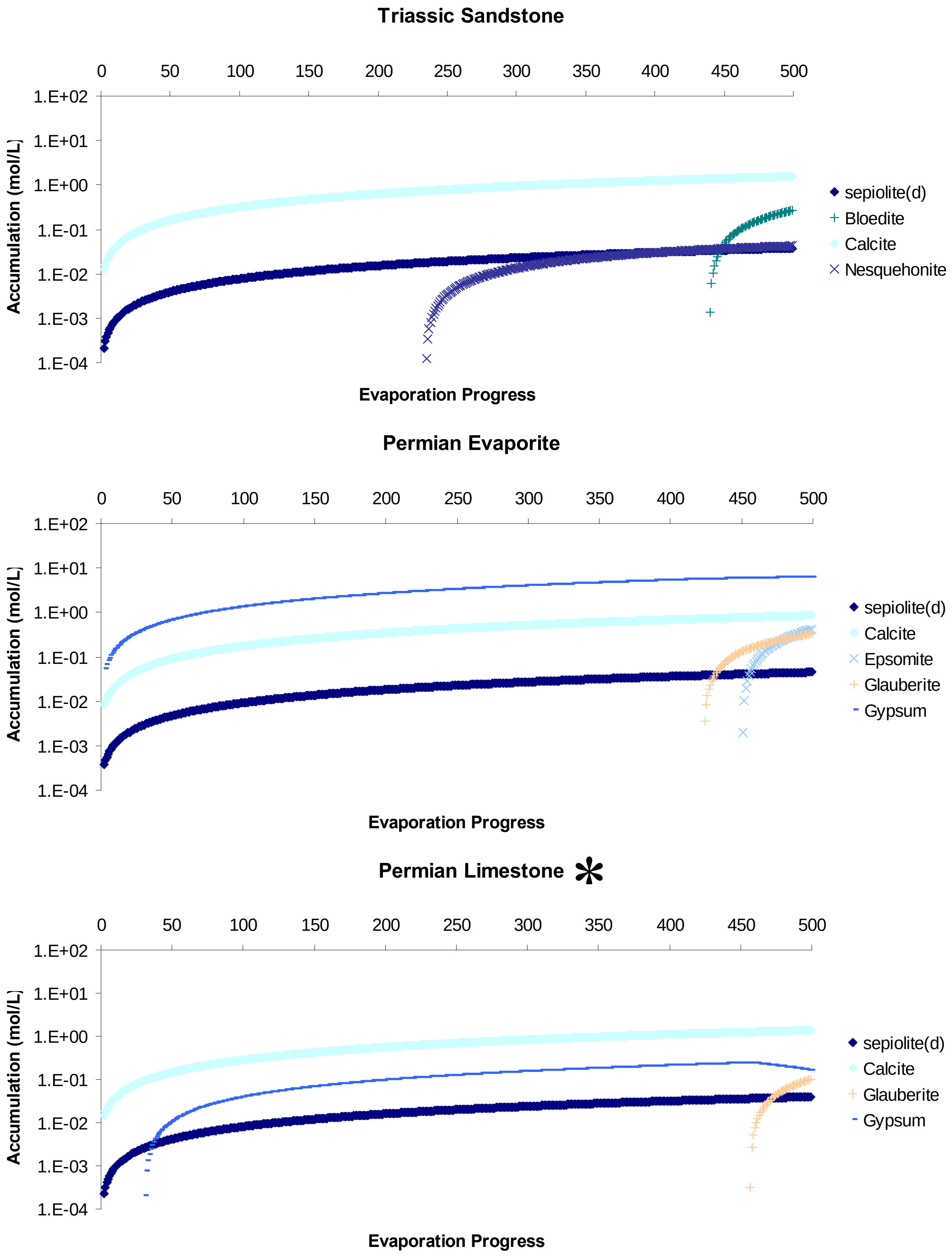


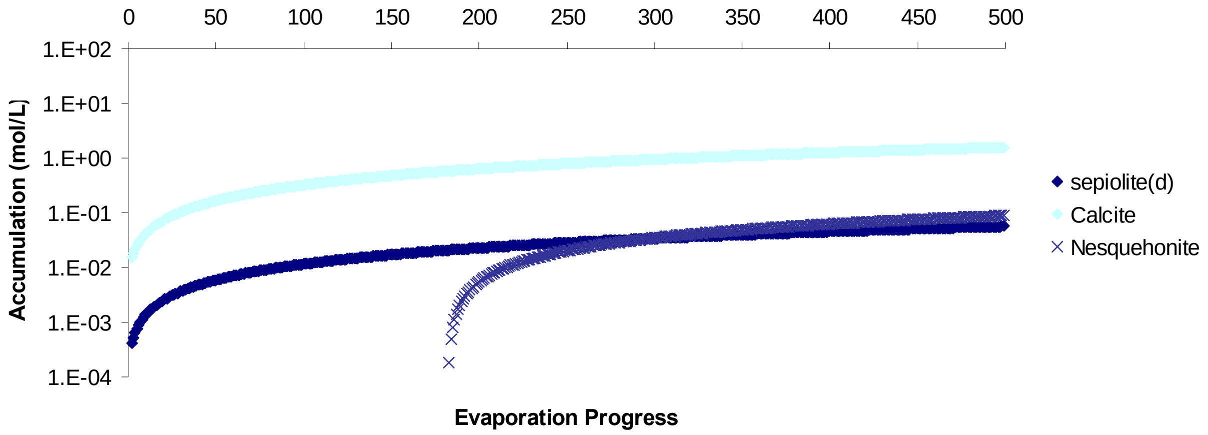
Figure 15-1. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions (continued)



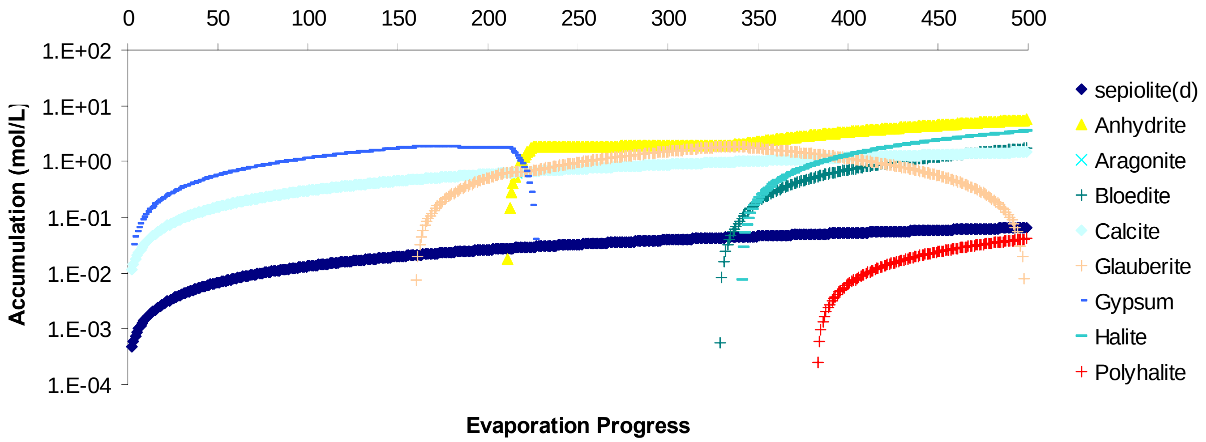
* Results obtained with the LLNL database not the Pitzer database

Figure 15-1. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions (continued)

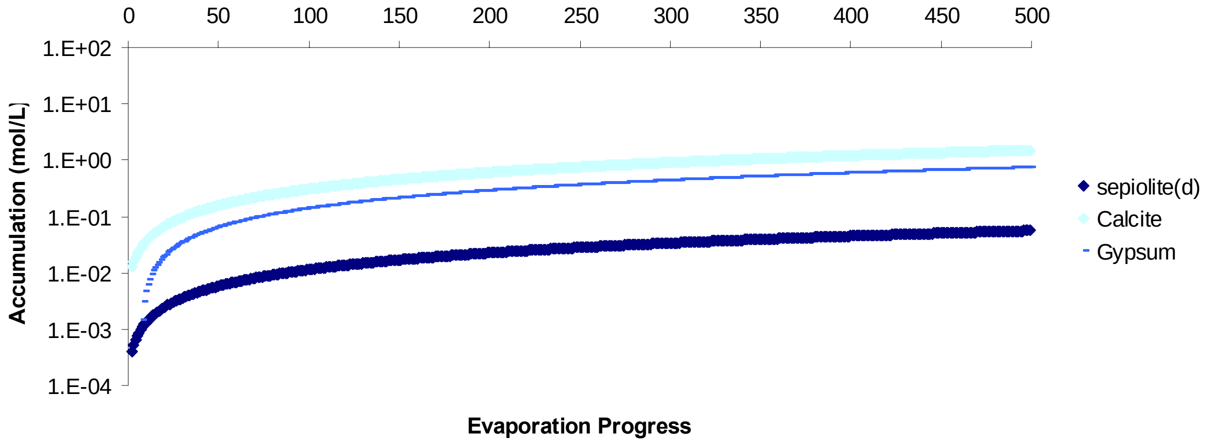
**Permian Sandstone** *



**Bone Spring – Victorio Peak**



**Capitan Reef**



* Results obtained with the LLNL database not the Pitzer database

Figure 15-1. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions (continued)

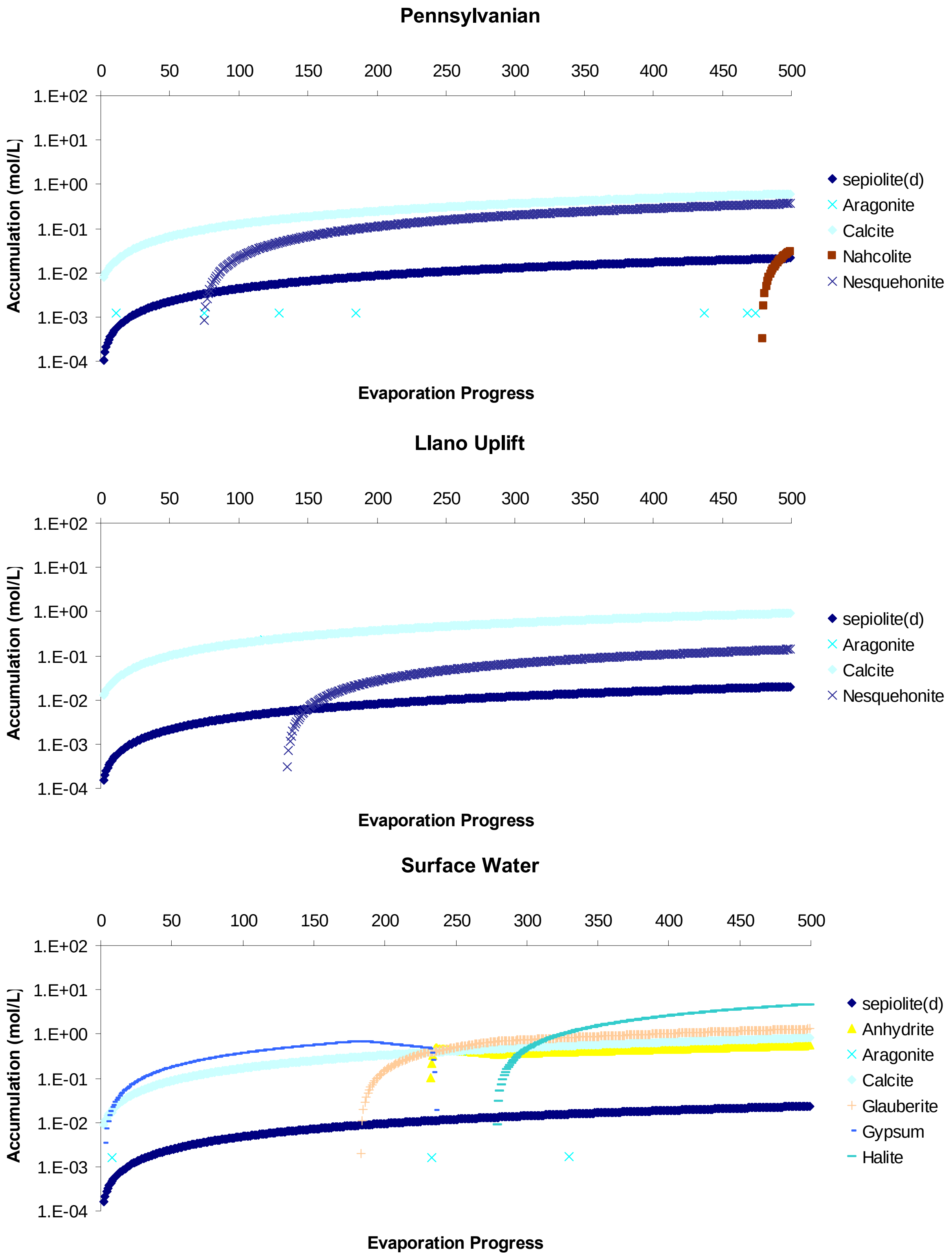


Figure 15-1. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions (continued)

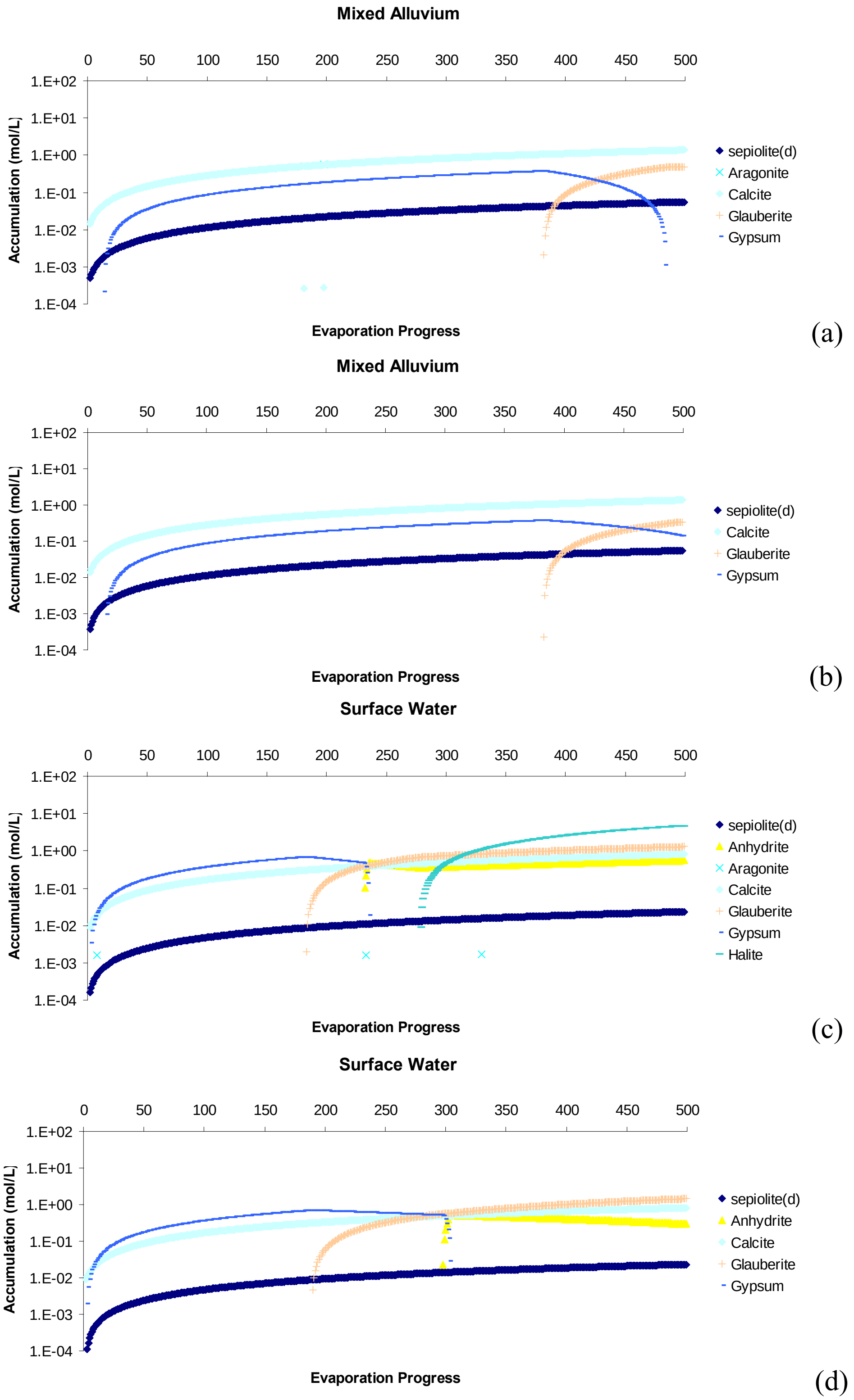


Figure 15-2. Comparison of results of selected groups run with different databases: mixed alluvium with Pitzer (a), mixed alluvium with LLNL (b), surface water with Pitzer (c), and surface water with LLNL (d)

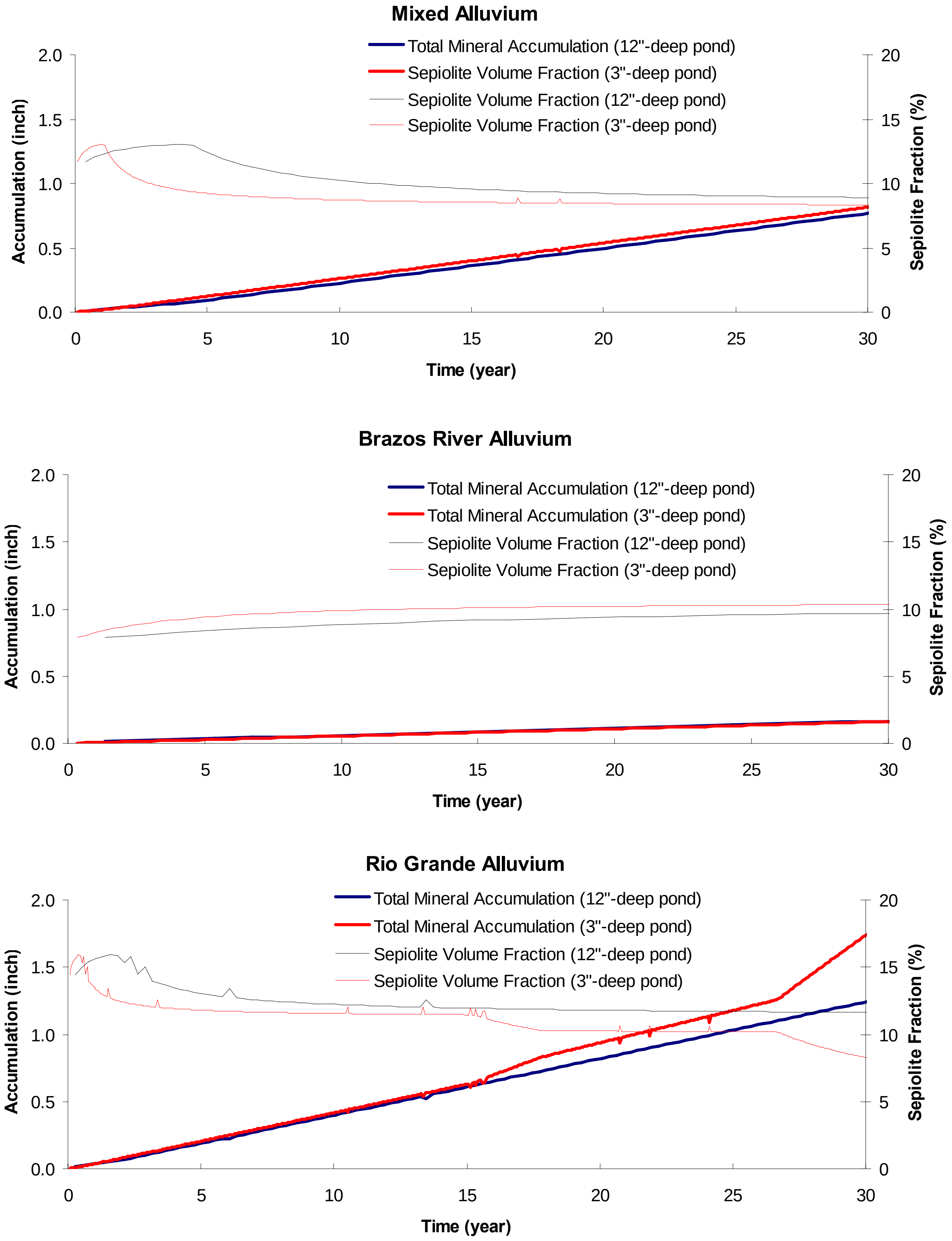
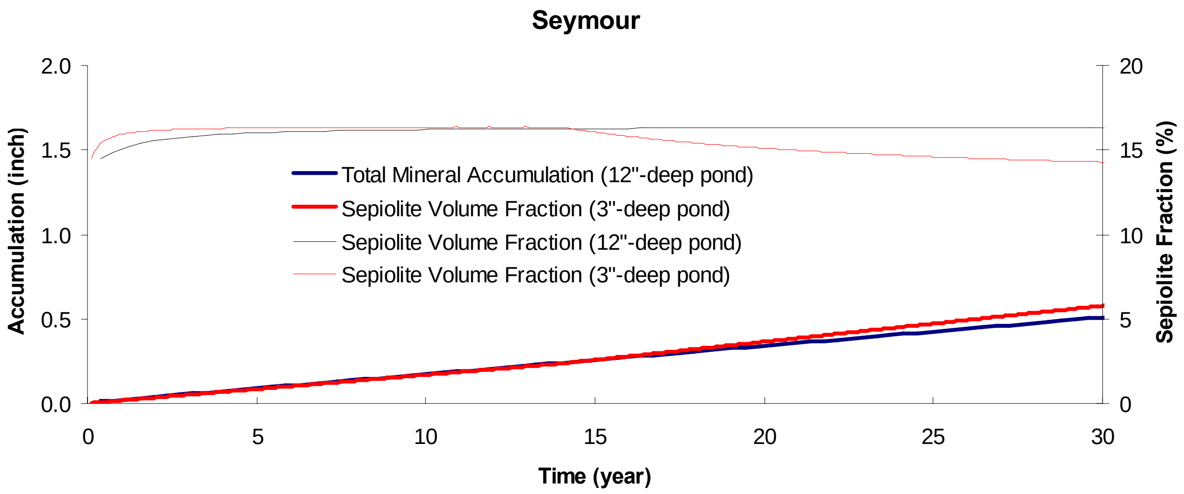
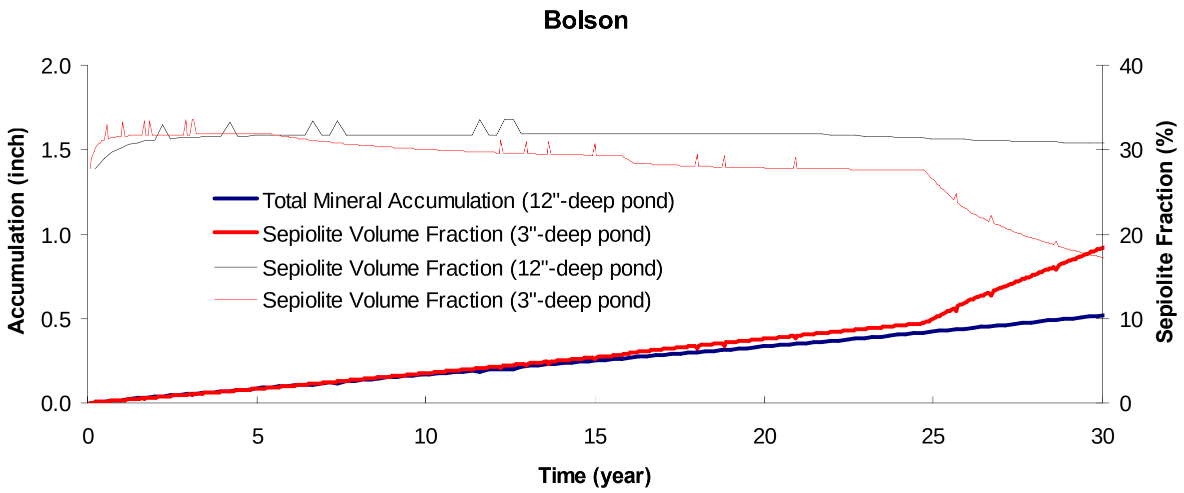


Figure 15-3. Specific accumulation (inches) and sepiolite fraction in accumulation for two pond depths (3 and 12 inches) for all water groups





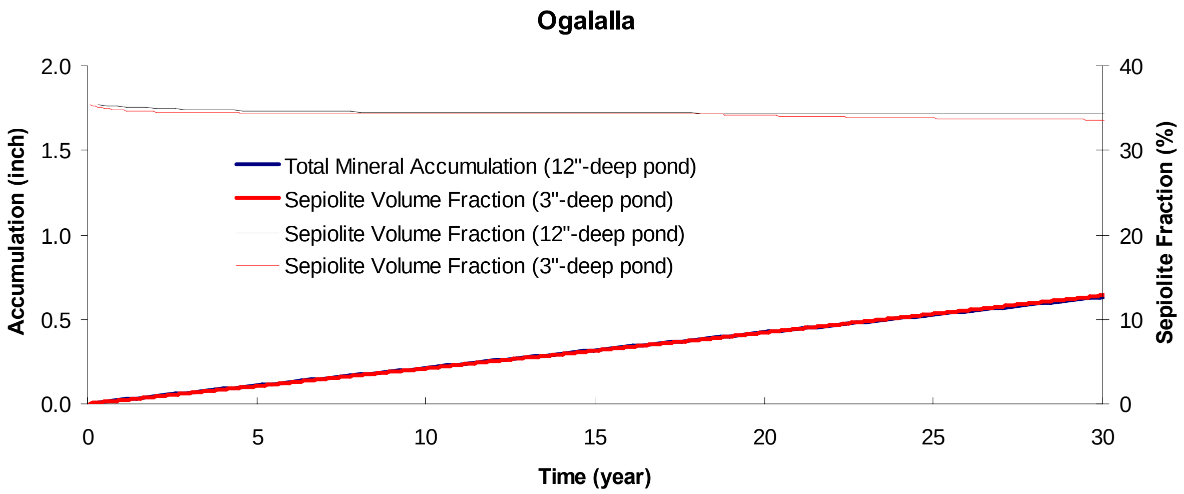
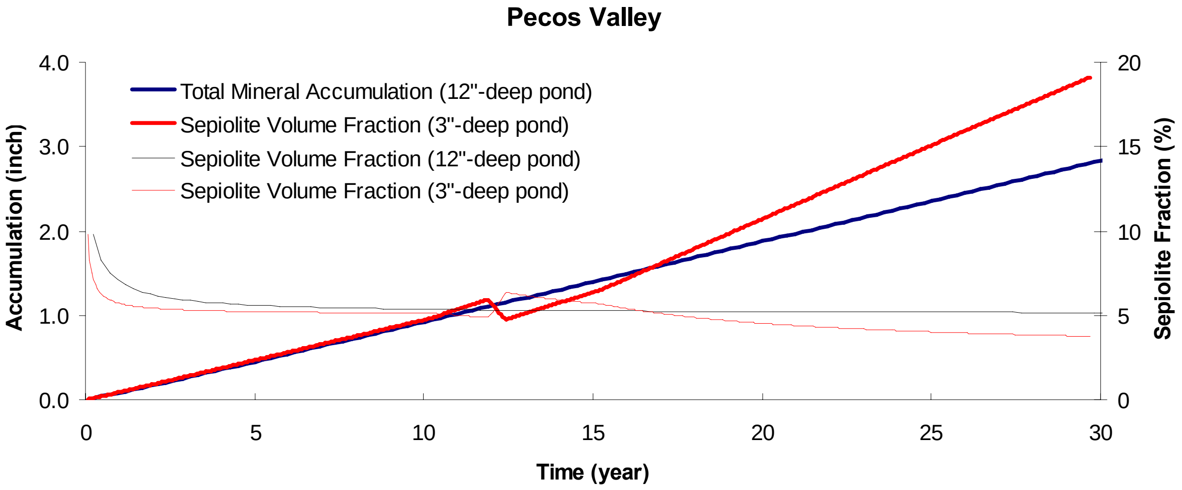
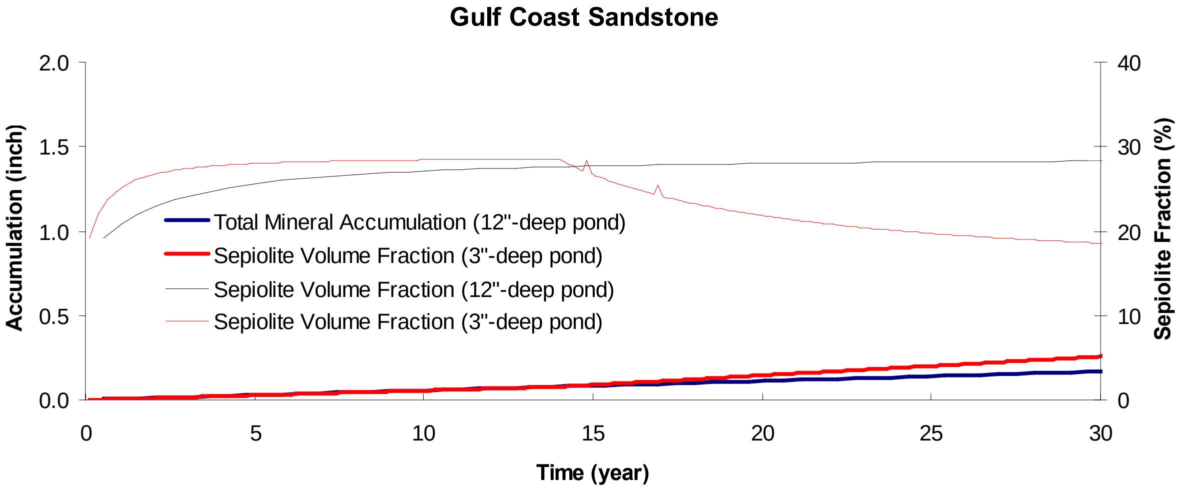


Figure 15-3. Specific accumulation (inches) and sepiolite fraction in accumulation for two pond depths (3 and 12 inches) for all water groups (continued)





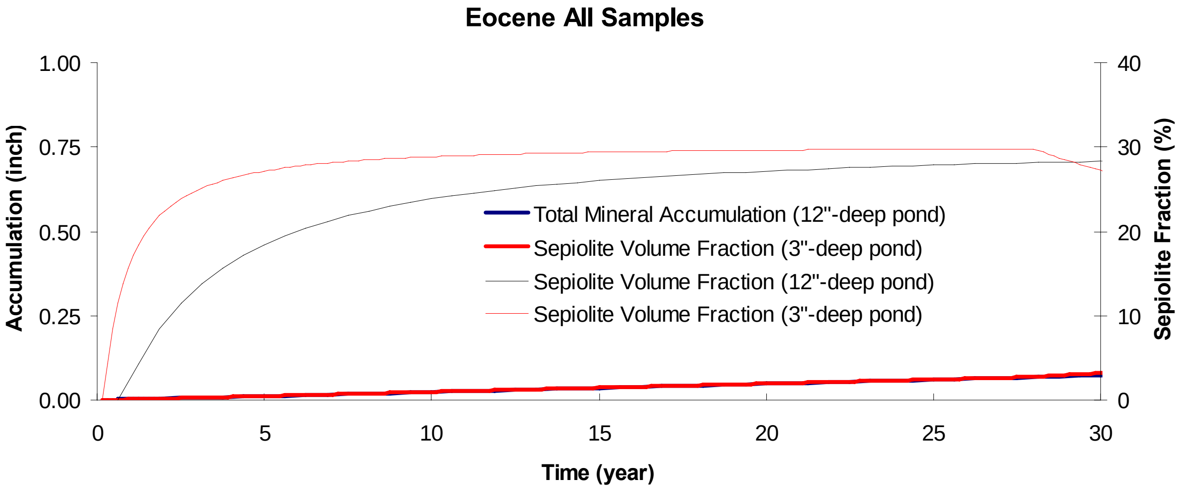
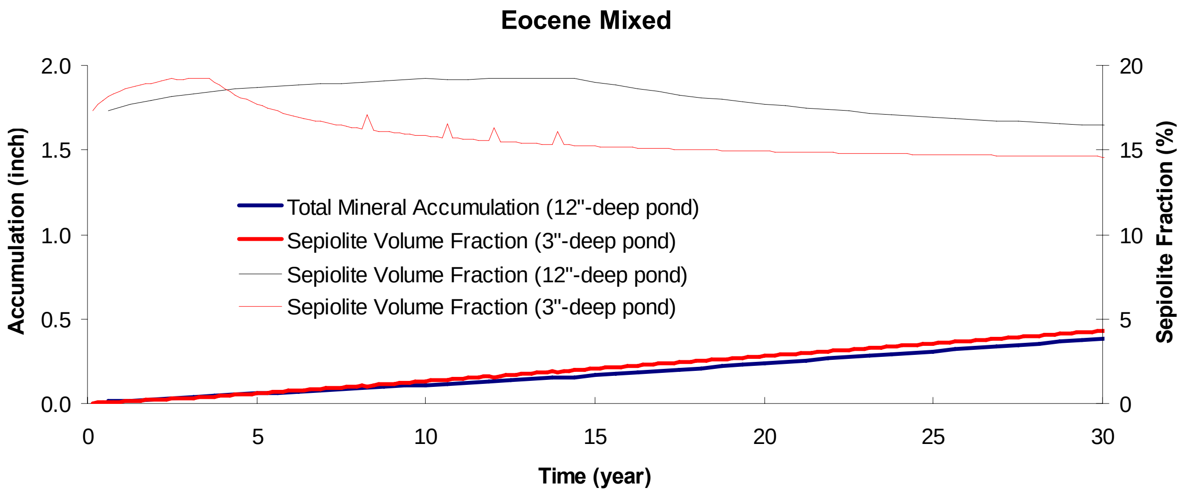
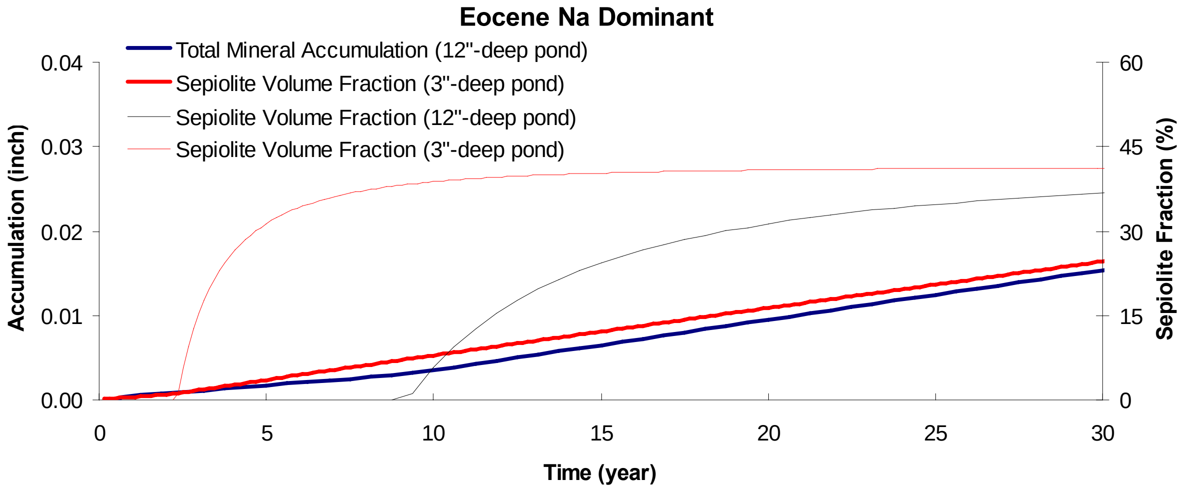


Figure 15-3. Specific accumulation (inches) and sepiolite fraction in accumulation for two pond depths (3 and 12 inches) for all water groups (continued)





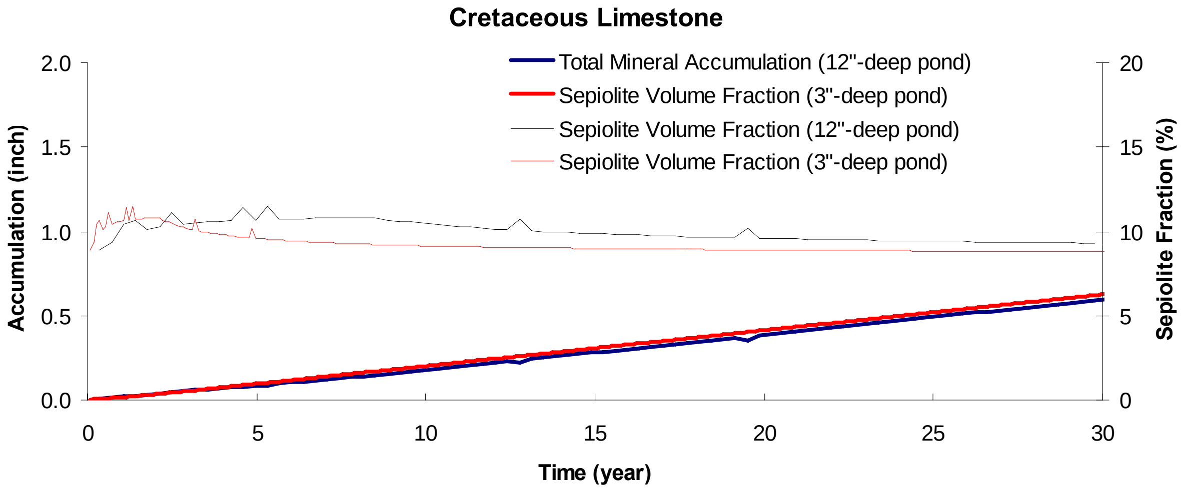
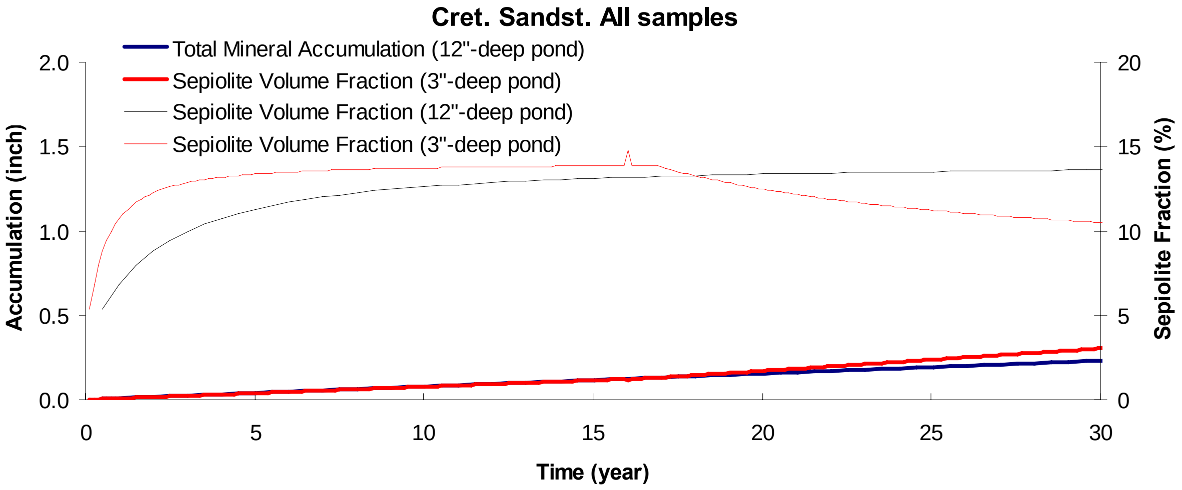
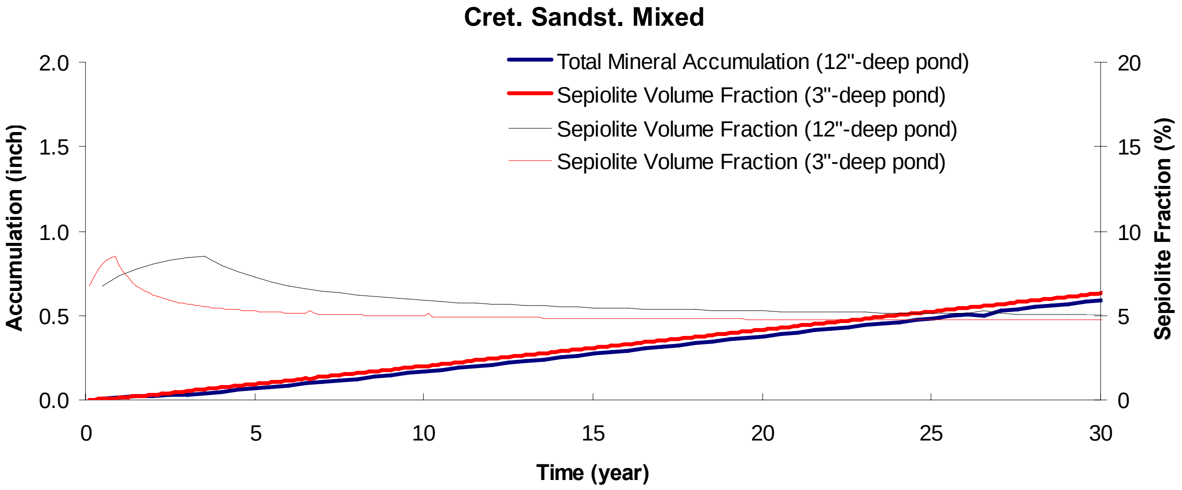


Figure 15-3. Specific accumulation (inches) and sepiolite fraction in accumulation for two pond depths (3 and 12 inches) for all water groups (continued)





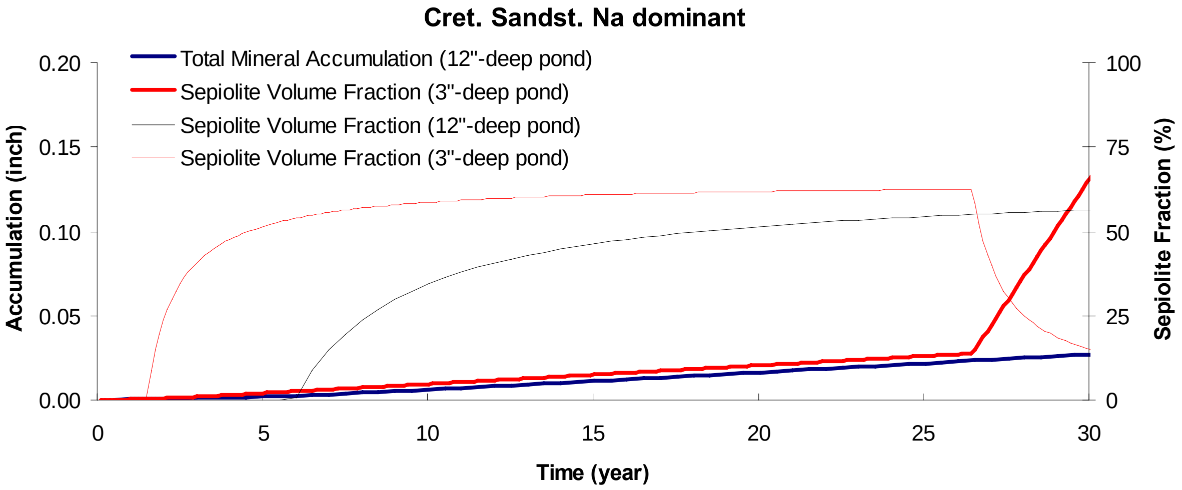


Figure 15-3. Specific accumulation (inches) and sepiolite fraction in accumulation for two pond depths (3 and 12 inches) for all water groups (continued)

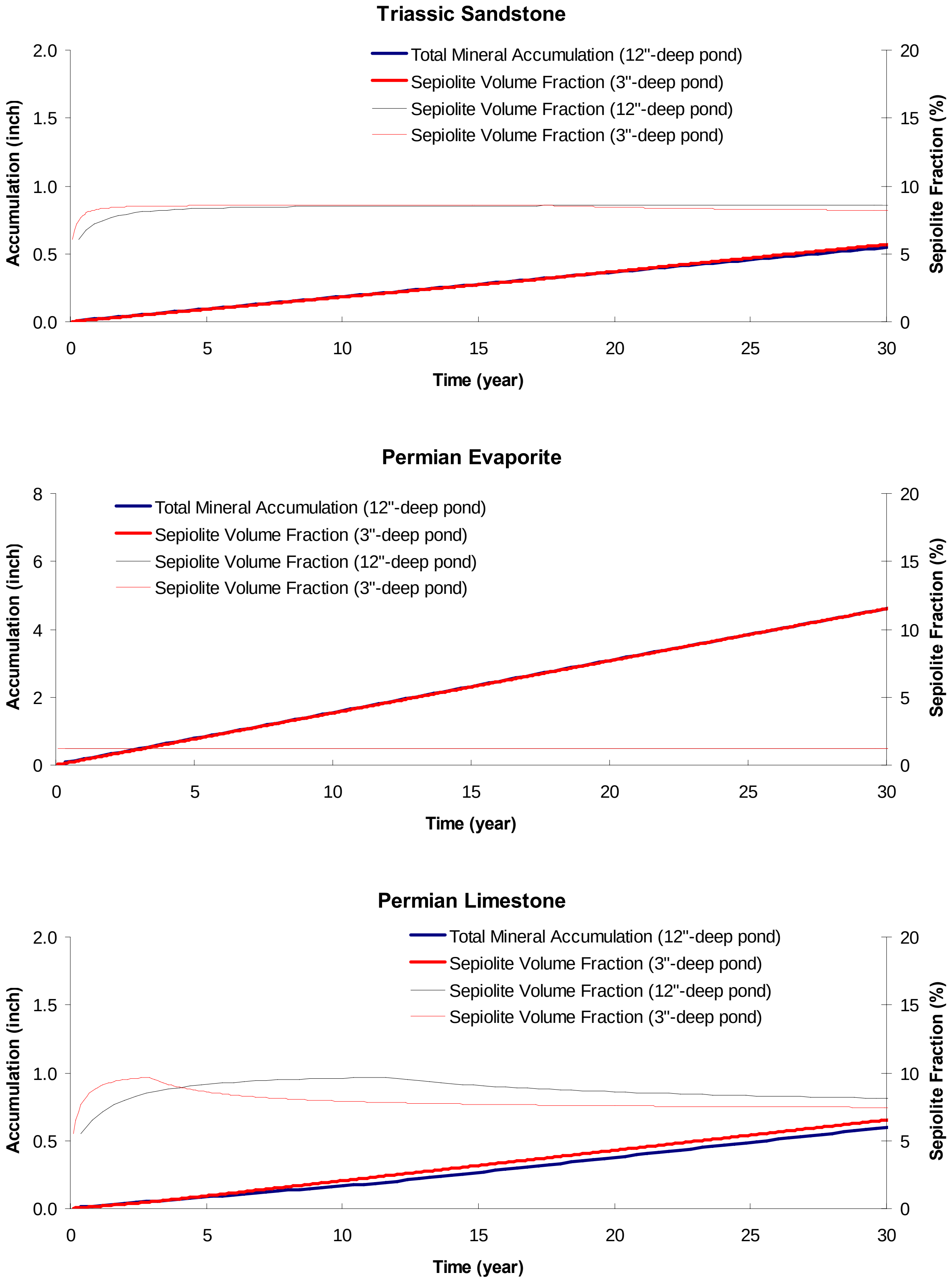


Figure 15-3. Specific accumulation (inches) and sepiolite fraction in accumulation for two pond depths (3 and 12 inches) for all water groups (continued)

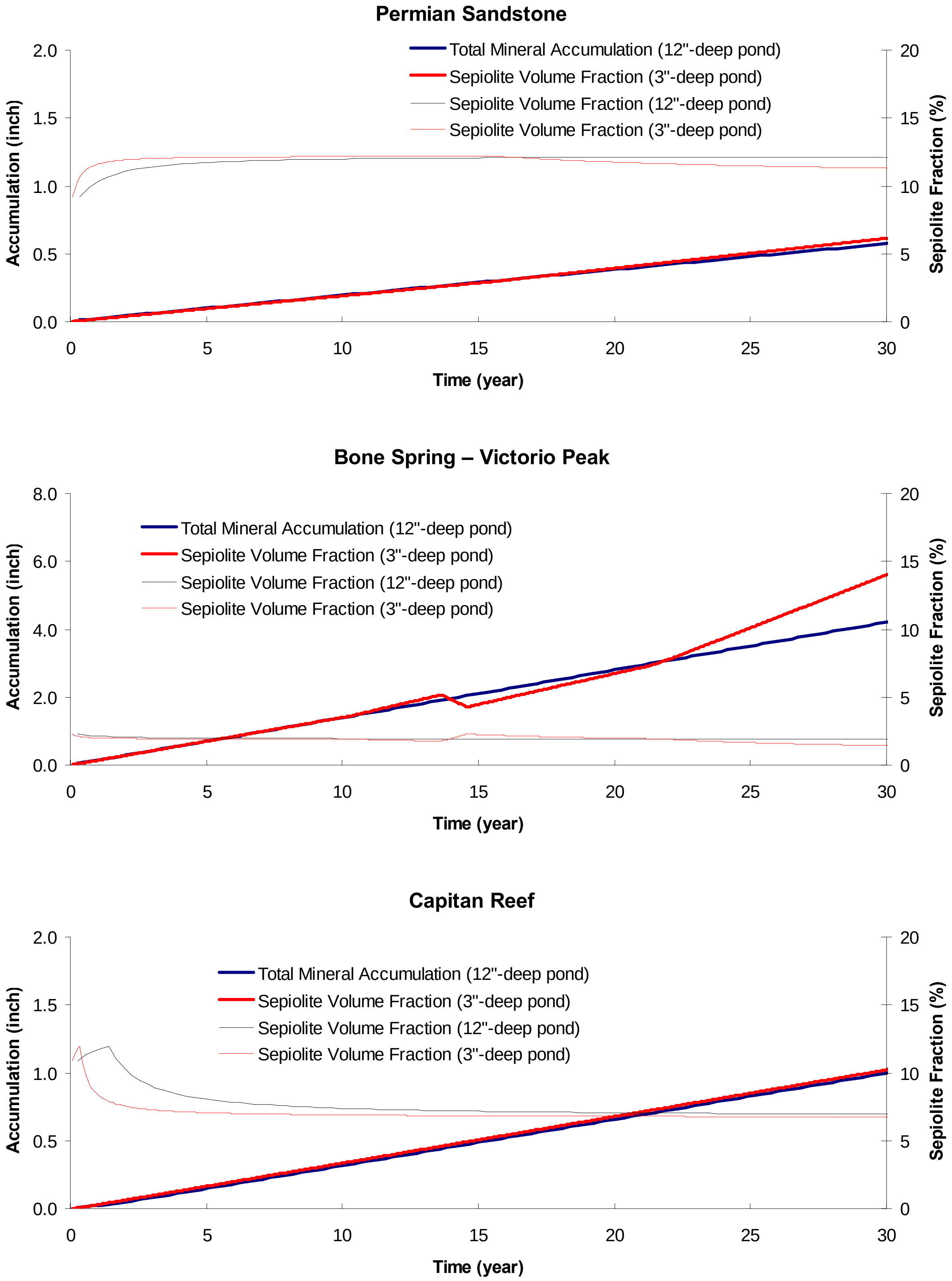
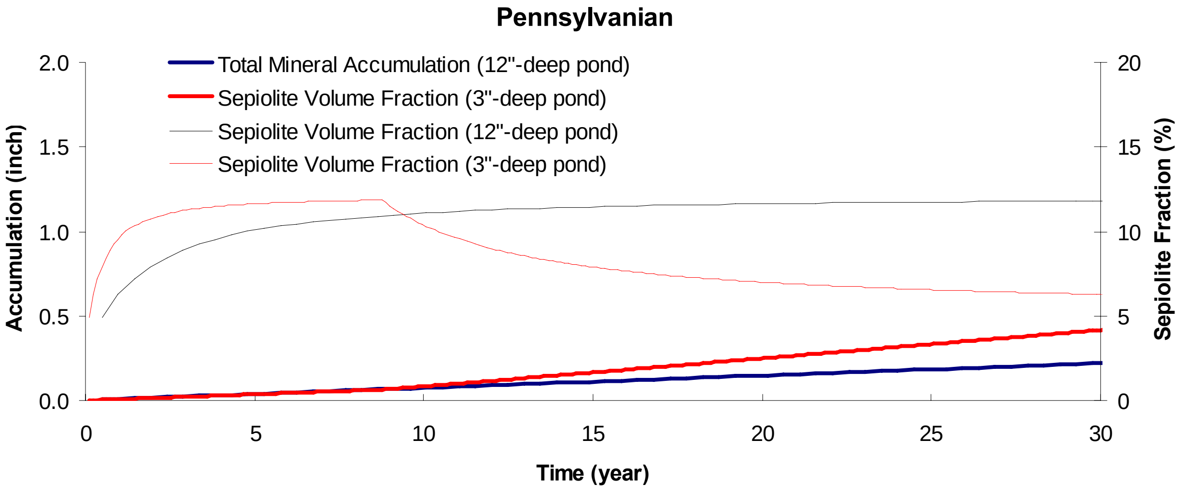
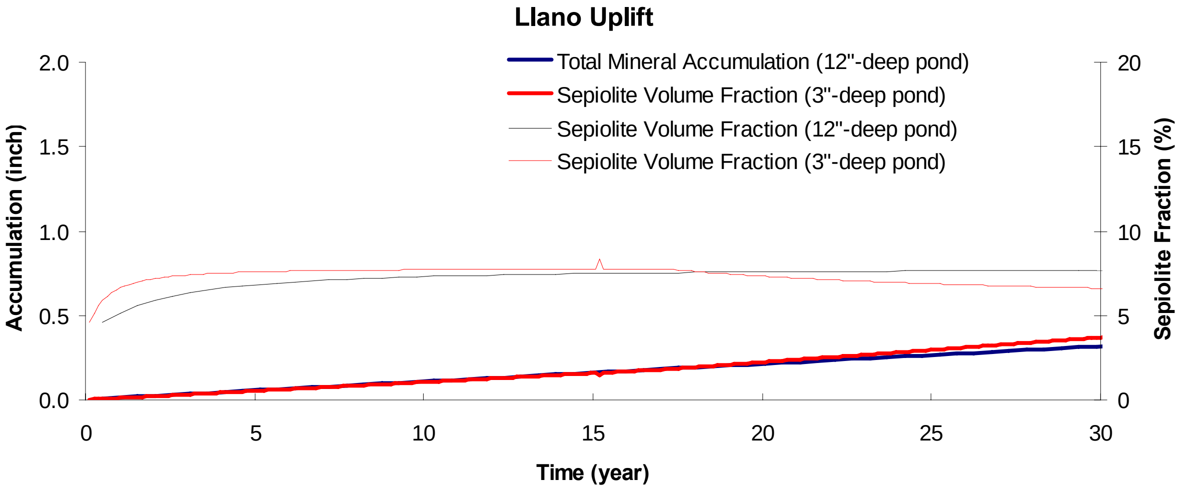


Figure 15-3. Specific accumulation (inches) and sepiolite fraction in accumulation for two pond depths (3 and 12 inches) for all water groups (continued)





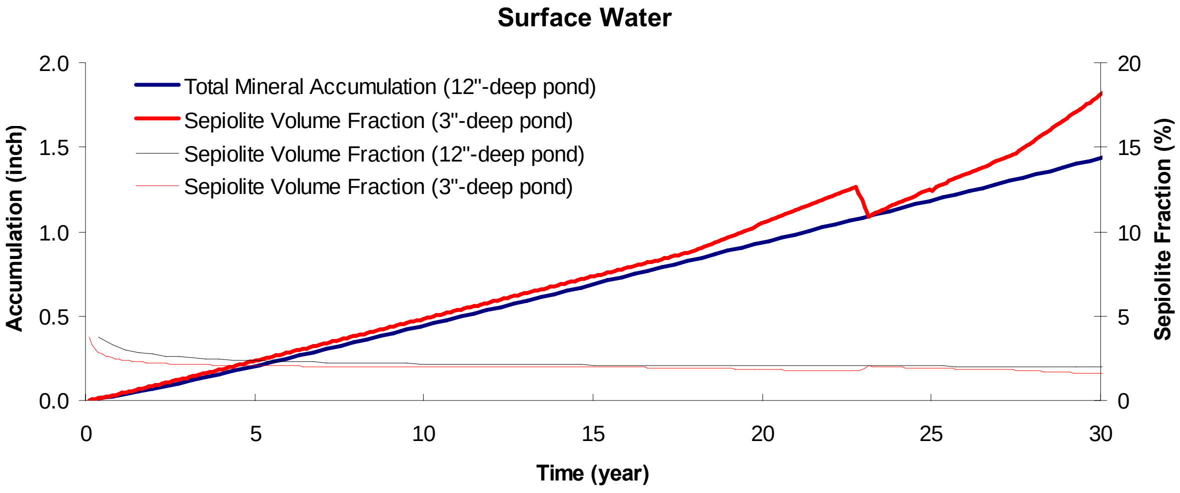


Figure 15-3. Specific accumulation (inches) and sepiolite fraction in accumulation for two pond depths (3 and 12 inches) for all water groups (continued)

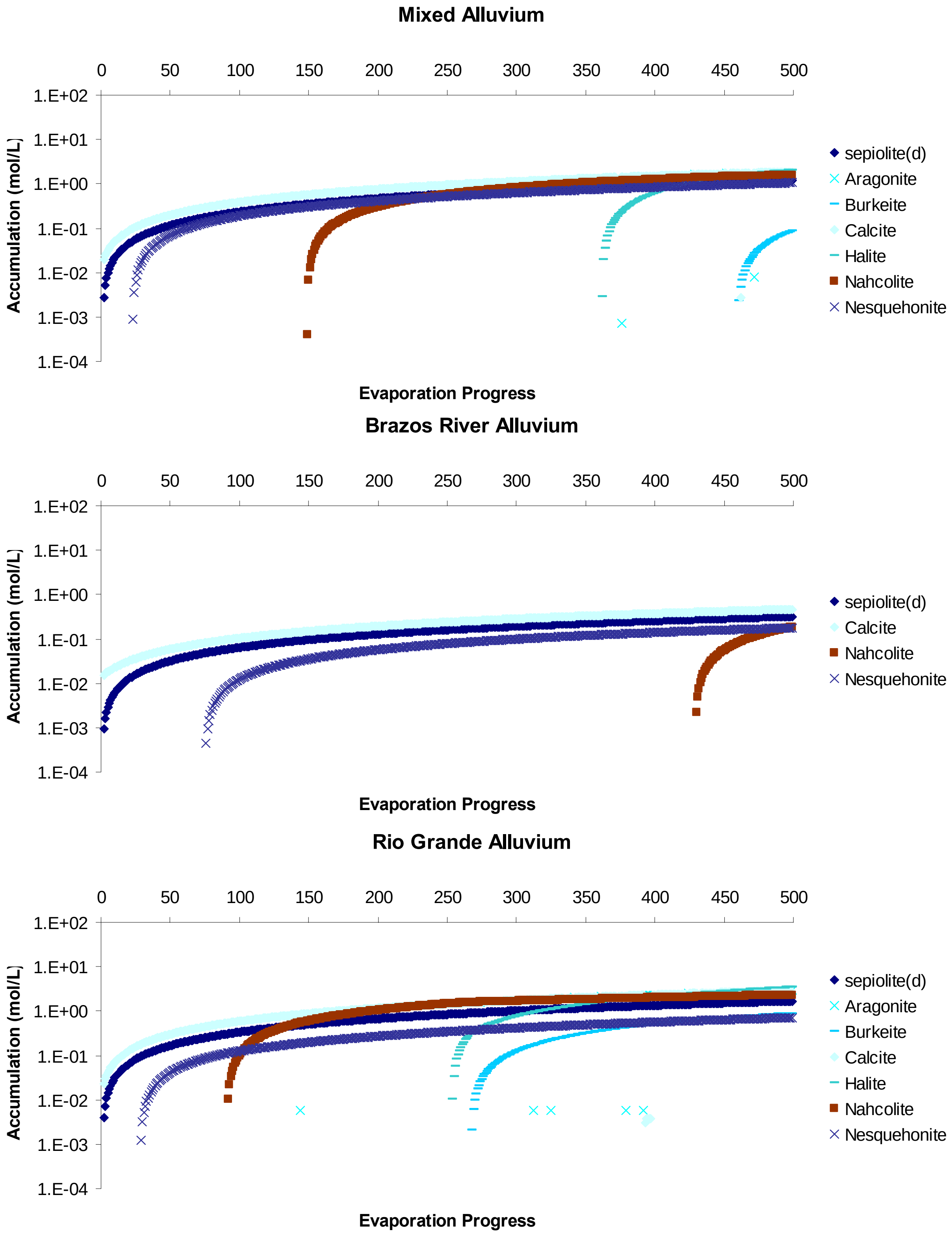


Figure 15-4. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in engineered conditions (0.01 mol/L of sepiolite precursor compounds)

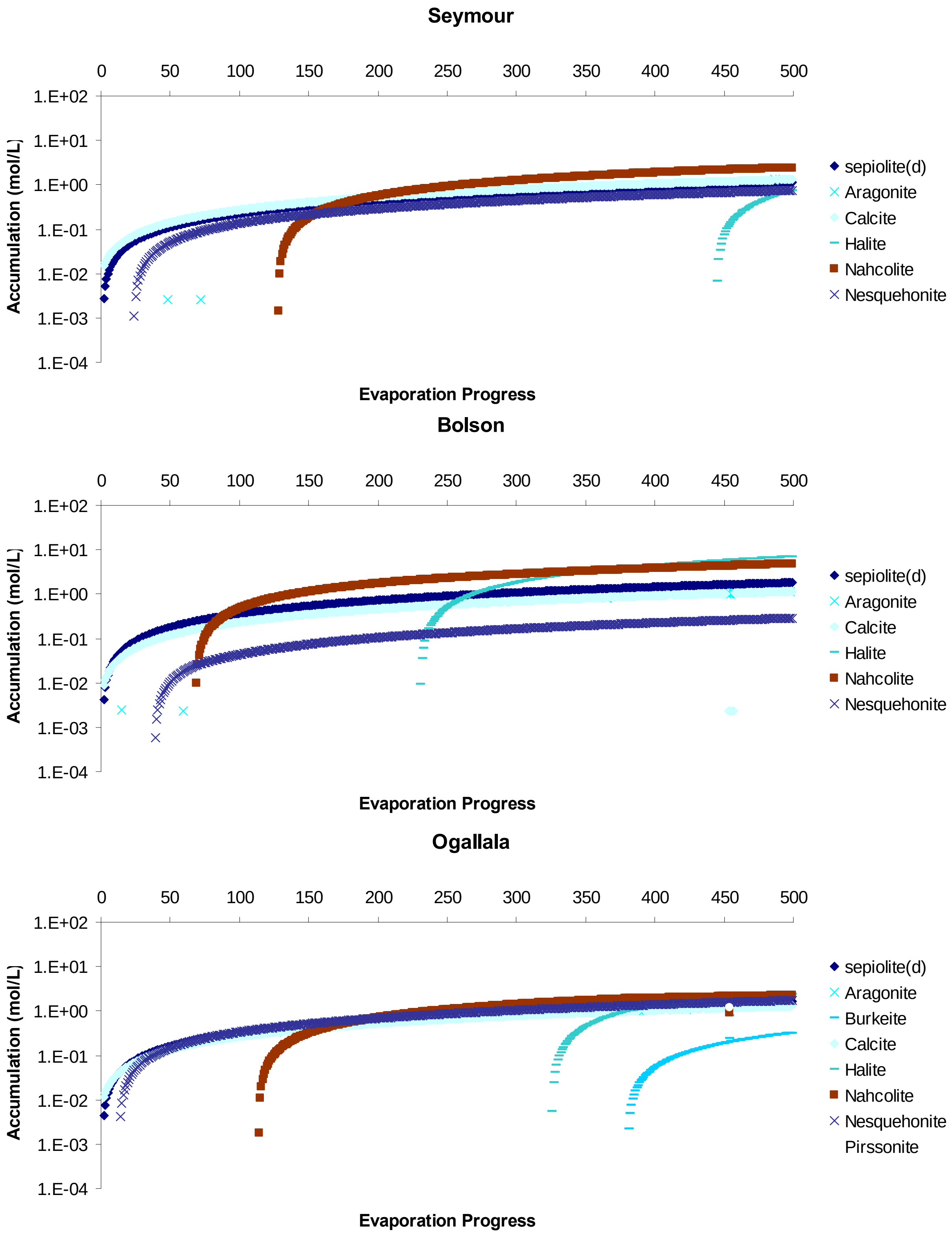


Figure 15-4. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in engineered conditions (0.01 mol/L of sepiolite precursor compounds) (continued)

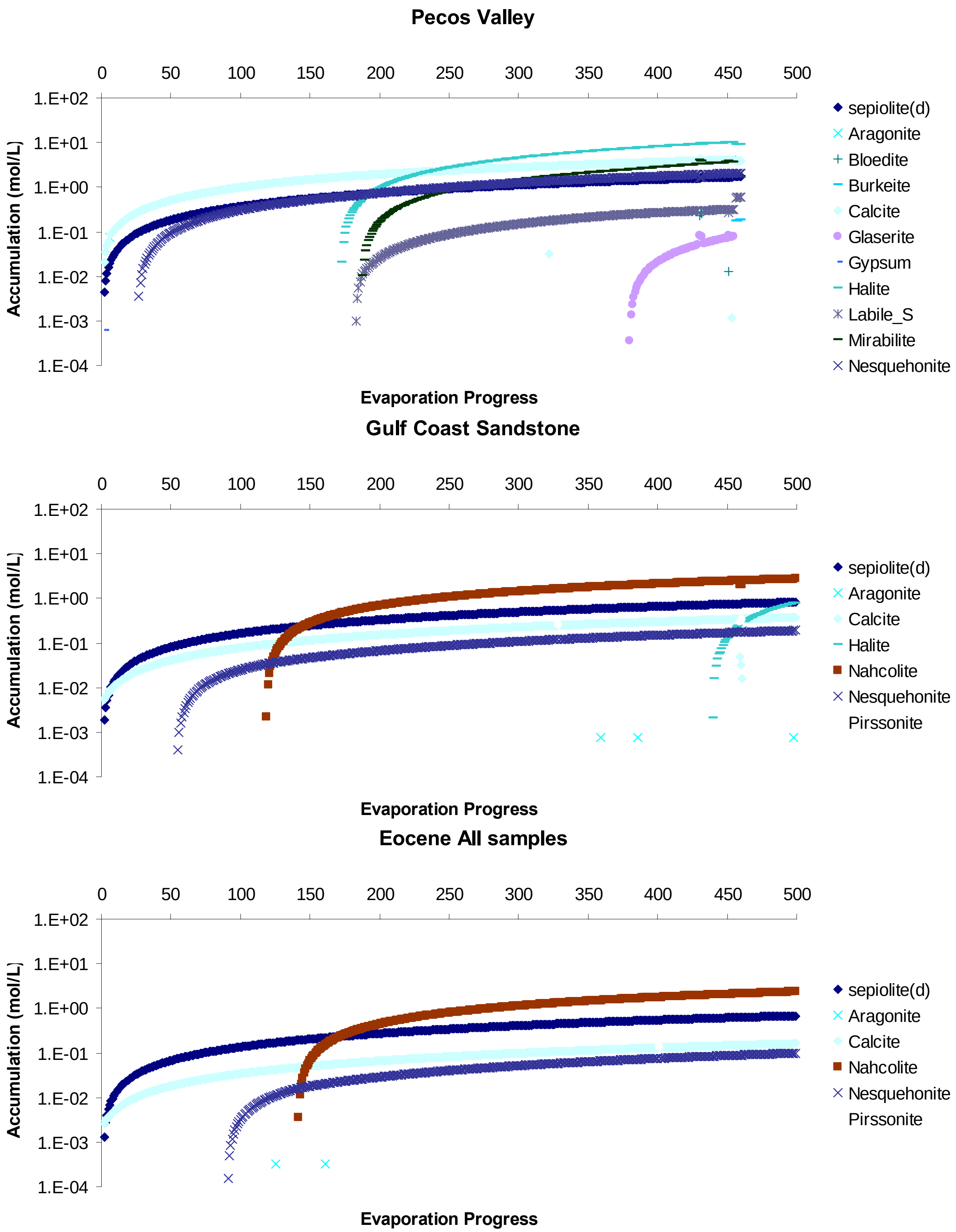
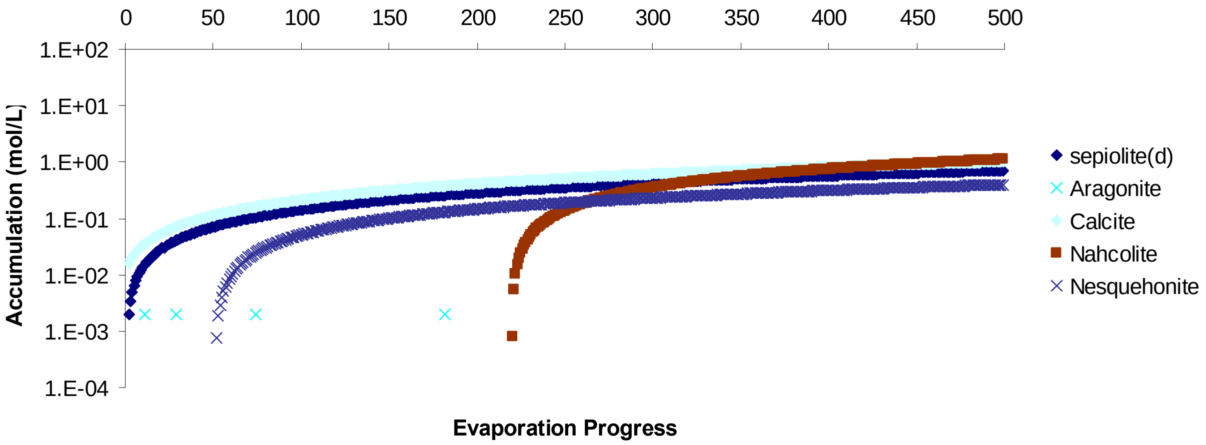
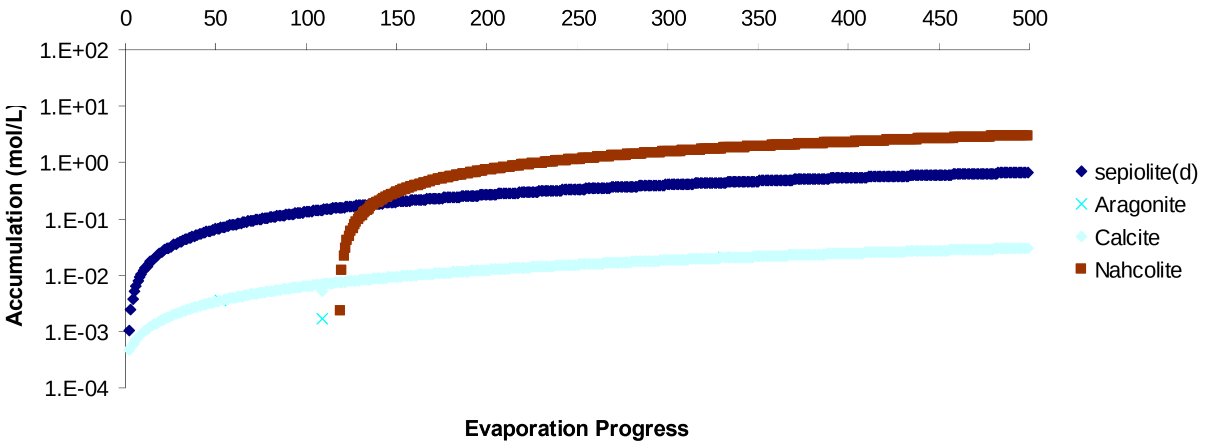


Figure 15-4. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in engineered conditions (0.01 mol/L of sepiolite precursor compounds) (continued)

**Eocene Mixed**



**Eocene Na dominant**



**Cretaceous Limestone**

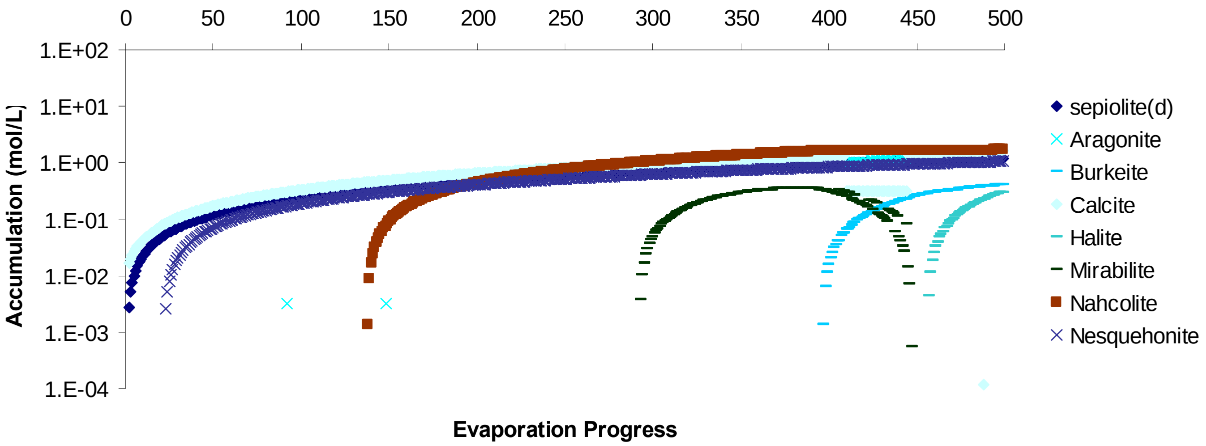
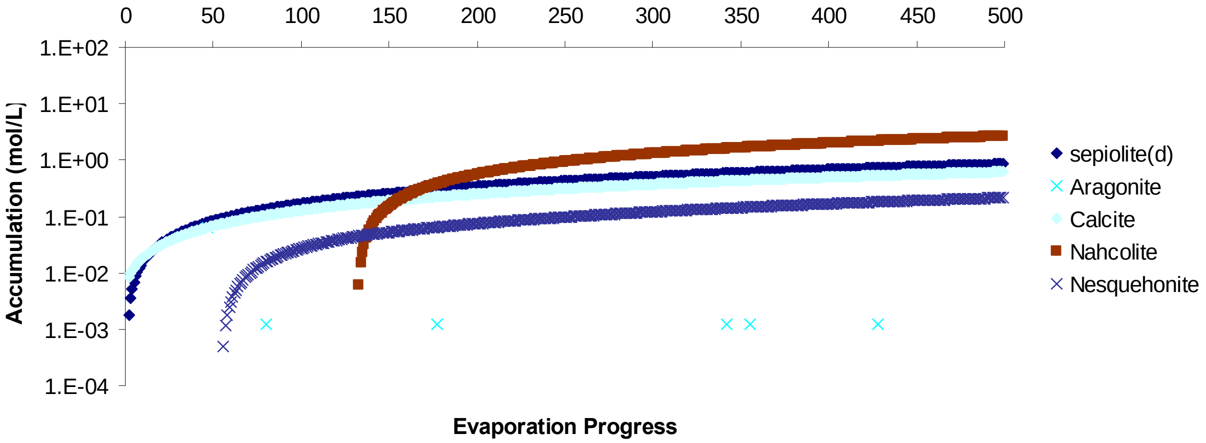
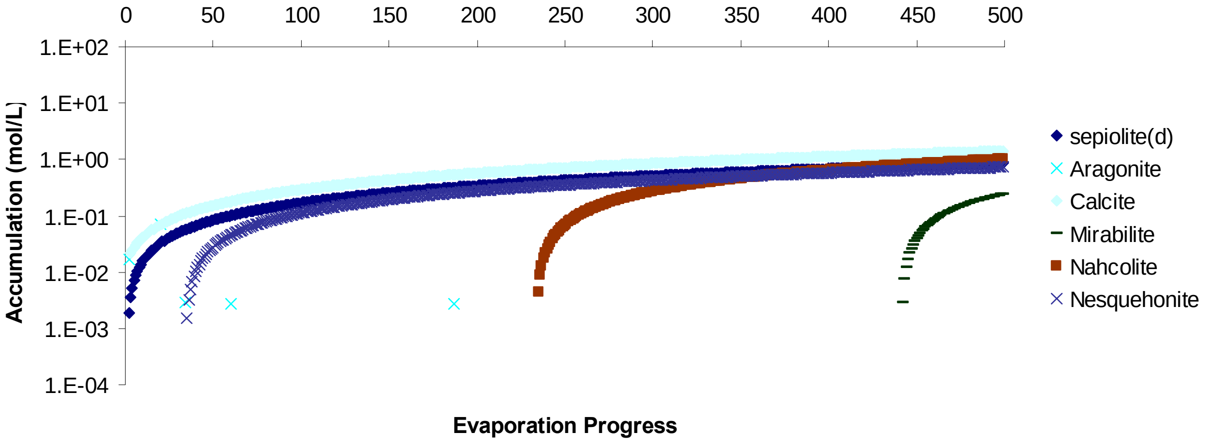


Figure 15-4. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in engineered conditions (0.01 mol/L of sepiolite precursor compounds) (continued)


Cret. Sandst. All samples


Cret. Sandst. Mixed

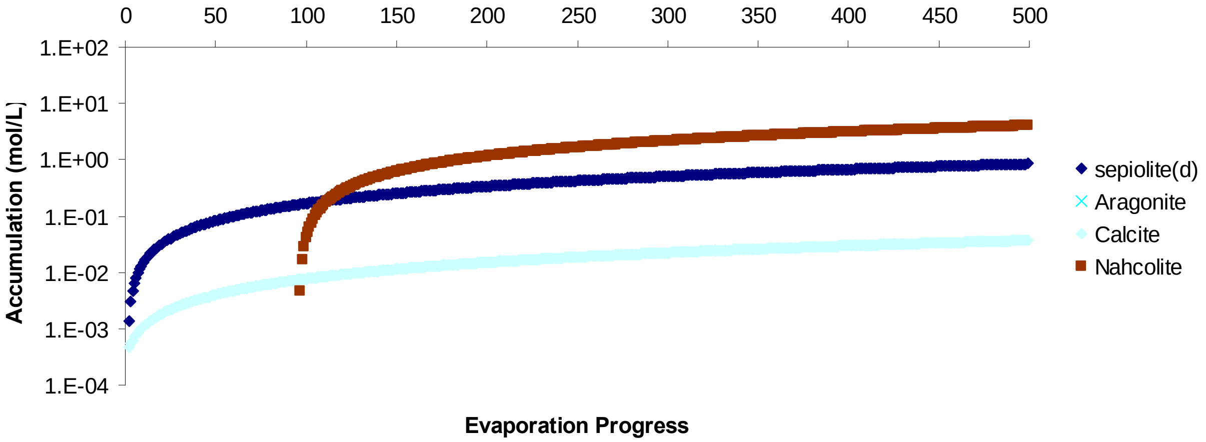

Cret. Sandst. Na dominant

Figure 15-4. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in engineered conditions (0.01 mol/L of sepiolite precursor compounds) (continued)

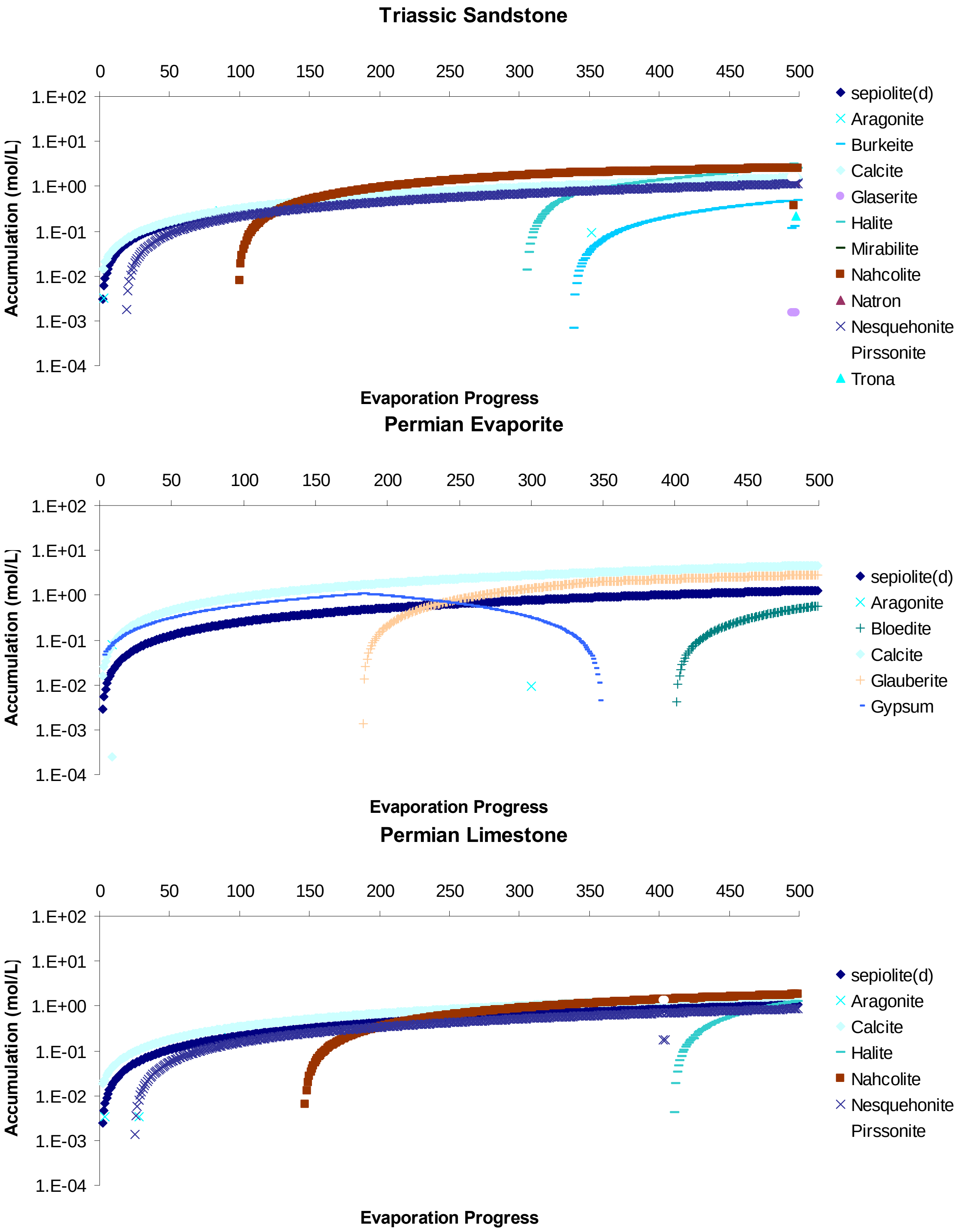


Figure 15-4. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in engineered conditions (0.01 mol/L of sepiolite precursor compounds) (continued)

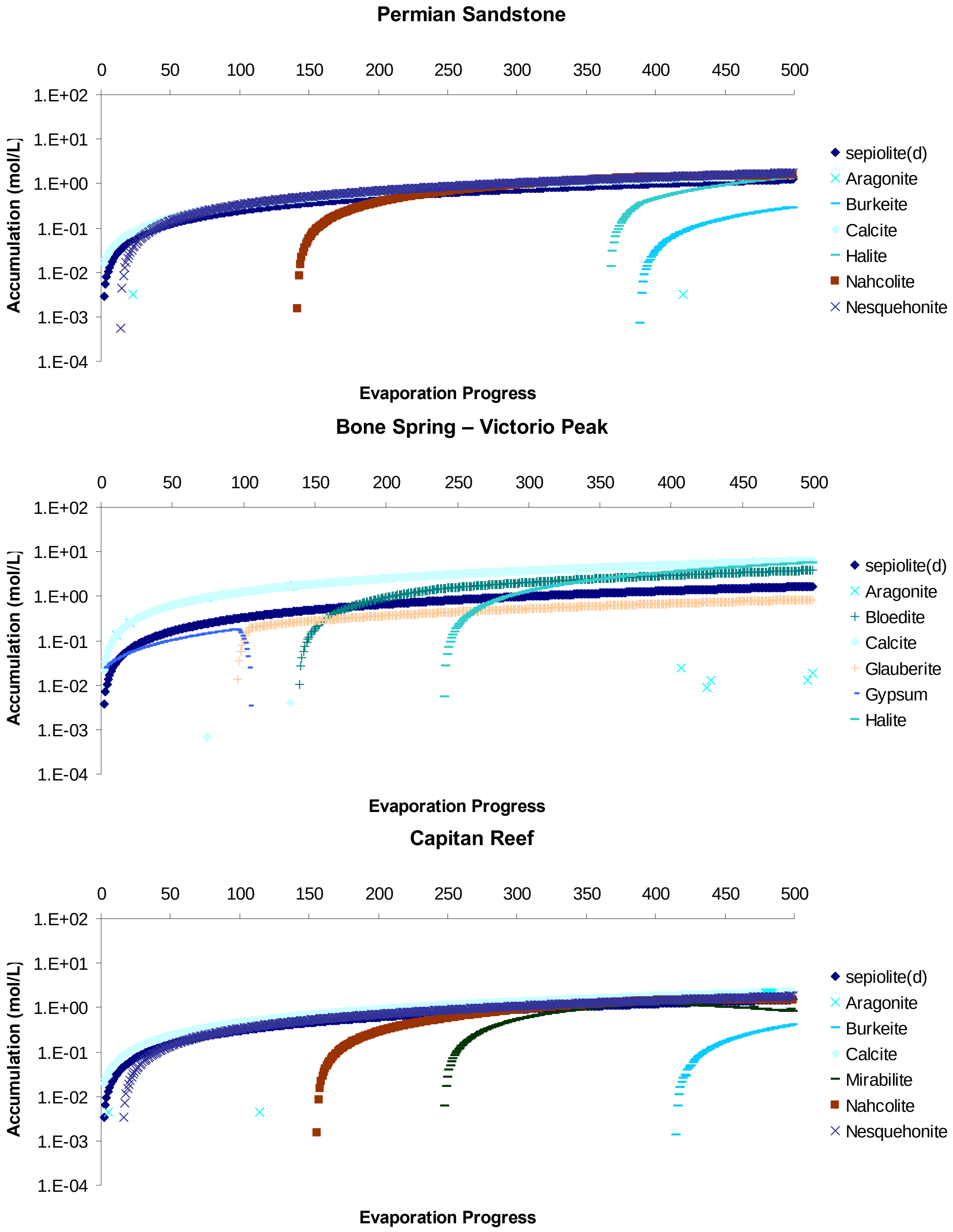


Figure 15-4. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in engineered conditions (0.01 mol/L of sepiolite precursor compounds) (continued)

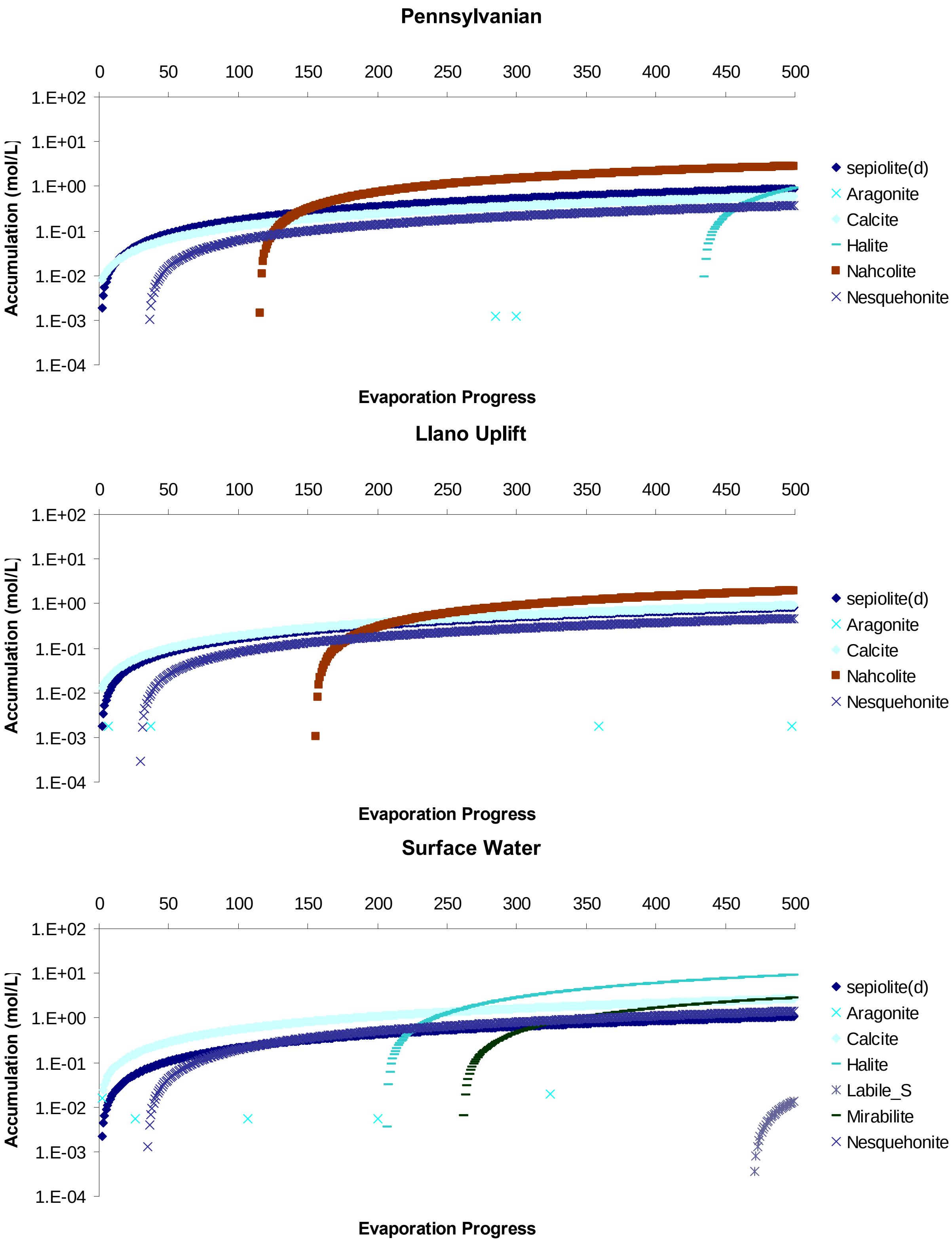


Figure 15-4. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in engineered conditions (0.01 mol/L of sepiolite precursor compounds) (continued)

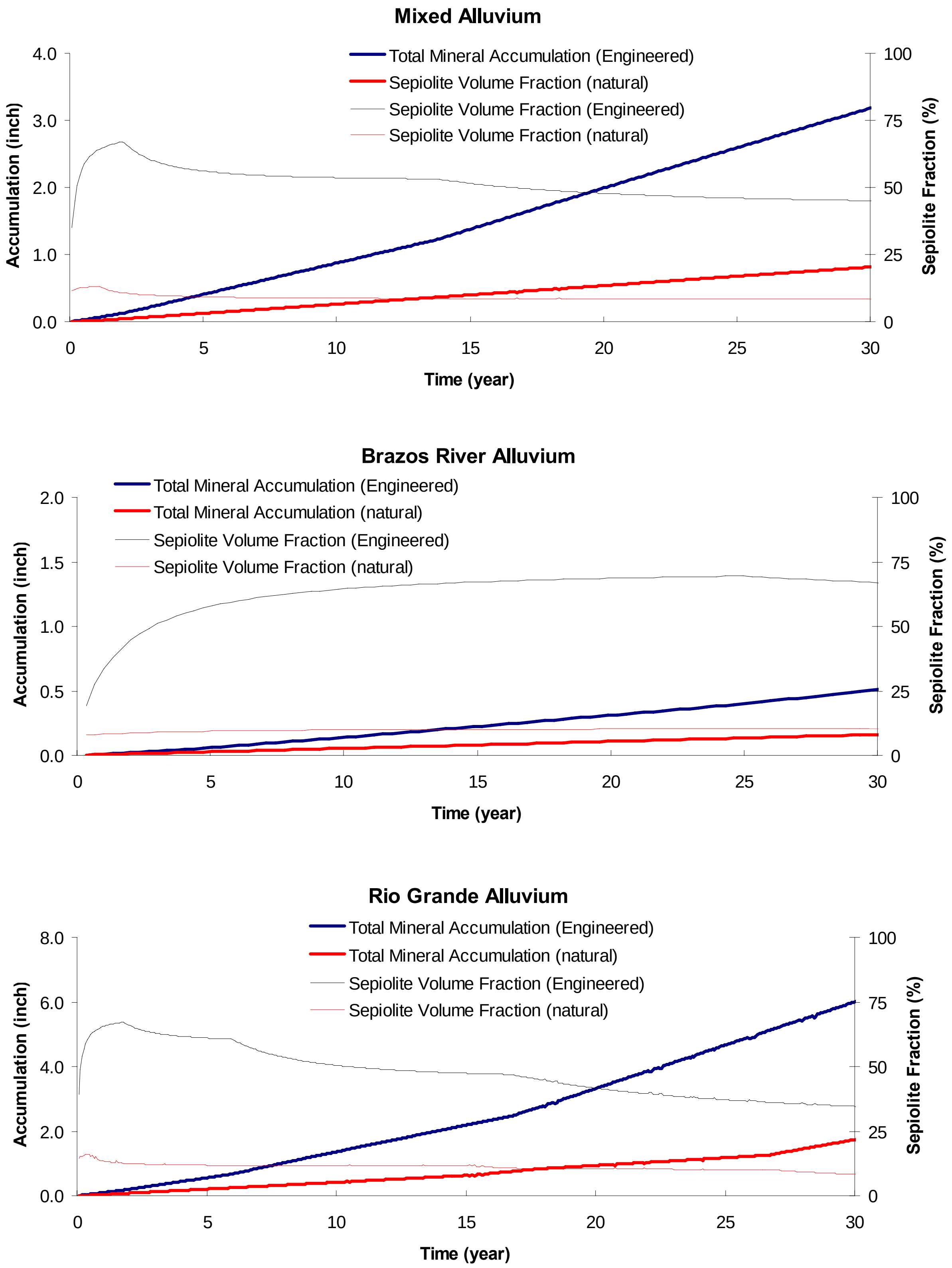


Figure 15-5. Specific accumulation (inches) and sepiolite fraction in accumulation for all water groups in engineered and natural settings (pond depth is 3 inches)

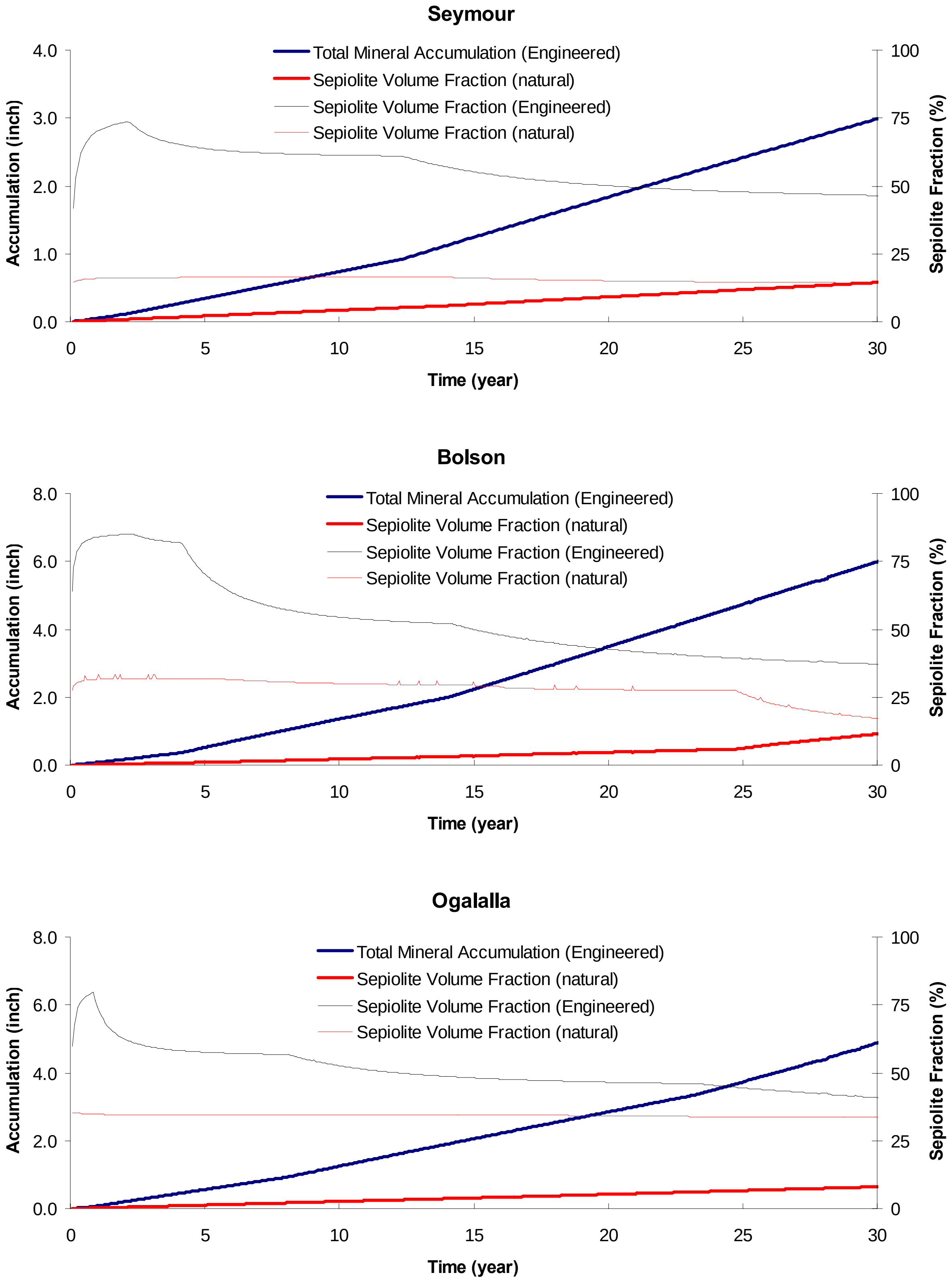


Figure 15-5. Specific accumulation (inches) and sepiolite fraction in accumulation for all water groups in engineered and natural settings (pond depth is 3 inches) (continued).

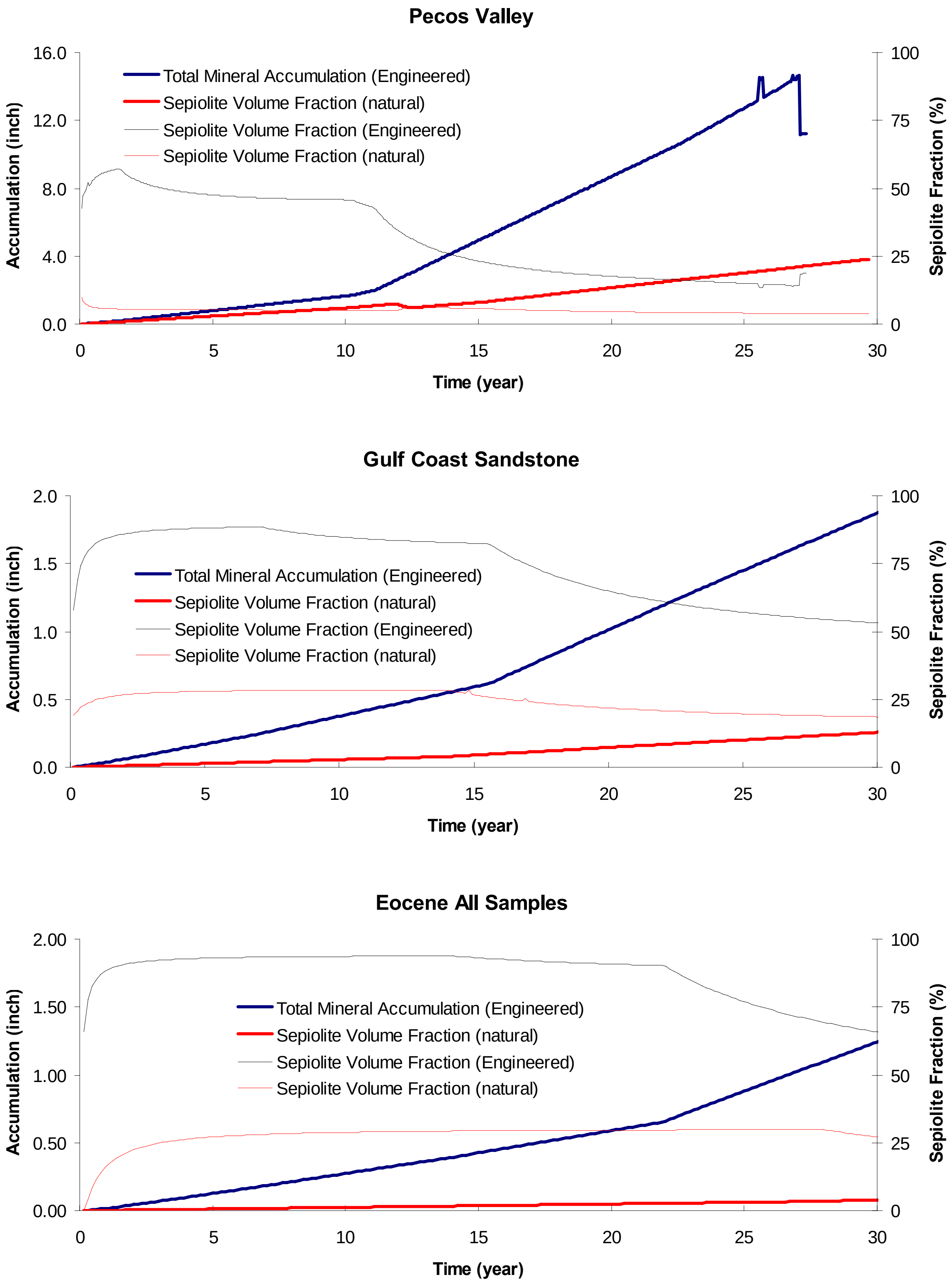
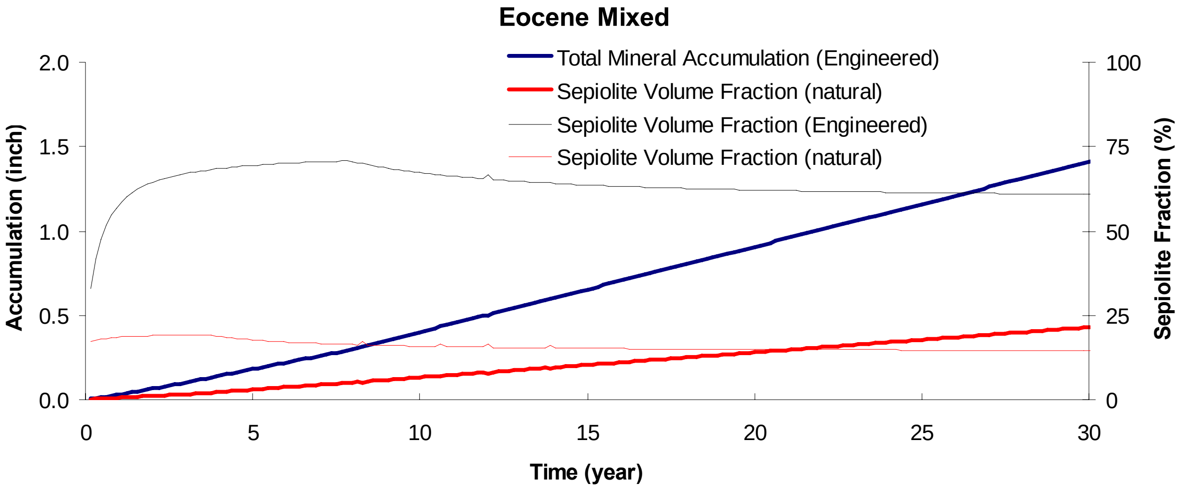
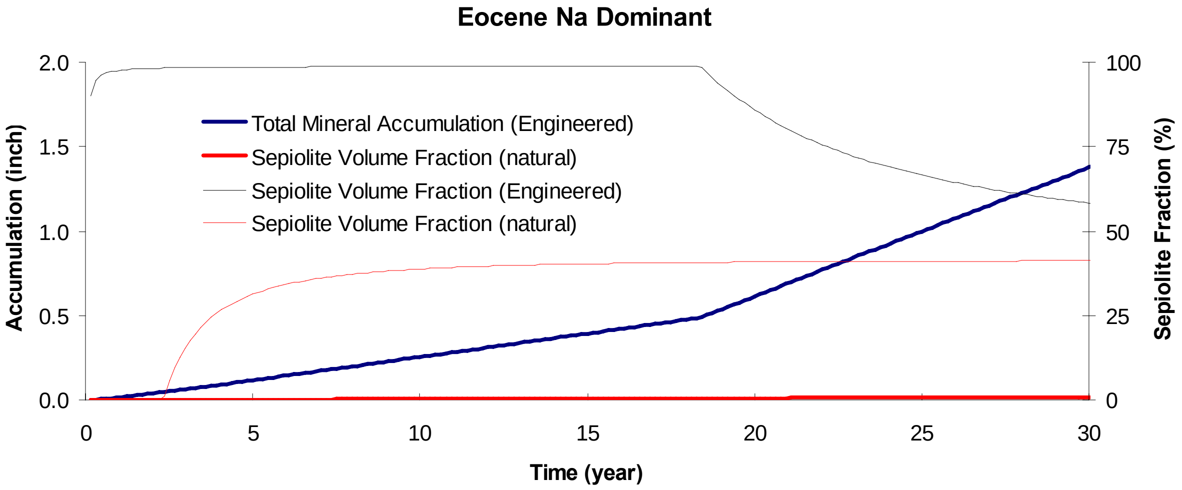


Figure 15-5. Specific accumulation (inches) and sepiolite fraction in accumulation for all water groups in engineered and natural settings (pond depth is 3 inches) (continued)





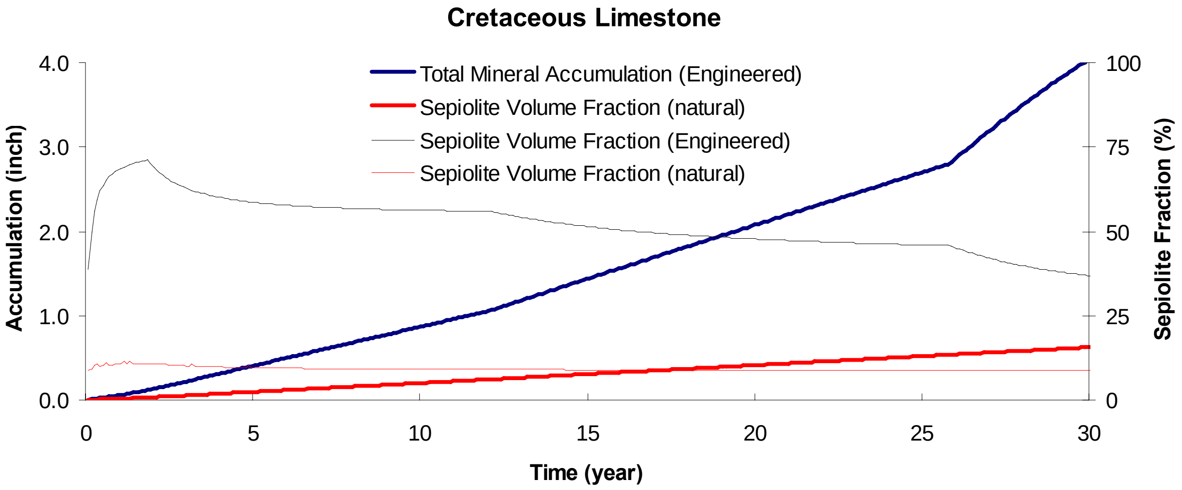
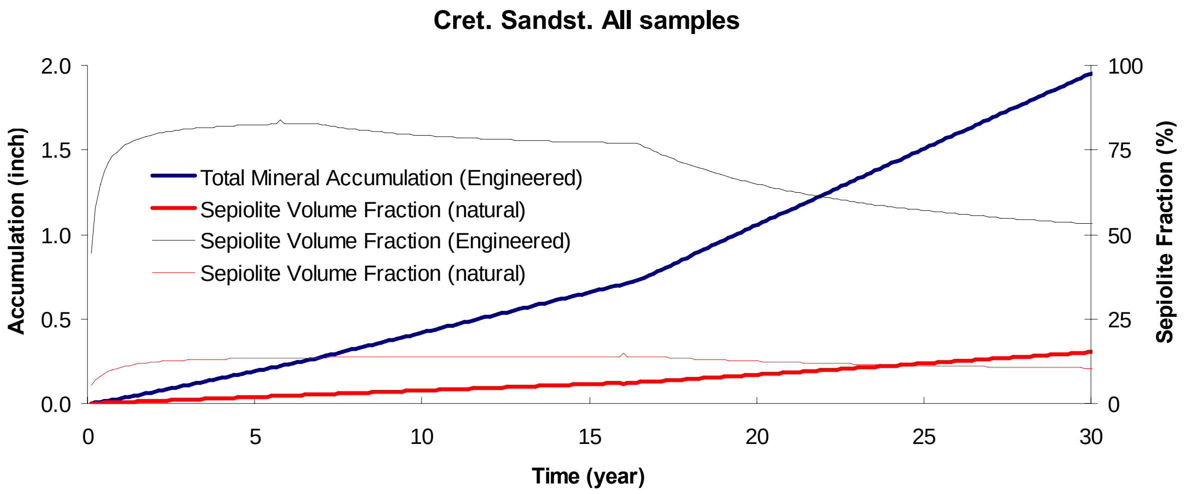
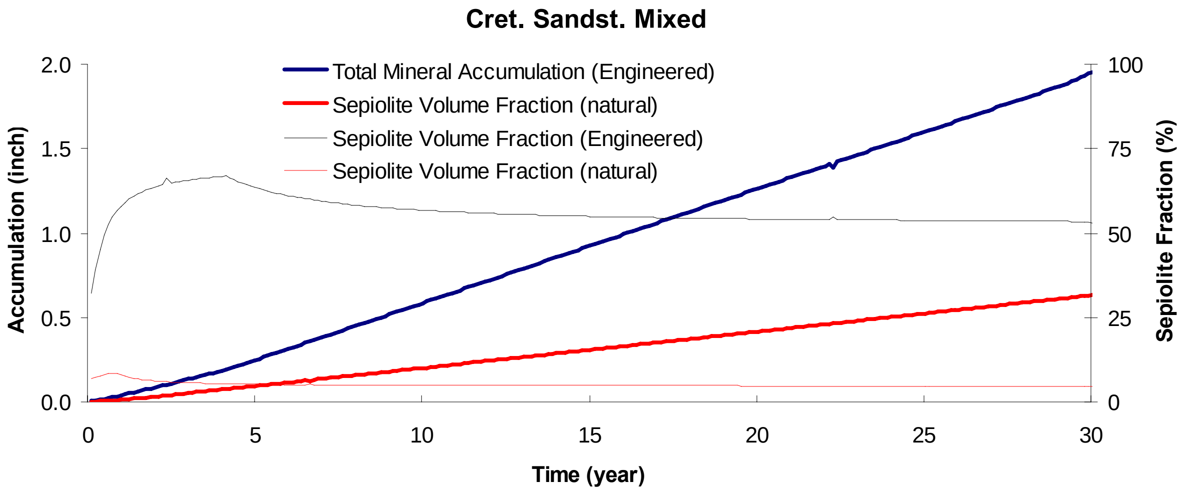


Figure 15-5. Specific accumulation (inches) and sepiolite fraction in accumulation for all water groups in engineered and natural settings (pond depth is 3 inches) (continued)





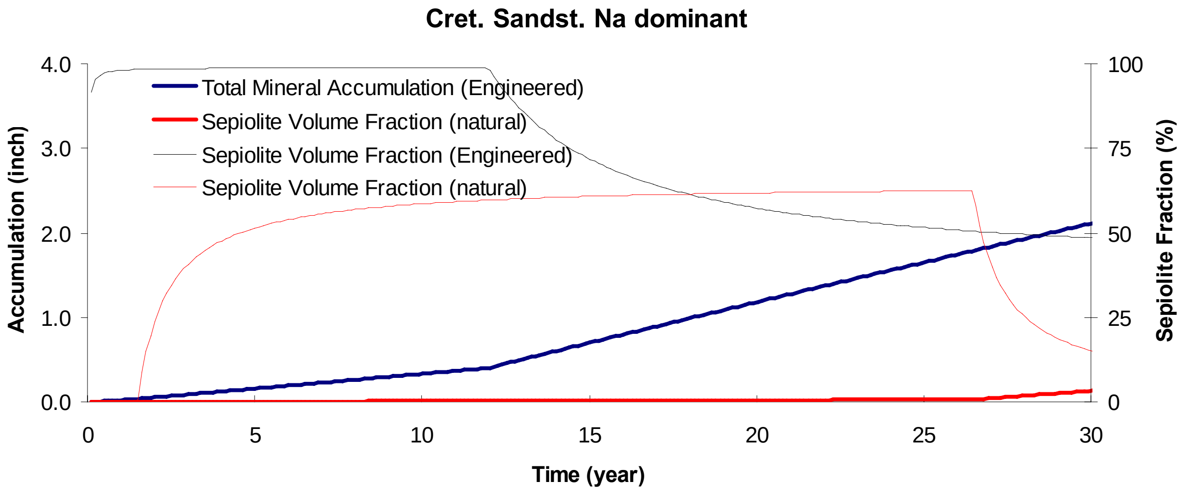


Figure 15-5. Specific accumulation (inches) and sepiolite fraction in accumulation for all water groups in engineered and natural settings (pond depth is 3 inches) (continued)

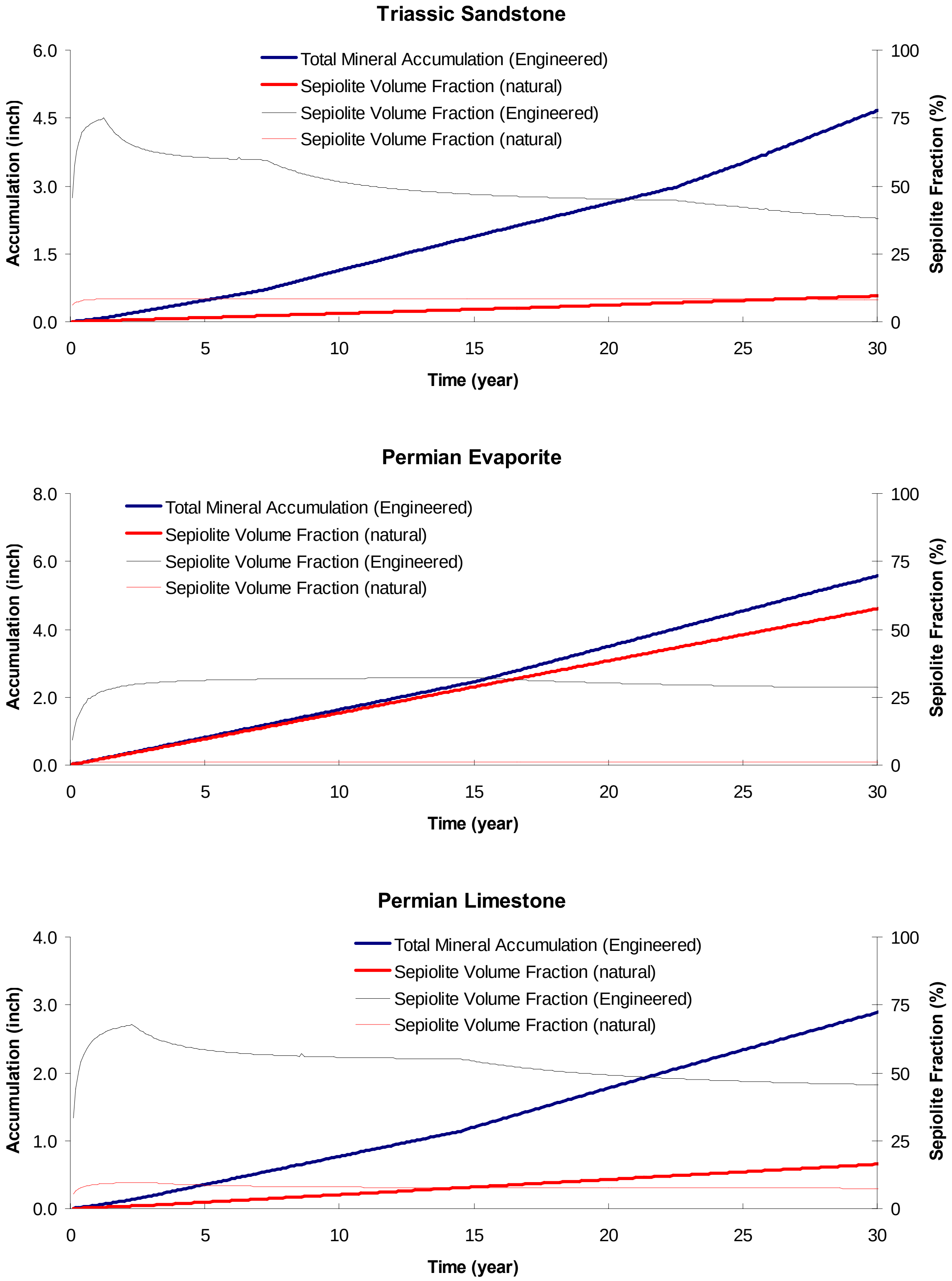
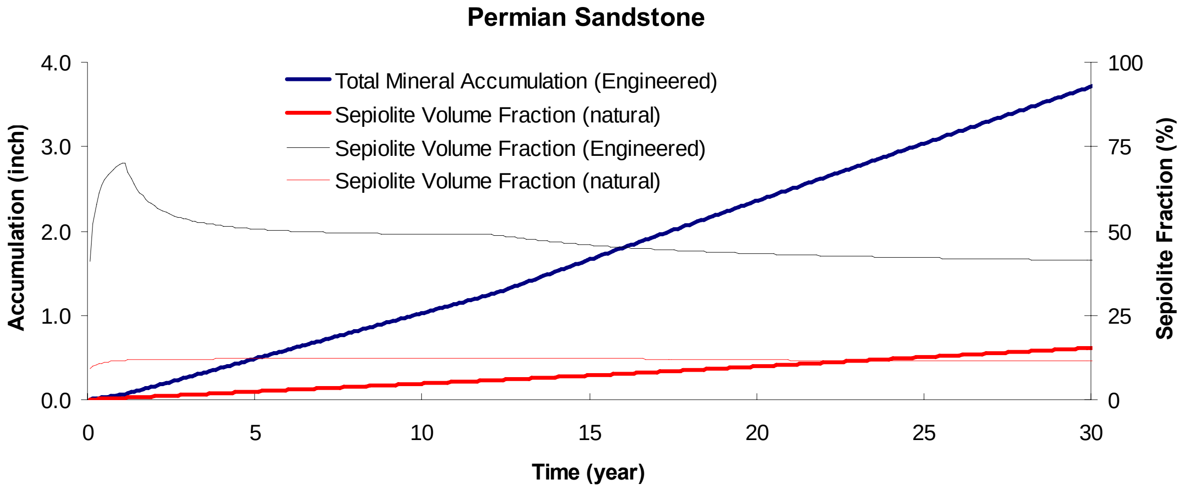
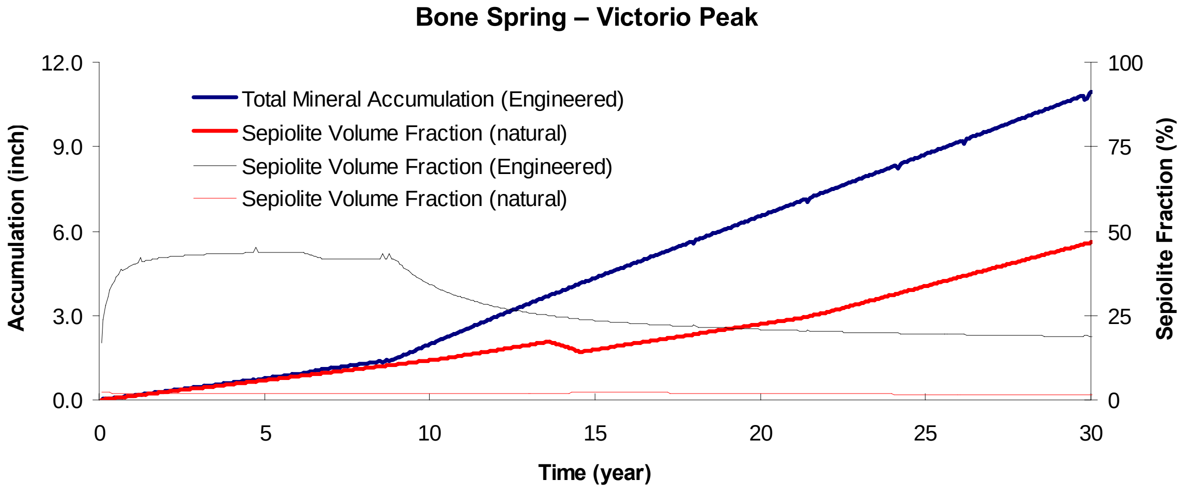


Figure 15-5. Specific accumulation (inches) and sepiolite fraction in accumulation for all water groups in engineered and natural settings (pond depth is 3 inches) (continued)





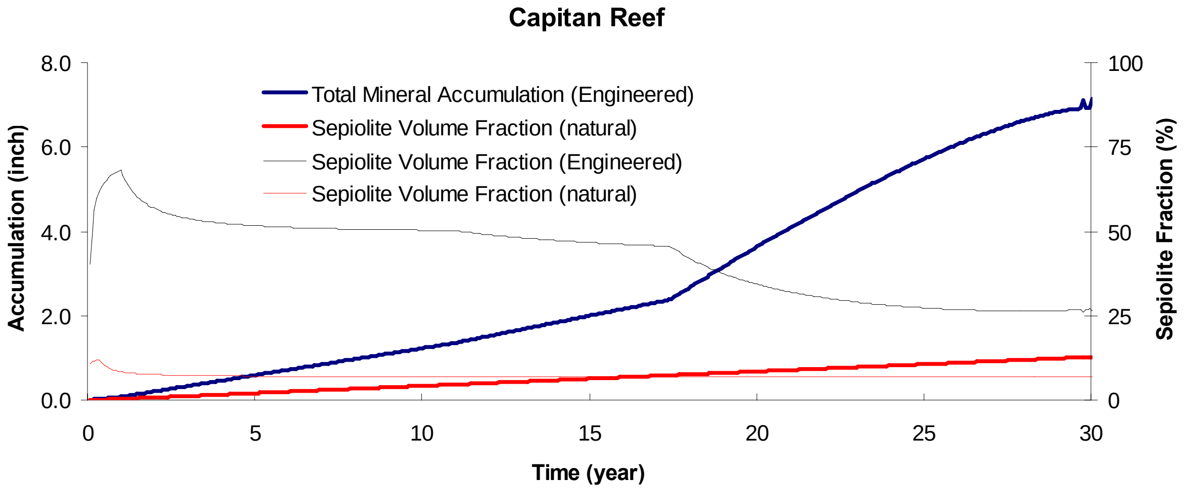
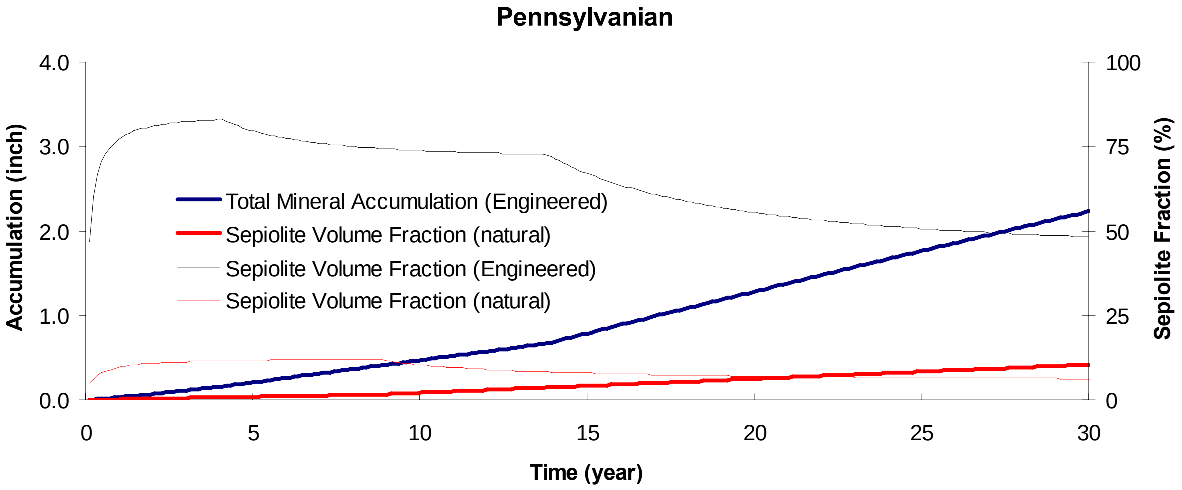
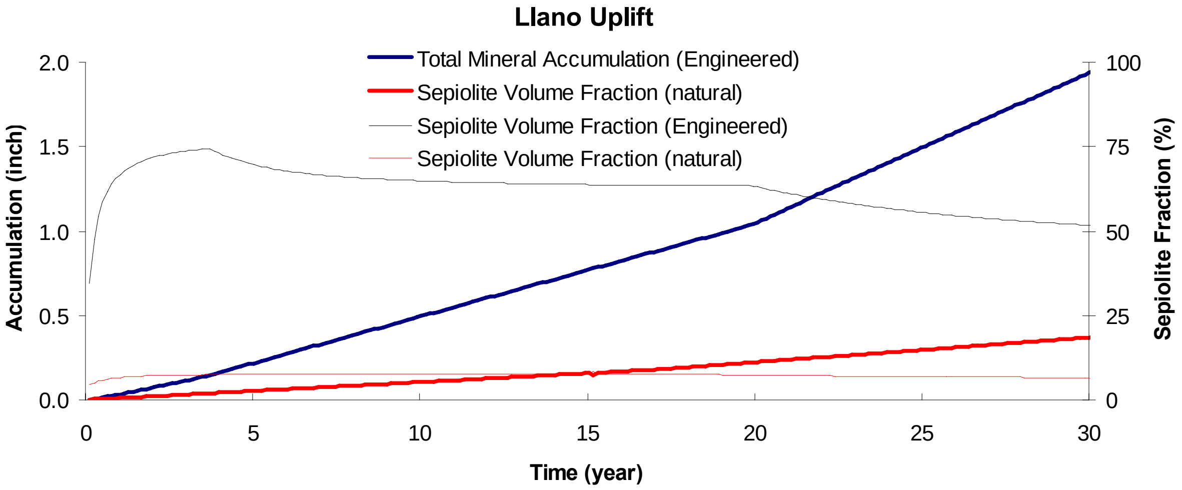


Figure 15-5. Specific accumulation (inches) and sepiolite fraction in accumulation for all water groups in engineered and natural settings (pond depth is 3 inches) (continued)





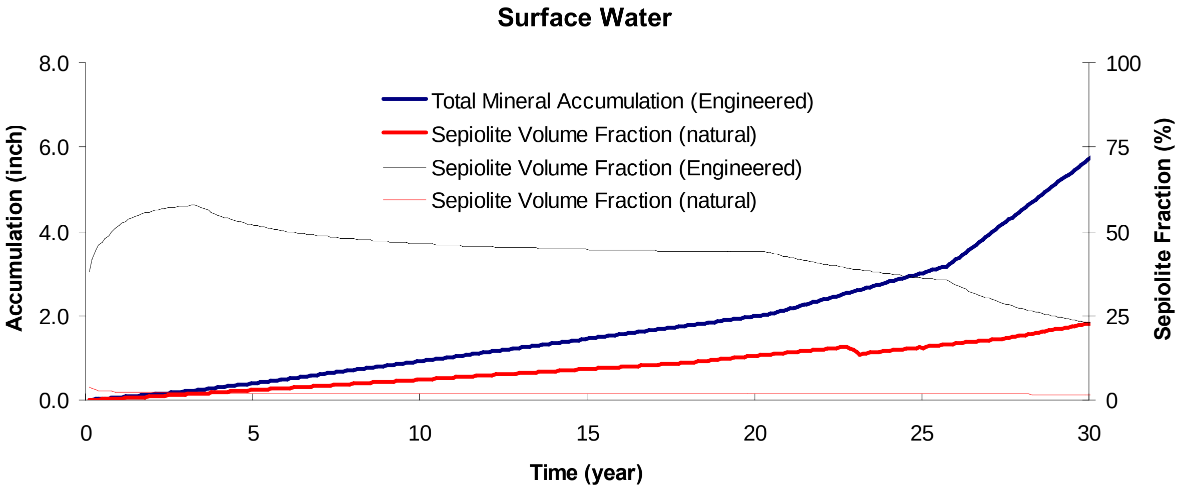


Figure 15-5. Specific accumulation (inches) and sepiolite fraction in accumulation for all water groups in engineered and natural settings (pond depth is 3 inches) (continued)

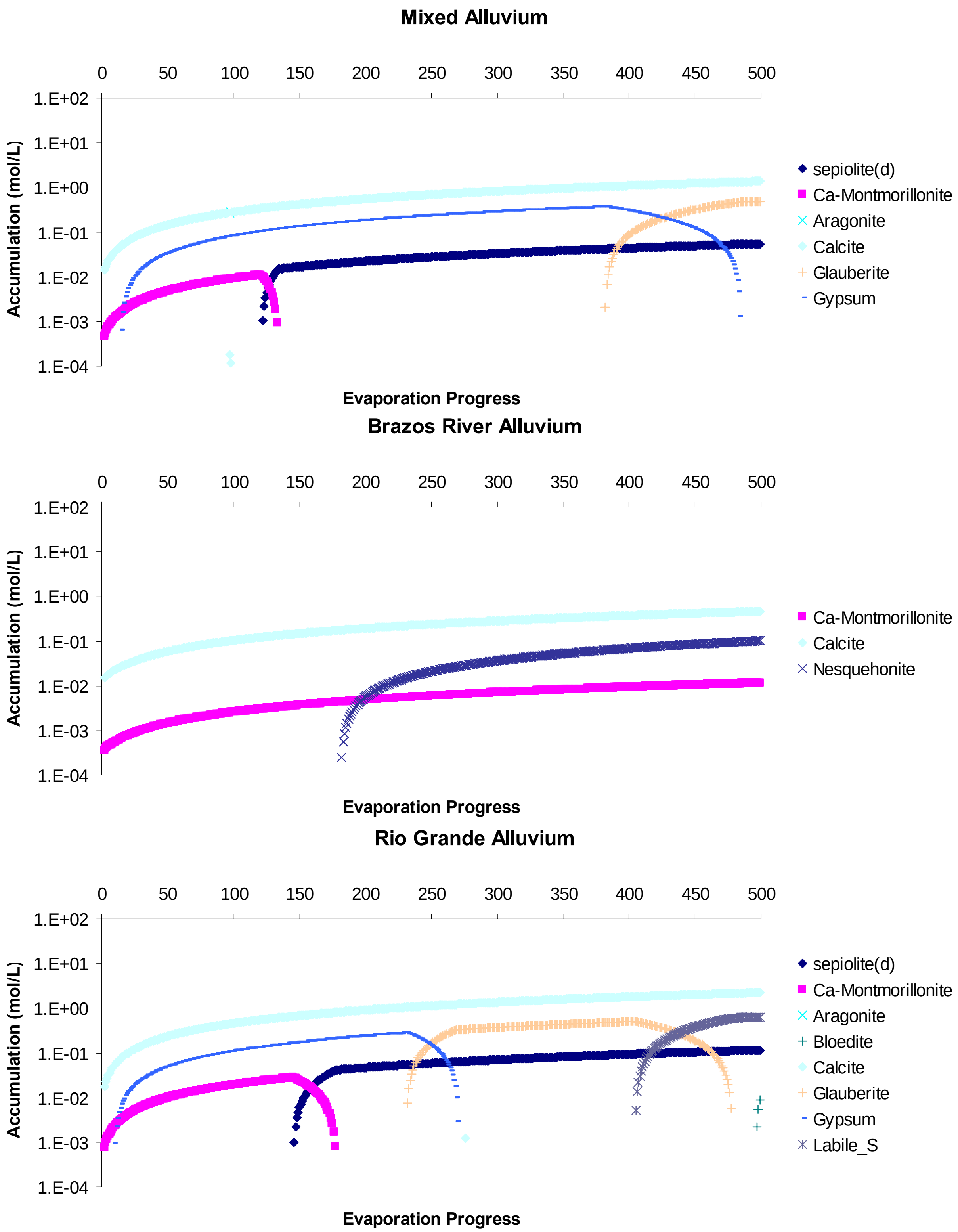
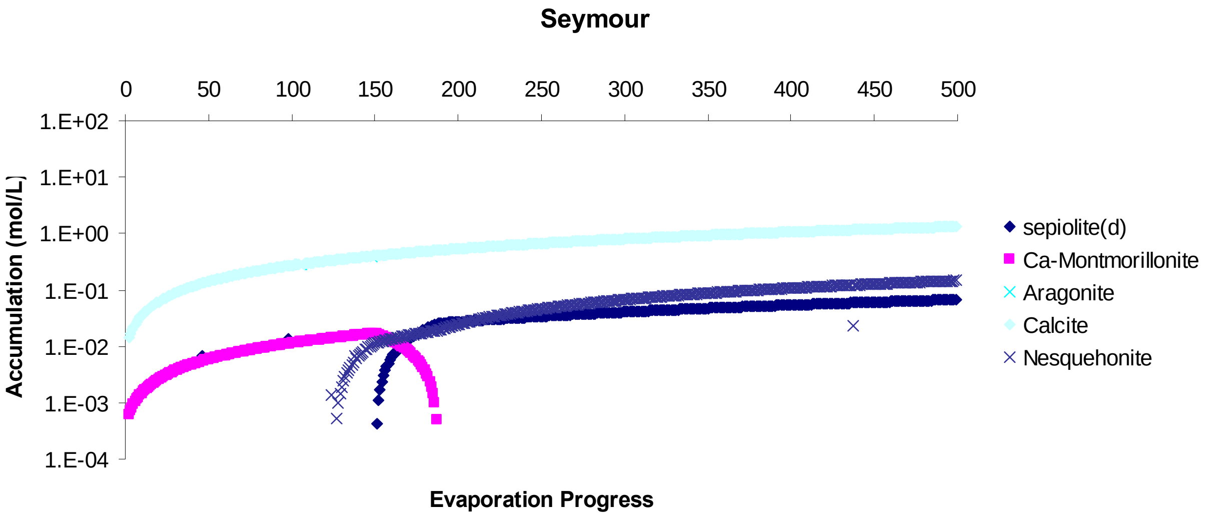
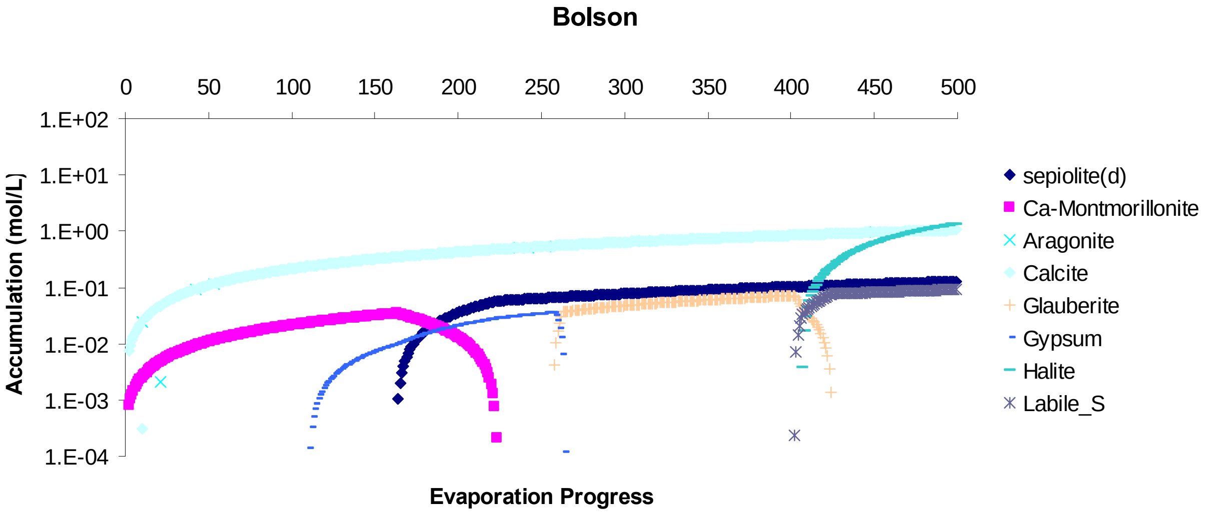


Figure 15-6. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions—Ca-Montmorillonite(d) is allowed to precipitate





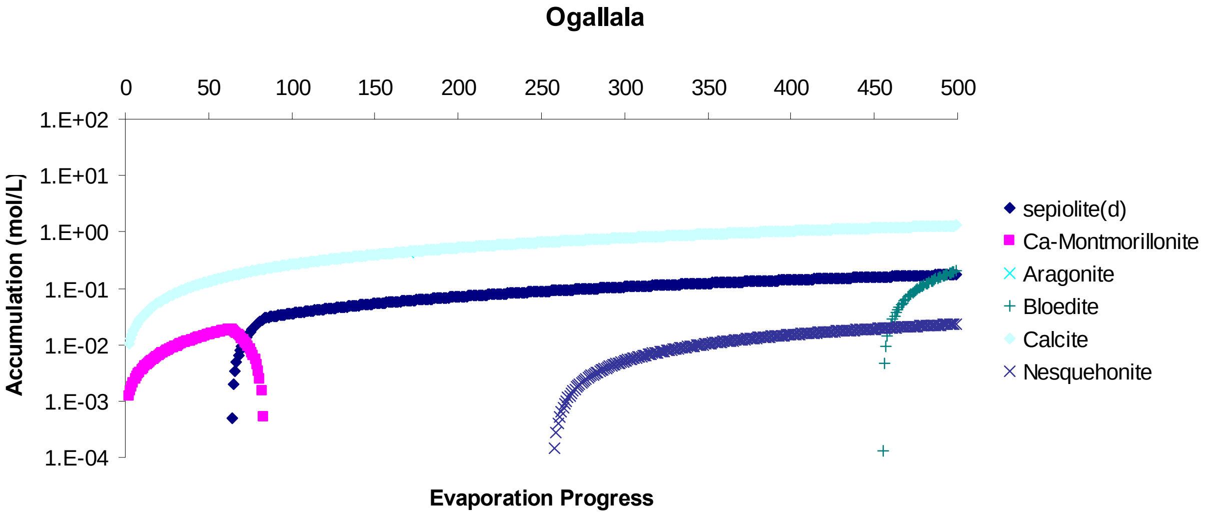
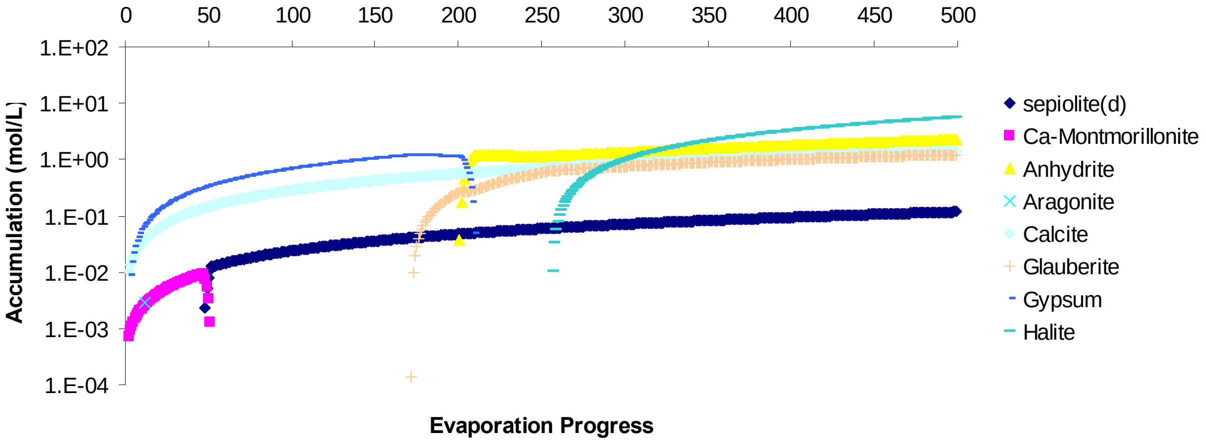
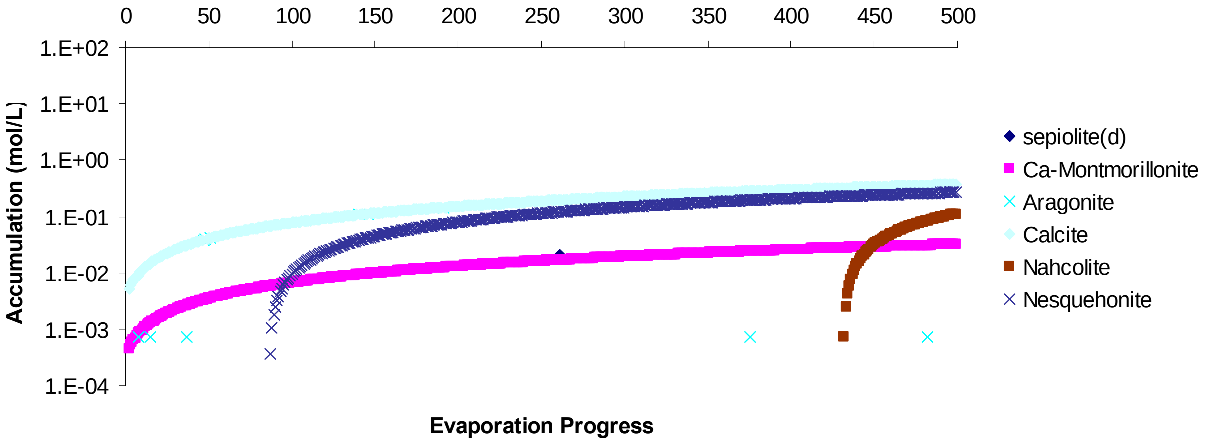


Figure 15-6. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions—Ca-Montmorillonite(d) is allowed to precipitate (continued)

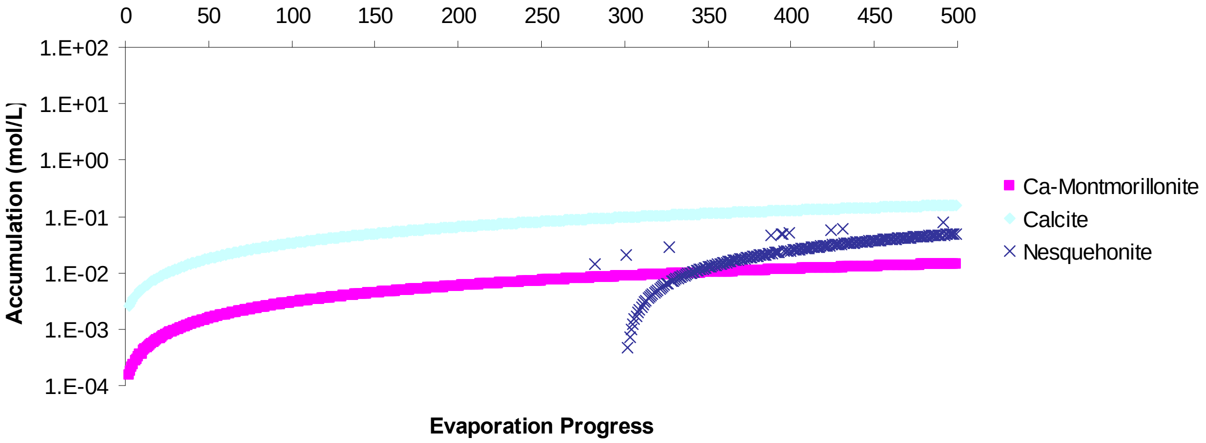
Pecos Valley



Gulf Coast Sandstone



Eocene All samples *



* Results obtained with the LLNL database not the Pitzer database

Figure 15-6. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions—Ca-Montmorillonite(d) is allowed to precipitate (continued)

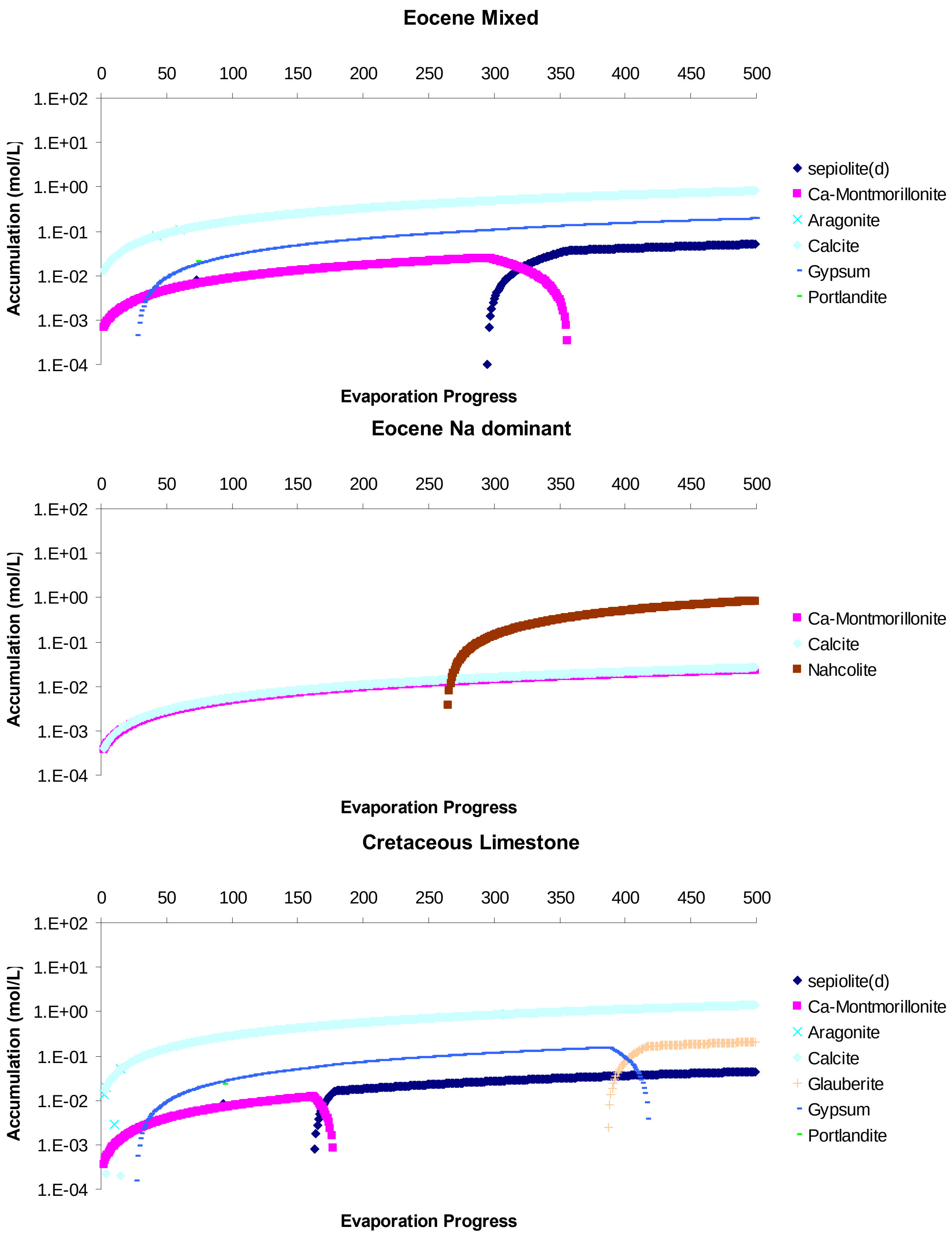


Figure 15-6. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions—Ca-Montmorillonite(d) is allowed to precipitate (continued)

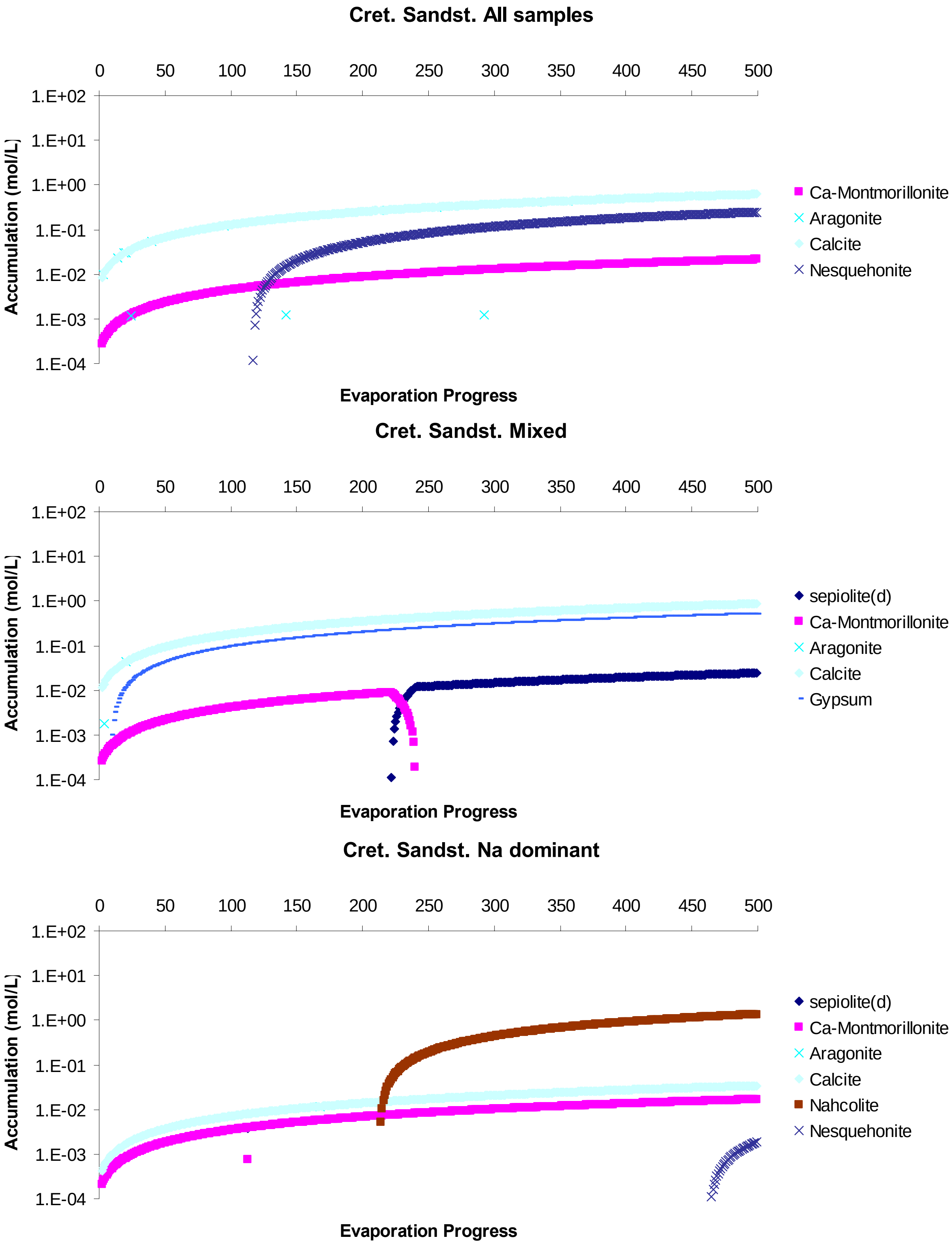


Figure 15-6. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions—Ca-Montmorillonite(d) is allowed to precipitate (continued)

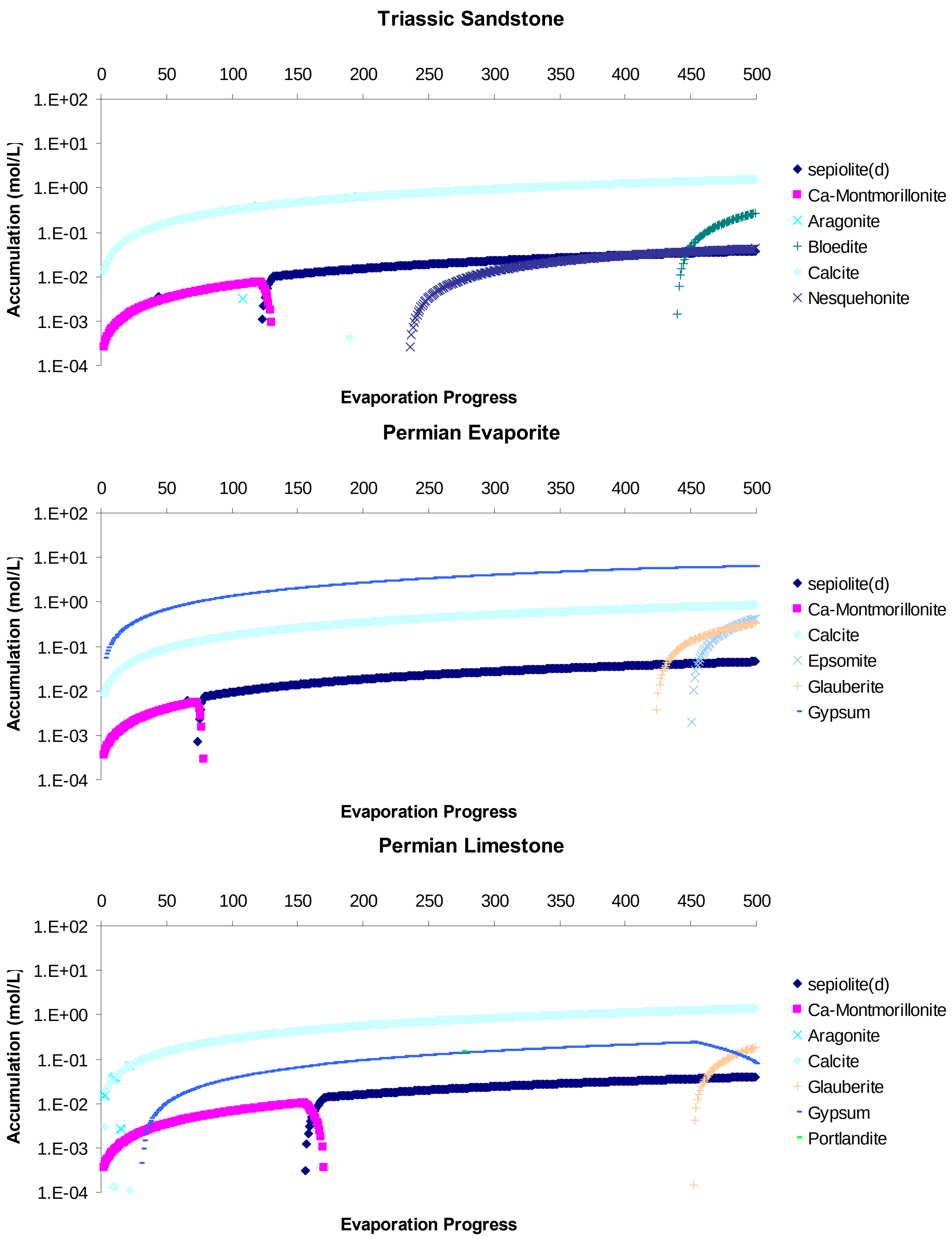
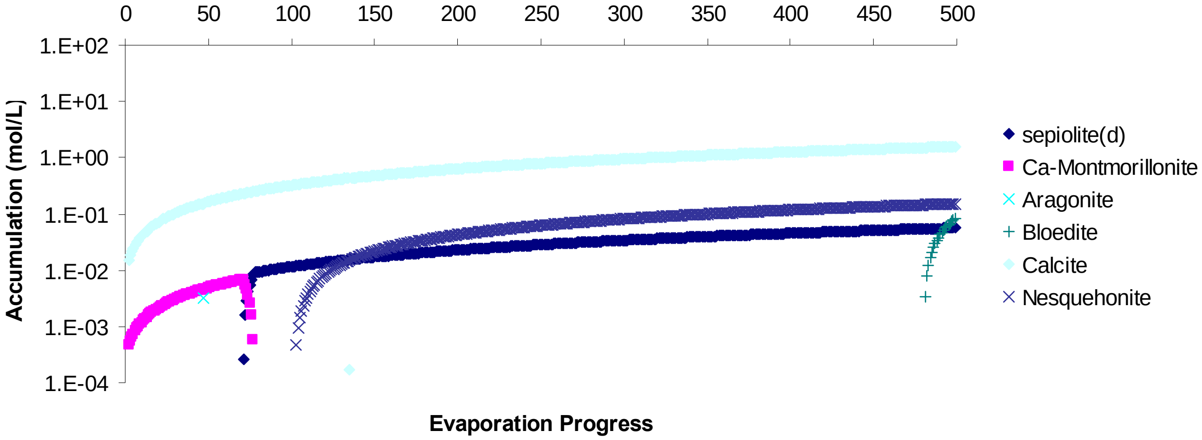
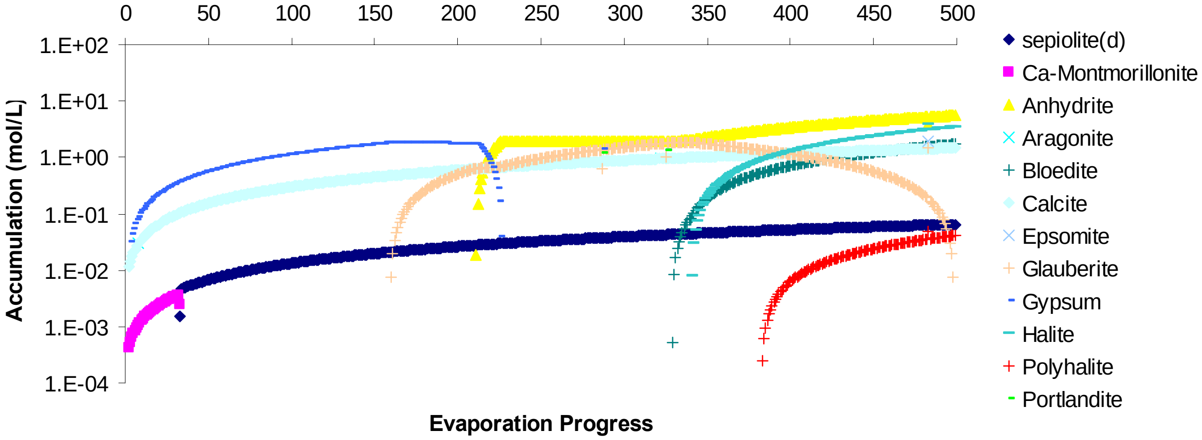


Figure 15-6. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions—Ca-Montmorillonite(d) is allowed to precipitate (continued)

Permian Sandstone



Bone Spring – Victorio Peak



Capitan Reef

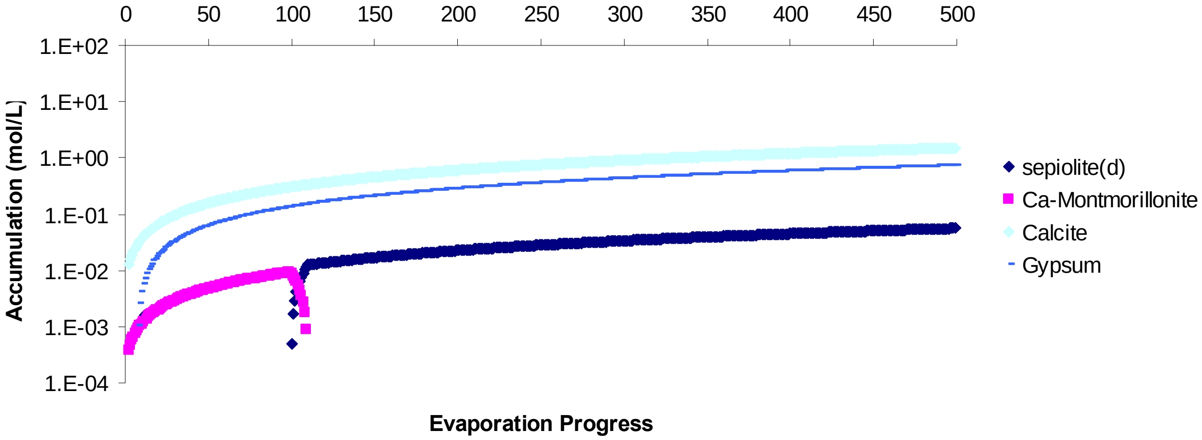
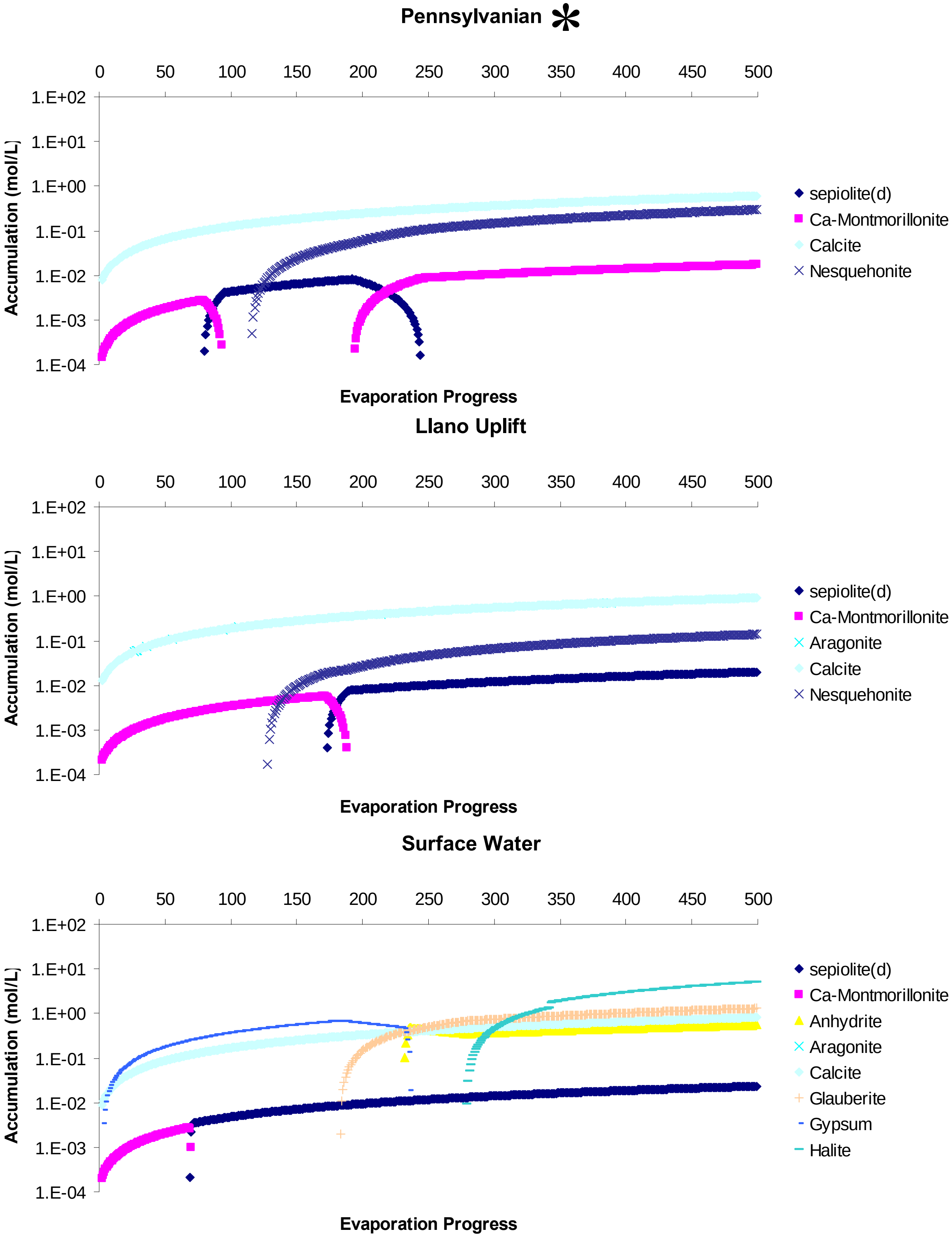


Figure 15-6. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions—Ca-Montmorillonite(d) is allowed to precipitate (continued)



* Results obtained with the LLNL database not the Pitzer database

Figure 15-6. Mineral precipitation sequence as evaporation progresses using computed concentrate as the source in nonengineered conditions—Ca-Montmorillonite(d) is allowed to precipitate (continued)

# 16 Appendix I:
# Disposal of As-Rich Residuals as Hazardous Wastes

Residuals from the desalination process that accumulate on the bottom of evaporation ponds must be removed and disposed of during facility closure activities and, possibly, periodically as part of normal maintenance. The disposal of residual waste may be needed for all conventional and alternative liner technologies in order to maintain the effective volume of the evaporation ponds. If the water being processed contains contaminants, such as arsenic, heavy metals, radionuclides, etc., these constituents will concentrate in the residual sediments. Once these residuals have been removed from the evaporation ponds, they may be considered Hazardous Waste under the Resource Conservation and Recovery Act (RCRA), if the concentrations of certain contaminants exceed levels of toxicity prescribed by Federal regulations (40 CFR 261). If this is indeed the case, some stabilization method would have to be used before the pond residuals are sent to an RCRA landfill. The relevant metric is not the amount of contaminant in the sludge but the amount that is expected to be mobilized and leached under the aggressive conditions found in a landfill.

A solid waste, including evaporation pond sludge, exhibits the characteristic of toxicity if, using the Toxicity Characteristic Leaching Procedure (TCLP), test Method 1311 in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW–846, the extract from a representative sample of the waste contains any of the contaminants at a concentration equal to or greater than the respective value given in the table in 40 CFR 261.24. Most of the contaminants listed are manufactured, organic compounds, but also include arsenic (5.0 mg/L), barium (100.0 mg/L), cadmium (1.0 mg/L), lead (5.0 mg/L), mercury (0.2 mg/L), selenium (1.0 mg/L), and silver (5.0 mg/L). Radionuclides are not included. Those regulatory levels for contaminants in the extract were typically derived by computing 100 times the MCL. As far as we can tell so far, the regulatory limit for arsenic is still 5.0 mg/L (in accordance with 40 CFR 261.24) using the TCLP Method 1311, despite the decrease of the arsenic MCL from 50 to 10 mg/L. The TCLP procedure is commonly applied on a variety of wastes and consists of testing the fluid leached from the waste in a 20:1 liquid:solid ratio (weight basis). Nonvolatile waste samples with interstitial water at pH>5 (as it is likely for evaporation pond sludges) are submitted to hot acid ($50^oC$) at low concentration for a short duration (10 minutes). Although most of the arsenic is typically sorbed onto mineral surfaces (clay and metal oxides), such a treatment will most likely desorb most of it. Typical sequence extraction procedures to desorb arsenic from crystalline Fe and Mn oxides involve aggressive conditions (low pH and temperature in the range of 70 to $100^oC$ for several hours) (e.g., Keon et al., 2001, and references therein). The TCLP procedure is likely to mobilize all arsenic recently attached to particles, that is, most of the amount discharged into the pond.

Consultation of Scanlon et al. (2005) suggests that an upper bound for average arsenic concentration in the feedwater for those aquifers located in areas with elevated arsenic concentrations (Panhandle and south Gulf coast) is 50 ppb, which translates into an arsenic concentration for the concentrate of $C_{As}$=200 ppb. The amount on a pond unit surface area at time $t$ is $C_{As} \times e \times t \times \rho_w (\times 1 \text{ m}^2)$, where $e$ is the net evaporation rate (30 inches/year), $t$=30 years is the facility life time, and $\rho_w$=1kg/L is feedwater density. Section 4.3.4 of the main report shows that a precipitate thickness of $h$=1 inch after 30 years is reasonable. It is conservative to use a small bottom sediment thickness because it will yield a larger arsenic concentration in the solid phase. If material density (not accounting for porosity) is about $\rho_{ssl}$=2,400 kg/m$^3$, the arsenic concentration in the solid sludge $CSl_{As}$ is given by

$$CSl_{As} = \frac{C_{As} \times e \times t \times \rho_w}{h \times \rho_{ssl}}$$ in a consistent system of units.

The regulations call for analyzing the liquid extract obtained with a 20:1 liquid:solid ratio. The resulting arsenic concentration in the liquid extract $CLe_{As}$ is $CLe_{As} = MF \times CSl_{As}/20$, where $MF$ is the fraction of arsenic mobilized during the extraction procedure. The resulting

$$CLe_{As} = \frac{MF \times C_{As} \times e \times t \times \rho_w}{20 \times h \times \rho_{ssl}} <?\ CTox_{As}$$ where $CTox_{As}$

is the concentration beyond which the bottom sediments are regulated as hazardous wastes. The $CTox_{As}$ concentration is approximately equal to 5 ppm for arsenic. Using the numerical values suggested above and assuming full leaching of the arsenic, we obtain $CLe_{As}$=4 ppm—that is, residual bottom sediments are NOT considered hazardous wastes.

# 17 Appendix J:
# Conceptual Drawings of Evaporation Ponds

This appendix presents a conceptual drawing of a generic evaporation pond modeled after precipitation / evaporation characteristics of quadrangle 608 (as defined by TWDB, 2006a), corresponding to the Brady site (Figure 17-1).

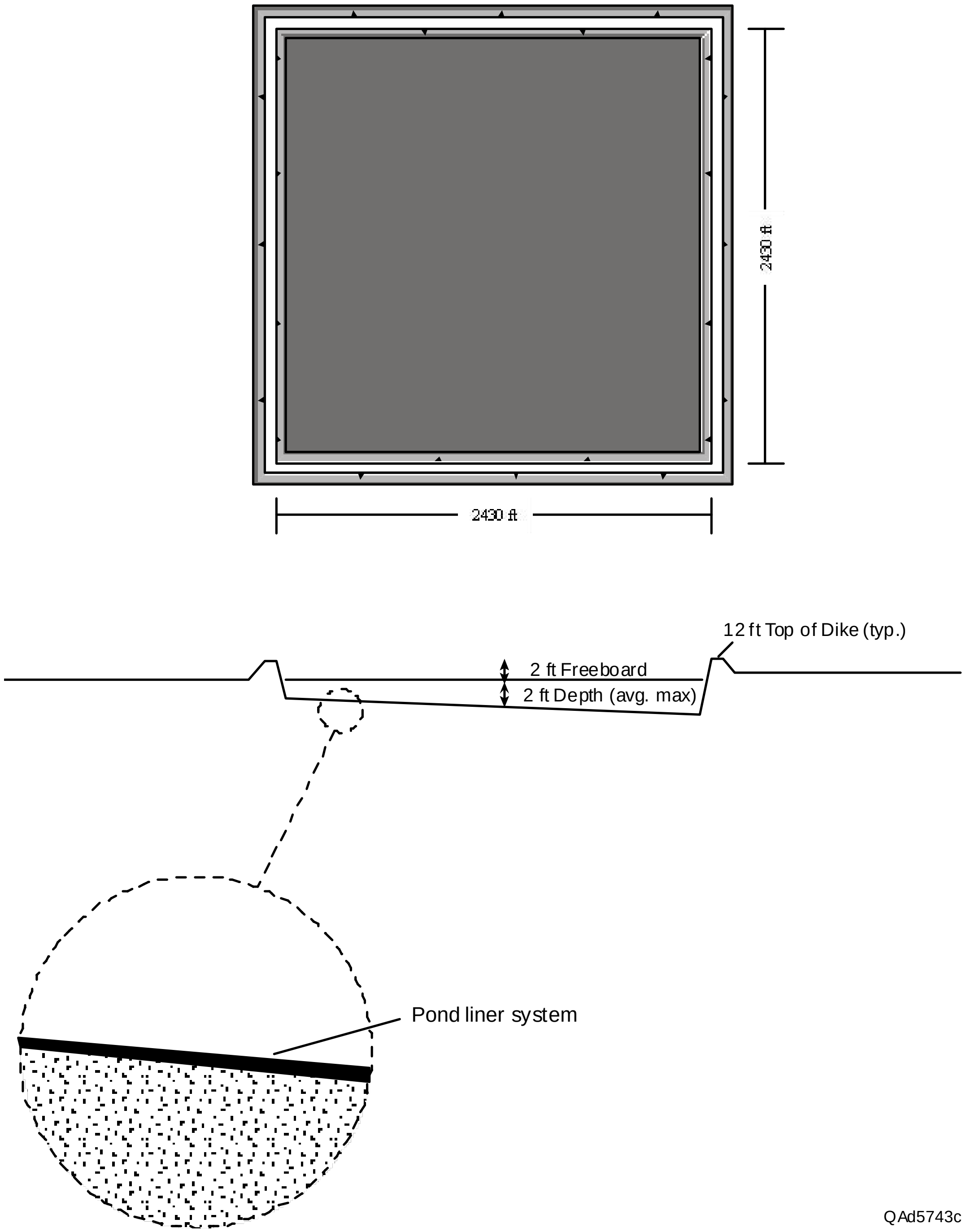


Figure 17-1. Conceptual drawing (layout and cross-section) of evaporation pond for generic facility in quadrangle 608

The pond's shape is assumed square with an area of 135.60 acres (~2430 ft × ~2430 ft) but it could be rectangular depending on local conditions (access, presence of buildings, topography, optimization of excavation costs, prevailing wind directions, etc.). The use of multiple ponds separated by baffles with a total area equal to that of the single basin presented in Figure 17-1 is also possible. The slope of each side of the berm is determined by the geotechnical characteristics of the material used to construct the pond. The pond is generally built with a slight slope to the pond bottom for easier maintenance. Maximum pond depth and freeboard height (to accommodate storm rainfall) are generally imposed in the permit and are determined by local weather conditions. The pond liner system can be either a geomembrane, generally coupled with a leak detection system, or a clay liner (in-situ clay or native clay). The details of the liner construction vary according to the nature of the material used.

# 18 Appendix K:
# Responses to Review Comments

## Responses to Review Comments

The report deals with a complex subject, and it was difficult for reviewers to clearly understand the conclusions of the study. Please revise the report to explain the study's findings and recommendations. The report needs editing to correct the typos, and to improve its structure and readability.
*The structure of the report was revised following TWDB's request. Conclusions were rephrased and could be summarized by the following: (1) There is no regulatory barrier. (2) Although there are many feasible techniques (some described in the report), they all come at an extra cost. Only the "do almost nothing" approach, that is, add some cheap additives to the concentrate stream, satisfies the requirement of no cost increase (case of prescriptive liners).*

Executive Summary - The executive summary needs to be re-written to better summarize the study findings and recommendations for a wider, non-scientific audience.
*The executive summary has been rewritten.*

Please provide specific information and recommendations on sealants that could be used for evaporation ponds, and pertinent construction details.
*We do not think that the word "sealant" properly describes the additives that could be used in the self-sealing process. It is true that sealants can be added after construction and before the start of operations. Many other improvements can also be executed, and some are described in the report. However, and this is a common thread throughout the report, those improvements all add to the cost of the pond. They go against the premise of this report and the whole idea of self sealing, which is to let the concentrate do the work. This is also the reason that there are NO construction details specific to a self-sealing pond when compared to a conventional pond.*

Please provide complete information on the types of permits required for self-sealing evaporation ponds (please include details such as the name of the Division to be contacted at the Texas Commission on Environmental Quality (TCEQ), permit requirements, and permit procedures).
*Information added.*

It is indicated in the report that sepiolite has many advantages, however, the techniques on how sepiolite (and any other sealants) can be beneficially used for self-sealing of ponds are not discussed. Please include this information.
*There is no specific technique to be used. Sepiolite precursors are added to the concentrate stream. Sepiolite is a self-sealing material; that is, it will precipitate by itself, initially seal the bottom liner, and seal any opening that may appear during the life of the pond. Many operational combinations of additive concentrations, amounts, products aiding nucleation can be tried, they, however, require laboratory and pilot scale work. The whole issue of this report lies in engineering ponds at a cost no higher than that of ponds constructed using common practices. Although many additives could seal the liners, they will not be "self sealing" and will be more expensive than the conventional approach.*

Please clarify the significance of the statement "Self-sealing properties appear to be most useful with constructed clay liner".
*Sentence changed; the statement contrasted usefulness of self-sealing properties for clay liners and geomembranes.*

Please be specific on the additives/compounds you recommend for "self-sealing" of ponds
*The report focuses on one type of additive: Mg (magnesium chloride) and silica (sodium metasilicate) because their combination generates sepiolite, a potential self-sealing agent. However, chemical composition of the concentrate is very specific to each evaporation pond, suggesting that additives could be tailored to each pond. There is no across-the-board, cost-effective solution that would work in each and every evaporation pond.*

Look at both currently operating evaporation ponds and hypothetical ponds in West Texas: Partially Addressed (could not find section on hypothetical ponds in West Texas)
*The whole report is about evaporation ponds in West Texas and elsewhere in the state.*

Additives needed to reduce hydraulic conductivity to $10^{-9}$ m/s: Not clearly addressed or explained
*Additives will favor precipitation of material that should show a conductivity* $<10^{-9}$ *m/s, as specified in the regulations. No conductivity measurement was performed in this study.*

Consider arsenic as a potential contaminant: Not Addressed
*No data are available on arsenic content of evaporation ponds in areas with elevated arsenic concentrations. We added a section and simple guidelines to address the possibility of pond residuals being classified as hazardous wastes.*

Depending on the success with sampling, measure the hydraulic conductivity of sludge: Not Addressed
*No sludge was sampled.*

Examine the chemical nature of solids, grain size, and surface area: Not Addressed
*X-ray analyses were performed (see Appendix E).*

"Ultimate goal of this project is to make evaporation ponds cheaper to build and operate"…..: Not accomplished
*The "goal" of this project was to determine whether self-sealing mechanisms had the potential to lower the cost of building and operating evaporation ponds. We successfully evaluated this premise to the extent of the existing data.*

Contact USEPA and TCEQ for opinion on permitting retention and evaporation basins: Partially Addressed (only TCEQ contacted)
*No need to interview EPA because this is strictly a state issue, as explained in the report.*

Collaborate on a listing of policy, regulatory, and statutory shifts needed to overcome regulatory hurdles, make projections….: Partially Addressed
*As stated in the report, no regulatory hurdles exist, so such a list seems unnecessary. Permitting is dependent upon effective technical demonstration of equivalency with existing performance criteria.*

Help in getting samples from actual evaporation ponds: Not being done by consultant, most site visits had to be arranged by TWDB
*Four sites were sampled; two visits were arranged by TWDB after a suggestion by TWDB to facilitate the sampling. However, BEG did all physical sampling, chemical analyses, and interpretation of the data.*

Determine general pond size requirements for a 1-MGD facility using Mickley work sheets: Not adequately Addressed
*General pond size requirements for a 1-MGD facility using Mickley's work were calculated. As realistic examples, areas of generic ponds having the climatic characteristics of the four facilities having evaporation ponds visited (and an average inflow rate of 0.3 MGD of concentrate) were computed. The area varies between 2.35 (Horizon MUD) and 5.85 (River Oaks Ranch) acres. As noted in the report, a self-sealing pond is no different from a regular pond.*

Prepare conceptual drawings to illustrate plan view and cross-section of evaporation pond: Not Addressed, Need drawings/blueprints
*Several techniques and processes are available to self-seal ponds; however, the request of having them constructed and operated cheaper than a regular pond severely constrains available approaches. Only the chemical nature of the pond influx will differentiate a generic conventional pond and a cheaper, generic, self-sealing one. A self-sealing evaporation pond would not be constructed differently from a regular evaporation pond. Generic drawing/blue-print of a generic self-sealing evaporation pond has been added.*

Develop preliminary cost estimates for materials including additives: Not Addressed, Need cost estimates
*Cost of additives had been given in report. General costs of a regular evaporation pond have been added.*

If appropriate, consider novel technologies such as solar ponds: Not Addressed
*As noted in the report, solar ponds are nothing like self-sealing evaporation ponds. Solar ponds could be an energy-saving feature but have little to do with self-sealing characteristics, are delicate to operate properly, and are unlikely to be a money-saving measure for disposing of the concentrate. This is not the direction that self-sealing should be taking.*

p.8. In all figures starting from this one, the Source must be shown BELOW the figure caption (not above the caption).
*I could not find such a requirement in the TWDB suggested format*

p.13. What is llnl ?
*llnl (changed to LLNL) stands for Lawrence Livermore National Laboratory. LLNL.dat is a database generated by using data put together by LLNL.*

p.18. Consider changing the second green and red dots in legend: hard to distinguish shades of green and red

*Fig. 3-4 has been changed. In addition, Fig. 3-5 has been updated (Brady feedwater source is SW, not GW—see note at bottom of Table 3-2)*

p.31. Explain in simple language why TLAP is required (self-sealing ponds do not involve land-application, such as animal waste and sludge)
*See inserted text.*

p.35. Please specify clearly what permits are required, which division, etc. Are these ponds considered "no-discharge" facilities? Regulatory/Legal aspects need to be re-written more clearly.
*See inserted text. Only a State TLAP permit is needed from the "Water Quality" division. Evaporation ponds are "no-discharge" facilities.*

p.37. Summarize and state exactly what you recommend to be added for "self-sealing of evaporation ponds" (the main objective of this study)
*The report does not recommend specific additives. Each evaporation pond is a specific case. The report does suggest that sepiolite precursors could work, but this small project did not perform the field tests needed to give true recommendations. Suggestions for future studies that could lead to explicit recommendations are presented in the conclusions section.*

p.39. Explain the significance of any of the constituents in this table to "self-sealing". What does the table show?
*This table has no particular significance relative to self-sealing. It shows that concentrate has a chemical composition similar to that of feedwater; that is, the ratio of major ion concentration in the concentrate to that of the feedwater is more or less constant. This ratio is used as a general input to the geochemical calculation in which the assumption that the concentrate chemical composition can be derived simply from the chemical composition of the feedwater is made.*

p.43. "Analogs" is unusual terminology. Replace with more understandable terms.
*Analog is an accepted geologic and engineering term, it is now defined at the first instance of its use in the report.*

p.43. Consider replacing "permeability" with "hydraulic conductivity"
*Change made when "permeability" was associated with a value in cm/s; cm/s is not an intrinsic permeability unit but a (hydraulic) conductivity unit. However, official TCEQ permits do use permeability (as opposed to intrinsic permeability) as synonymous with hydraulic conductivity.*

p.61. Conclusions unclear - Please state your recommendations clearly for the average reader
*Explanations added*

p.61. Desalination spelling is incorrect !
*Desalination, desalinization, and desalting are perfectly correct and accepted words describing the same process. Changed to desalination for consistency*

p.62. Provide specific recommendations on the chemical amendments needed for self-sealing of ponds.

*This section does not discuss the specific nature of the additives. Some are suggested elsewhere in the report. However, this report cannot pretend to give an exhaustive list of possible additives.*

p.86-104. Please consider removing symbols in legend (e.g., blue dots) that do not appear on the maps
*All blue dot symbols (">5,000ppm TDS") removed from legends*

p.115. Twin Lakes reported in Table 10-2 is not shown in Table 10-1 and Figure 10-1. Please include.
*Twin Lakes location has been added to Figure 10-1. No water analysis had been performed on this saline lake. It was dry at the time bottom sediment samples were taken*

p.120. Please explain the significance of the different size of circles on the map. *Explanation is given in note: "symbols are proportional to the facility size". It has no special significance and is only a reminder for the reader of the relative size of the facilities.*

p.122. Please explain the blank page or remove.
*"Blank page" was explained in the short note. Some X-ray diffraction patterns added.*

# 19 Appendix L: List of Changes in Revision 1

## List of Changes in Revision 1:

Since the publication of the initial version of this report in March 2007, a few errors have been found and corrected in this new revised version. It should be noted that no additional work was performed, only corrections to the initial report. This appendix documents the changes due mostly to a typo in excel spreadsheets computing the size of evaporation ponds.

Cover page and title page:
Added revision number

Table of contents:
Added this appendix

Abstract:
Deleted the following text:
"Cost of a 5-acre evaporation pond, following prescriptive rules for municipal wastewater is in the $250,000-350,000 range, not accounting for land purchase."

Section 4.4.1 Pond Sizing and Table 4-9 (p.66):
The following text:
"The smallest pond, with an area of 2.35 acres and depth (including freeboard) of 45 inches, was calculated for quadrangle 601 (Horizon MUD) (Table 4-9). Pond designs for the other three quadrangles ranged from 4.22 to 5.8 acres in surface area, with a depth of 48 inches. They cover a representative sample of net evaporation conditions expected across the state. As expected, calculated pond size is proportional to net evaporation rate. A representative evaporation pond area for a 1-MGD desalination facility can be estimated at 5 acres.
Table 4-9. Generic pond size for 1-MGD facilities located near the sampled ponds

| **Public Utility** | **Pond Area (acres)** | **Representative of USGS Quadrangle** |
|---|---|---|
| River Oaks Ranch | 5.85 | 709 |
| Brady | 4.52 | 608 |
| Abilene | 4.22 | 508 |
| Horizon MUD | 2.35 | 601 |

"was substituted by:

The smallest pond, with an area of 70.5 acres and depth (including freeboard) of 45 inches, was calculated for quadrangle 601 (Horizon MUD) (Table 4-9). Pond designs for the other three quadrangles ranged from 126.6 to 175.5 acres in surface area, with a depth of 48 inches. They cover a representative sample of net evaporation conditions expected across the state. As expected, calculated pond size is proportional to net evaporation rate. A representative evaporation pond area for a 1-MGD desalination facility can be estimated at 125 acres.
Table 4-9. Generic pond size for 1-MGD facilities located near the sampled ponds

| **Public Utility** | **Pond Area (acres)** | **Representative of USGS Quadrangle** |
|---|---|---|
| River Oaks Ranch | 175.5 | 709 |
| Brady | 135.6 | 608 |
| Abilene | 126.6 | 508 |
| Horizon MUD | 70.5 | 601 |

### Table 4-10, 4-11, 4-12, and 4-13 (p. 67 to 70):

These tables now display the correct pond area

### Table 4-14 (p. 73):

Changed from:

| Equivalent Containment Type | If Minimum Pond Depth (1.1 inch) | If Possible Pond Depth (1 foot) |
|---|---|---|
| Clay liner | ***Rate must be <1.2 inches/yr***<br>— 616 m$^3$/year over 5 acres —<br>Translates into a single precipitant layer with $k<1\times10^{-8}$ cm/s | Precipitant $k<1\times10^{-9}$ cm/s |
| Prescriptive geomembrane liner (order of magnitude)<br>3 holes per acre | Rate is 14 inches/year/hole distributed over 1 acre<br>N/A with precipitant – defective liner<br>— ~21,000 m3/yr = 0.015 MGD — | Rate is 45 inches/year/hole distributed over 1 acre<br>N/A with precipitant – defective liner<br>— ~70,000 m3/yr = 0.05 MGD — |
| 0.15 inches of precipitant with $k = 1\times10^{-4}$ to $1\times10^{-6}$ cm/s and geomembrane liner<br>(order of magnitude)<br>3 holes per acre | Rate is 0.002 to 0.06 inches/year/hole/acre<br>— ~1 to 23 L / yr over 5 acres — | Rate is 0.08 to 2.4 inches/year/hole/acre<br>— ~1 to 95 L / yr over 5 acres — |

to:

| Equivalent Containment Type | If Minimum Pond Depth (1.1 inch) | If Possible Pond Depth (1 foot) |
|---|---|---|
| Clay liner | ***Rate must be <1.2 inches/yr***<br>— 123 m$^3$/yr/acre<br>= 0.0001 MGD/acre—<br>Translates into a single precipitant layer with $k<1\times10^{-8}$ cm/s | Precipitant $k<1\times10^{-9}$ cm/s |
| Prescriptive geomembrane liner (order of magnitude)<br>3 holes per acre | Rate is 14 inches/yr/hole distributed over 1 acre<br>N/A with precipitant – defective liner<br>— ~4,300 m$^3$/yr/acre<br>= 0.003 MGD/acre— | Rate is 45 inches/yr/hole distributed over 1 acre<br>N/A with precipitant – defective liner<br>— ~13,900 m$^3$/yr/acre<br>= 0.01 MGD/acre — |
| 0.15 inches of precipitant with $k = 1\times10^{-4}$ to $1\times10^{-6}$ cm/s and geomembrane liner<br>(order of magnitude)<br>3 holes per acre | Rate is 0.002 to 0.06 inches/yr/hole distributed over 1 acre<br>— ~0.6 to 18.5 m$^3$/yr/acre<br>= 0.45 to 13.4 gal/D/acre— | Rate is 0.08 to 2.4 inches/yr/hole distributed over 1 acre<br>— ~25 to 740 m$^3$/yr/ acre<br>= 18 to 536 gal/D/acre— |

### Section 4.4.4 Cost Analysis:

Formulas on p.74 have been updated to the correct pond area (125 acres instead of 5 acres)

$\$Cost/acre = 1.392 \times CI \times (8077 + 465 \times mil)$ and $\$Cost/acre = 1.55 \times CI \times (8077 + 465 \times mil)$ have been replaced by: $\$Cost/acre = 1.11 \times CI \times (8077 + 465 \times mil)$ reflecting the smallest cost per acre for a larger pond.

Table 4-15 (p.76):
The table now focuses on the cost per acre. Column with total cost for a 5-acre pond was deleted.

Conclusions (p.77):
Total cost changed to cost/acre.

Appendix list:
New Appendix L added

Appendix J: Conceptual Drawings of Evaporation Ponds
Dimensions corrected from 450 ft × 450 ft (4.52 acres) to 2430 ft × 2430 ft (135.6 acres)