EVALUATIONS OF RADIONUCLIDES OF URANIUM, THORIUM, AND RADIUM ASSOCIATED WITH PRODUCED FLUIDS, PRECIPITATES, AND SLUDGES FROM OIL, GAS, AND OILFIELD BRINE INJECTION WELLS IN MISSISSIPPI

Final Report

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ABSTRACT

Naturally occurring radioactive materials (NORM) are known to be produced as a by-product of hydrocarbon production in Mississippi. The presence of NORM has resulted in financial losses to the industry and continues to be a liability as the NORM-enriched scales and scale encrusted equipment is typically stored rather than disposed of. Although the NORM problem is well known, there is little publically available data characterizing the hazard. This investigation has produced base line data to fill this informational gap.

A total of 329 NORM-related samples were collected with 275 of these samples consisting of brine samples. The samples were derived from 37 oil and gas reservoirs from all major producing areas of the state. The analyses of these data indicate that two isotopes of radium (^{226}Ra and ^{228}Ra) are the ultimate source of the radiation. The radium contained in these co-produced brines is low and so the radiation hazard posed by the brines is also low. Existing regulations dictate the manner in which these salt-enriched brines may be disposed of and proper implementation of the rules will also protect the environment from the brine radiation hazard.

Geostatistical analyses of the brine components suggest relationships between the concentrations of ^{226}Ra and ^{228}Ra, between the Cl concentration and ^{226}Ra content, and relationships exist between total dissolved solids, $BaSO_4$ saturation and concentration of the Cl ion. Principal component analysis points to geological controls on brine chemistry, but the nature of the geologic controls could not be determined.

The NORM-enriched barite ($BaSO_4$) scales are significantly more radioactive than the brines. Leaching studies suggest that the barite scales, which were thought to be nearly insoluble in the natural environment, can be acted on by soil microorganisms and the enclosed radium can become bioavailable. This result suggests that the landspreading means of scale disposal should be reviewed. This investigation also suggests 23 specific components of best practice which are designed to provide a guide to safe handling of NORM in the hydrocarbon industry. The components of best practice include both worker safety and suggestions to maintain waste isolation from the environment.

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INTRODUCTION

Naturally occurring radioactive materials (NORM), produced along with oil and gas production, are often concentrated at some point in the hydrocarbon production process. These concentrated NORM deposits could be referred to as technically enhanced naturally occurring radioactive materials or TENORM. In this investigation both NORM and TENORM are included under the NORM acronym and so both will be referred to simply as NORM.

This project was begun in 1996 when the initial ideas of characterization of NORM in Mississippi were conceived. The driving force behind the idea of the project was the maneuvering of the legal industry and the reaction of the regulatory agencies; all of which were proceeding without adequate knowledge of NORM issues or an adequate database regarding NORM in Mississippi. The Mississippi Office of Geology put together the initial research team, consulted with the U.S. Department of Energy (USDOE), and submitted a preproposal for the consideration of the U.S. Department of Energy.

Comments from the review by the USDOE were incorporated into a formal proposal that was submitted in April of 1997 for consideration. The project was funded and the initial brine sampling was begun in September of 1997. The project continued under the leadership of the Mississippi Office of Geology until June of 2000. Personnel changes at this point required the NORM research team to be reorganized and lead agencies changed.

In May of 2002, the final phase of the project was finalized under the leadership of the Mississippi Mineral Resources Institute (MMRI). The final phase research team was also expanded to consider aspects of spatial and geostatistical relationships. Final sampling, chemical analyses and modeling were completed and the technology transfer task was initiated. A no-cost extension was granted in June 2003 extending the project through the end of the calendar year.

The primary overall goal of this set of investigations was to fill a significant informational gap by providing base line data regarding NORM in Mississippi and to distribute this information. It is hoped these data and the conclusions derived from them, will be used by the industry, regulatory agencies, as well as the public. The research goals can be summarized into the three listed below. Notes have been added to the description to provide insight as to how the research goals fulfilled the project's overall goal.

1) - Characterize NORM-containing petroleum by-products in Mississippi

- the ions resulting in radioactive by-products were identified
- the distribution of radioactive by-products was determined

- brines, sludges, and scales were sampled and their radioactive components were characterized
- limited leaching studies were conducted to provide insight into behavior of radioactive scales in the environment

2) - Develop a model to predict the occurrence of chemical conditions that may lead to the production of radioactive by-products
- a geographic information system (GIS) database was constructed to manage information and to investigate potential spatial relationships between NORM and areas of production
- the potential relationships between NORM and geological structure and the formational source of the fluids were investigated

3) - Transfer these findings to the industry, regulatory agencies, and to the public.
- information transfer *via* informational briefings, publication (print and electronic), and through the websites of the University of Mississippi
- an industry briefing was held on May 22, 2003 and a public briefing was held in August of 2003
- the NORM database derived from this investigation is available to the public through the MMRI website

To meet these goals, a total of 329 samples were collected from oil and gas fields in Mississippi. The total number samples included brine, biological, salt, scale, sludge, and soil samples. The majority, 275 samples, were of brines co-produced with hydrocarbons. Unfortunately, quality control considerations resulted in some the brine samples being rejected for analysis. Some were unuseable due to excess oil and inadequate brine in the sample, for example. Whereas, some samples contained nearly fresh water and were rejected after it was determined the flow line and stock tanks had recently been steam cleaned.

The brine samples represent 37 different reservoirs and were derived from all major producing areas in Mississippi, *i.e.* the Black Warrior Basin, Mississippi Interior Salt Basin and the Wilcox Trend (Figure 1). Reservoir age varies from Mississippian units in the Black Warrior Basin to Tertiary units in the Wilcox Trend. Reservoir rock types vary widely from well consolidated Paleozoic sandstone to poorly consolidated Tertiary sands. Thirty-eight operators have aided the investigation by allowing their wells to be sampled.

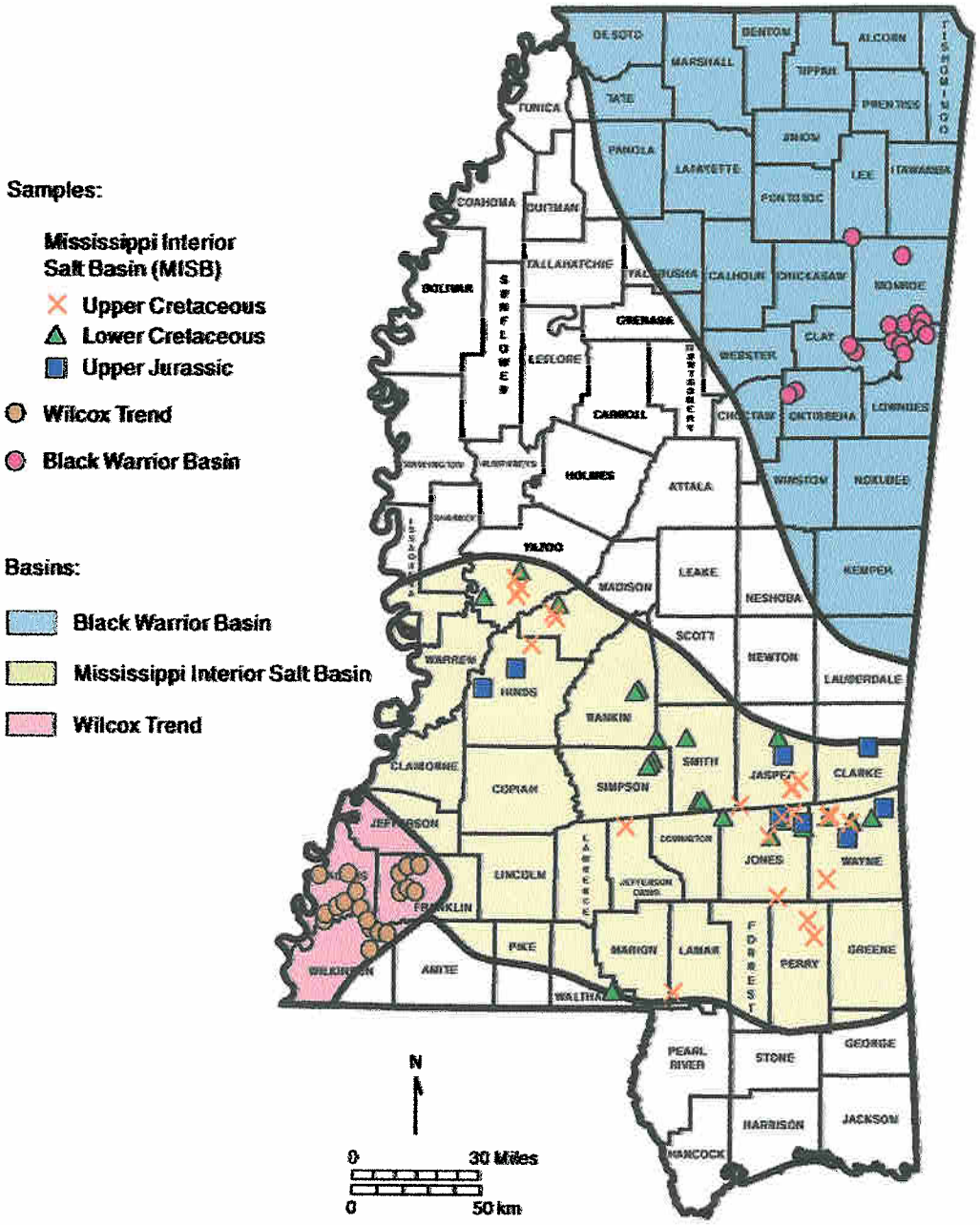


Figure 1 - Map of sampling locations and producing areas in Mississippi.

The radioactive component (^{226}Ra and ^{228}Ra) is, of course, the major environmental concern that has resulted in significant economic loss to the industry and continues to be an economic concern and a legal liability. Exxon and ChevronTexaco, for example, have both been involved in multimillion dollar law suits involving NORM. In the case of Exxon, the dollars were in excess of one billion. NORM- related legal costs to both major oil companies continue as decisions are appealed and other suits are filed. NORM- related costs and liability also extends to the smaller independent producers such as those which produce most of Mississippi's hydrocarbons. To the small independent operators, there is the cost of maintaining NORM storage areas, the increased cost of doing business in fields which produce NORM as well as the continued legal liability represented by NORM in storage and NORM-enriched scale present in equipment currently being used. So, there is little doubt of an economic incentive to better understand NORM and its characteristics.

The U.S. Geological Survey (USGS) and the USDOE have contributed significant knowledge of NORM resulting from hydrocarbon production but, their studies, as others, have seldom included the problems associated with the NORM produced in the southeastern U.S., focusing instead on the western portion of the country. Oddly, there is little known of the characteristics, geographic distribution, concentration of radioactive components or how NORM reacts to the humid environments such as Mississippi. A review of published literature indicates that Mississippi-specific NORM investigations are essentially nonexistent. As a result of this informational gap, the most relevant works to this investigation are the investigations conducted by Fisher (1995, 1998) in Texas.

The underlying significance of knowing the isotopic distributions of ^{226}Ra and ^{228}Ra lies in the relative decay half-lives of the two radium isotopes and their radioactive-decay products, and hence their persistence in the environment and in disposal facilities. The ^{226}Ra isotope has a half-life of approximately 1,620 years and ^{228}Ra has a half-life of approximately 5.8 years. None of the radioactive-decay products from either of these radium isotopes has a half-life that is as long as the parent radium nuclide, and therefore, the radioactivity of the decay chain will not persist significantly longer than the parent radium isotope. Thus, as radium-based NORM and TENORM wastes age, the contributions due to ^{228}Ra will diminish relatively rapidly while the contributions due to ^{226}Ra will remain relatively unchanged.

Both ^{226}Ra and ^{228}Ra produce radon as a radioactive-decay product. ^{222}Rn, a decay product of ^{226}Ra, has a half-life of 3.82 days. This half-life allows ample time for this gaseous element to "emanate" from its source into the atmosphere where it is available for inhalational exposure. ^{220}Rn, a decay product of ^{228}Ra, has a half-life of 56 seconds. Thus, very little of the ^{220}Rn that is produced will find its way into the atmosphere before it has decayed to nonvolatile

products. When considering persistence and the potential for exposure of the general population ^{226}Ra is the isotope of greatest concern.

Radium Isolation

At the time this study was initiated, there were essentially three methods available for analysis of radium in water samples. Each of these methods requires substantial concentration of the radioisotope being measured in order to achieve reasonable detection levels. These methods had all been originally developed for analysis of radioactivity in drinking water and other low salt content water samples. A purpose of this study was to adapt existing methodologies for accurately and reliably determining the amounts of the two main radium isotopes in complex solutions, as represented by the brines using commonly available radiation-detection equipment, and to subsequently employ the method developed to generate a primary, unbiased knowledge base from which rational and informed social, economic and environmentally sound decisions may be made in regard to the handling and disposal of NORM (and TENORM) contaminated wastes.

The three methods involve, respectively, isolation of the radioactive noble gas ^{222}Rn, the first decay product of ^{226}Ra (American Public Health Association, 1980); isolation of radium by co-precipitation with lead sulfate and/or barium sulfate (U.S. Environmental Protection Agency, 1980; American Public Health Association, 1985); and isolation of radium using Empore™ Radium Rad Disk technology (Smith et al., 1998). One major drawback of the ^{222}Rn method is that it cannot be used to determine the amounts of ^{228}Ra in the samples. The high concentrations of interfering solutes in brines cause problems with Rad Disks and the co-precipitation methods. With the lead and barium sulfate co-precipitation methods high concentrations of chloride or calcium interfere. In addition to the problems with interfering solutes, the lead and barium sulfate co-precipitation methods require several processing steps (Demorest & Wallace, 1992), which increase the labor and the potential for error. With the Rad Disk method relatively low concentrations of barium and potassium and high concentrations of several other solutes interfere (Smith et al., 1998).

Most of the methods that existed prior to development of the method reported here employed either alpha or beta counting techniques to quantify radium or its decay products. When beta counting is employed for quantification of ^{228}Ac it is necessary to physically isolate ^{228}Ac after aging of the samples since gamma emissions from ^{226}Ra and its decay products interfere with beta counting. Similarly, when alpha counting is employed, for example, for quantification of ^{222}Rn it is also necessary to physically isolate the emitting nuclide. Because of these procedural complexities, recoveries of the two isotopes can vary within the same analysis.

Lucas & Markun (1992) have described a method for quantifying both radium isotopes simultaneously from a variety of sample types by employing least-squares-gamma counting employing the entire gamma-emission spectrum.

The method reported here has been adapted from existing methods with some added innovations. It employs an initial clean-up step, which reduces the levels of some of the interfering solutes. This is followed by isolation of radium on Empore™ Radium Rad Disks. ^{226}Ra is then quantified from the freshly prepared Rad Disks by gamma counting for its 186-keV gamma emission, followed by aging of the Rad Disks and quantification of ^{228}Ra by gamma counting for the 911-keV and 969-keV gamma emissions of ^{228}Ac (Chu, Ekström and Firestone, 1999). This method allows accurate and reproducible evaluation of the two main radium isotopes and it can be accomplished with almost any available gamma counting equipment.

Generally, samples are spiked with known amounts of ^{226}Ra, which serves as an internal standard, to allow determination of recoveries of the unknown radium. In the lead and barium sulfate co-precipitation methods that employ beta counting for quantification of ^{228}Ac, the addition of ^{226}Ra can only serve as an internal standard for measurement of ^{226}Ra. In the method described here, the Radium Rad Disk method was adapted for analysis of brines by adding some relatively simple preprocessing steps to reduce interfering solutes to tolerable levels. In addition, isotope-detection strategies employing gamma counting were adapted that allowed detection and quantification of both of the radium isotopes from the same Rad Disk without further physical processing. This allows quantification of recoveries for both isotopes using only ^{226}Ra as the internal standard.

Leaching Of Radioactivity From Scale And Sludge Samples

The purposes of this portion of the study were to characterize the effects of environmental exposure on the solubilization of radioactivity and other components of radioactive scale and sludge samples produced as undesirable by-products during Mississippi hydrocarbon production. These samples were extracted with toluene, concentrated HNO_3, and artificial rainwater. They were also incubated with moist Mississippi top soils to determine what effects soil incubation have on solubilization of radioactivity and other components.
While brines are often disposed of by pumping into injection wells, one of the disposal methods currently acceptable by regulatory agencies for disposal of scale and sludge is land farming or landspreading. Landspreading is a method for disposal of low level, solid NORM wastes resulting from hydrocarbon production. The methodology involves spreading the material on the surface of the ground, tilling it into the surface layer, and then covering the NORM with a layer of "clean" soil such that the radioactivity is below governmental action levels, and the site

can be considered uncontaminated (Smith, Blunt and Arnish, 1998; Mississippi State Oil and Gas Board, 2001). One of the major assumptions of this method of disposal is that the radioactivity in these wastes is highly insoluble, and will, therefore, remain relatively immobile in the natural environment.

In this study, the assumption that barite scales remain insoluble and the radioactivity from these scales and sludges remains immobile after mixing with soils typical of Mississippi was tested. While the sulfates of Ba and Sr are highly insoluble, the sulfides and sulfites of these alkaline earths are relatively soluble (CRC Handbook of Chemistry and Physics, 1971). Sulfates may be converted to sulfides and sulfites under reducing conditions. Many soil microorganisms have the ability to reduce various minerals and have been shown to be capable of reducing sulfates (Bolze, Malone and Smith, 1974; Gilkeson, Perry and Cartwright, 1981). This activity would reasonably be expected to increase the solubilization of radium from scales and sludges when these are incubated with soil. In addition, soil microorganisms often produce chelators that are valuable to them for obtaining trace minerals from their environments (Barton and Hemming, 1993). These would also be likely to facilitate the solubilization of scale.
As noted by Postgate (2000), microorganisms flourish most abundantly in the presence of moisture and warmth. Environments that provide these two conditions should facilitate any microorganism-enhanced leaching. Based on precipitation records from 1990 to 2003, Mississippi had an average rainfall of 1.5 m, and an average temperature of 17^{0}C (NOAA, 2003). These data indicate that the Mississippi climate is suitable to microorganism growth. Thus, leaching models invoking a biological factor may be relatively more important in a warm, moist climate like that of Mississippi than would be true for locations with colder or dryer climates. The abundance of infiltrating precipitation moving through the soil zone, also provides a mechanism for moving any bioavailable radium to other locations.

EXECUTIVE SUMMARY

Prior to this investigation there was little information available to the public regarding NORM produced as a by-product of oil and gas production. As regulatory agencies make decisions regarding the public health, safety, and welfare, this deficiency of information becomes increasingly important. Decisions of this type may affect the public as well as industry and should be based on a set of objective and defensible data. A primary goal of this investigation has been to make these data available and thereby narrow this gap in our knowledge of NORM in Mississippi.

This investigation has primarily sampled brine co-produced with oil and gas. It has also sampled NORM-impacted soils, radioactive scale, and sludges. A total of 329 NORM-related samples were collected with 275 samples consisting of brines. The samples were derived from 37 geologically distinct oil and gas reservoirs. The sampling area included all the major producing areas in Mississippi, *i.e.* the Black Warrior Basin, Mississippi Interior Salt Basin, and the Wilcox Trend.

These samples were analyzed for various chemical components including radium, barium, sulphate, and chlorine (as chlorinity). Also data regarding the physical and locational aspects of the sampled well, such as name, operator, API number, field name, and producing reservoir were also added to the chemical data. This information was compiled as a data base, and was used for derivation of statistical parameters and other analyses. This collection of information represents the most extensive available to the public regarding NORM in Mississippi and is available through the Mississippi Mineral Resources Institute website (http://www.olemiss.edu/depts/mmri).

Radium is traditionally considered the primary source of radioactivity in oil field scale and sludge. Two isotopes of radium, ^{226}Ra and ^{228}Ra, are commonly present in scales and sludges, so it was necessary to determine the amounts of both isotopes in the collected brine samples. A new method of determining isotope concentrations was developed using available technology and innovative new laboratory techniques to determine the radium isotope concentrations in these brines.

Using this new methodology, it was determined that virtually all the co-produced brines contained small amounts of both ^{226}Ra and ^{228}Ra. The state-wide average radiation values were low *i.e.* 12.6 Bq/L for ^{226}Ra and 15.1 Bq/L for ^{228}Ra. Considering these low radiation values, the radiation hazard from brines appear minimal. Many of these brines also contain large quantities of NaCl (salt) which are the subject of various environmental regulations promulgated to minimize the release of salt-enriched brines to the surface environment. Adhering to these regulations regarding brine disposal also serves to address the radiation hazard in an environmentally sensitive manner.

Although the brines pose minimal radiation hazards, the scales are significantly more radioactive. The scales consist predominately of the mineral barite ($BaSO_4$), although some carbonate scales have been reported by oil and gas operators. Scale encrusted flow lines with as much as 60 μr/hr have been measured from the outside of the steel pipe. Interviews with field operators suggested that the production of radioactive scales was not uniformly distributed across the state. The Black Warrior Basin, for example, seemed to produce little, if any, scale. This observation was independently verified by both field investigations and records contained at the Mississippi State Oil and Gas Board. The brine studies indicated the presence of ^{226}Ra and ^{228}Ra in all basins. Barium is also present in all basins, so differences in the sulfate content of the brine was suggested as controlling the development of the scale. Chemical analyses of brines

for SO_4 ion concentration supports this suggestion. The Black Warrior Basin brines contain the smallest concentrations of SO_4 followed by the Wilcox Trend and finally the Mississippi Interior Salt Basin with the highest concentrations of the SO_4 ion. These SO_4 concentrations correlate with amounts of scale produced. The importance of this conclusion is that it offers a model to predict scale formation by determining the concentration of the SO_4 ion in a well's produced brine.

Mississippi has chosen to allow radioactive scale disposal by way of landspreading methods. Regulations controlling landspreading have been promulgated by the Mississippi State Oil and Gas Board, although only limited landspreading has taken place. A basic assumption of the landspreading methodology is that the barite scale remains insoluble under surface or near surface conditions. This assumption was tested by laboratory leaching studies using common solvents, including artificially generated "acid rain". It was determined that under these sterile laboratory conditions, it was difficult to extract any significant amounts of radium from the barite crystal lattice. This conclusion was expected.

It was theorized that mixing the barite scale with common soils would more closely replicate the field conditions encountered in landspreading and should provide insight to barite behavior in the environment. The barite scale was mixed with Mississippi soils and allowed to incubate. After incubation, the soils were extracted to determine the amount of radioactivity removed from the mixture using artificial rainwater as the solvent. All of the soil incubation conditions resulted in greater extraction of soluble radioactivity than were observed for percolation of artificial rainwater through the sterile NORM samples. The amounts of leached radiation is small. When the abilities of soils to complex soluble radium are considered, however, the indication is that substantial amounts of radium may have been released from the NORM samples through incubation with these moist top soils. The means of releasing the enclosed radium from the barite crystal lattice is thought to be by the action of soil microorganisms. This conclusion suggests that land use restrictions may be needed on areas where the scale has been disposed of by landspreading. Additional research is clearly needed in this area.

Considerable effort was contributed to understanding the relationships between the brine chemistries, producing formations, depth of production and geological controls. When compared with the work of Fisher (1995, 1998), the Mississippi brine chemistry demonstrated both differences and similarities. Fisher found that a strong correlation existed between concentrations of ^{226}Ra and ^{228}Ra in Texas brines. In Mississippi, the same correlation exists, but is only moderately correlated ($r = 0.63$ in Mississippi brines verses $r = 0.98$ in Texas). Both Texas brines and Mississippi brines containing high levels of Cl ,also contain higher levels of ^{226} Ra. Total dissolved solids and $BaSO_4$ saturation is also moderately correlated with Cl. The SO_4 ion is moderately correlated with $BaSO_4$, but weakly correlated with ^{226}Ra and ^{228}Ra. The variation of ^{226} Ra concentrations within formations is large, but variations across formations is small, *i.e.* similar means exist for all formations. Principal component analysis suggests that geological factors play a part in brine chemistry and evolution. The exact nature of the geological control could not be identified and is an area of study deserving additional research.

Using the information derived from the study and from discussions with field operators, a set of components of best practices was constructed. A total of 23 specific practices are described herein that should reduce monetary and physical exposure liability from NORM scales. The components of practice cover not only the handling and storage of NORM - enriched scales and equipment, but worker safety issues as well. This set of components are designed to provide the nucleus for a future, more complete best management plan that should be developed by industry.

EXPERIMENTAL METHODS AND PROCEDURES

Field Procedure And Sample Collection

The liquid hydrocarbon production system typically allows samples to be obtained from several locations. Some sample locations, such as at the well head, are superior to others for analytical purposes. So, a priority was established as to preferred sampling locations, so if multiple locations were possible the one best suited for analysis was consistently chosen. The sample location priority is 1) from the well head (most preferred sampling location), 2) from flow lines, 3) from the heater treater, and 4) from separation and storage tanks (least preferred). The natural gas production system allows only limited locations to sample produced waters, with the most common sample location consisting of the salt water storage tanks.

Field notes were maintained regarding the sampling procedure. The notes contained the time and date the sample was obtained, oil or gas well, field name, well name, API number, sampling location (such as well head), sample number (the sample number consisted of a unique field code and a numerical sample number), amount of sample obtained, and any special information which could be of use at a later date.

Approximately 8L of sample were obtained for laboratory analysis. The samples were typically a mixture of oil and water, so the mixture was allowed to separate and cool in a sampling container prior to bottling. The brine was taken from the bottom of the sampling container and placed into sample bottles. Custody sheets were maintained to document the handling of the sample throughout the field and laboratory analysis process.

Quantification Of Radium Isotopes From Brines

Sample Processing

Each 4-L container of brine was sampled before any processing to determine pH and total dissolved solutes in the aqueous portion. Thirty milliliters of brine were withdrawn from the unagitated container and filtered through Whatman #1 filter paper (Whatman International, Ltd., Kent, UK) under gravity flow to separate suspended particulates and oil from the brine. Ten milliliters of the filtered brine was transferred to a weighed, 125-mL Erlenmeyer flask. This flask was weighed again to determine the density of the brine sample. Next, the sample was placed in an oven at 120^{0}C for several hours until dry. The criterion for dryness was that the sample weight no longer changed over time. After cooling, the flask with the remaining nonvolatile solutes was again weighed to determine the amount of dissolved solutes from the sample. The remainder of the filtered sample was used to determine the pH.

Next, the volume of the aqueous portion of the sample from at least one of the 4L containers from each brine sample was measured and 100 mL/L of concentrated HCl was added. This was returned to the original container with the intent of dissolving any acid-soluble solids that remained in the container. Following acidification a 20 mL sample was removed and filtered and 11.0 mL of this was placed in a weighed, 125-mL Erlenmeyer flask. This was oven dried and weighed again to determine the amount of acid soluble solutes.

Carbonate Precipitation

The acidified brines were vacuum filtered through Whatman #1 filter paper to remove oil and suspended solids. Two 550-mL aliquots of the filtered, acidified brines were taken and placed in 2L Erlenmeyer flasks. One of these aliquots was then spiked with 925 Bq of ^{226}Ra by adding 50 µl of 1.85×10^4 Bq/mL $^{226}RaCl$. The filtered, acidified brine aliquots were stirred constantly and vigorously at room temperature throughout the Na_2CO_3 addition phase described below. Twenty eight grams of solid, anhydrous Na_2CO_3 were added gradually to each brine aliquot. Then 25% w/v anhydrous Na_2CO_3 solution was added drop-wise to each aliquot. The first 30 mL was added at the rate of 1 mL/min, the next 30 mL was added at the rate of 2 mL/min, all subsequent additions were at the rate of 3 mL/min. The suspended precipitates were then collected on Whatman #1 filter paper by vacuum filtration. The filtrates were returned to the original flasks and additional Na_2CO_3 solution was added as before in volumes of up to 125 mL until no further precipitate formed. After all of the carbonate precipitates from each aliquot were collected on a single filter paper, the filtrates were discarded.

Radium Isolation

The carbonate precipitates from each aliquot, along with the filter paper, were returned to the original flask, which still contained some of the carbonate precipitate that had condensed out on its inside surfaces. Eight hundred milliliters of 2 N HNO_3 were added to redissolve the carbonate precipitate. The resulting solution was then filtered through a Whatman 0.25 µm pore size cellulose-nitrate membrane to remove the paper and any suspended particulates that had not been removed by previous paper filtration steps. Additional 2 N HNO_3 solution was used for rinsing to ensure quantitative recovery and then 2 N HNO_3 solution was added to bring the volume to 1L. This solution was then vacuum filtered through an Empore™ Radium Rad Disk (3M Company, St. Paul, MN), which had been wetted with methanol, to collect the radium on the disk. Following filtration the Rad Disk was rinsed with acetone to dry it. The dried Rad

Disk was then immediately placed in a polystyrene tube and, within 90 min of collection, counted for 30 min in a Packard model 500C gamma counter, equipped with a 7.6 cm NaI crystal, with the counter window set to 15-500 keV for quantification of the 186-keV gamma emission of ^{226}Ra (Chu, Ekström and Firestone, 1999). Instrument background was determined by counting empty polystyrene tubes. This background was subtracted from the sample counts prior to further data manipulation. If the Rad Disks were allowed to age, radioactive decay products grew in and interfered with the quantification of ^{226}Ra. The recovery percentage for the radium in each sample was obtained by subtracting the radioactivity captured on the Radium Rad Disk from the unspiked aliquot from that of the spiked aliquot and dividing that by the total radioactivity of radium added.

The Rad Disks from the unspiked aliquots were then placed in a desiccator under vacuum with $CaSO_4$ desiccant and activated charcoal, and aged for 2 weeks to allow ^{228}Ac to grow in and equilibrate. Storage with desiccant and activated charcoal under vacuum was intended to provide an absorption bed for volatile ^{222}Rn, the first decay product of ^{226}Ra, and thus promote it's emanation from and separation from the rad disks. This was intended to minimize interference with quantification of the ^{228}Ac. The aged Rad Disks were then counted for 30 min in the gamma counter with the counting window set to 900-1000 keV to quantify the 911-keV and 969-keV gamma emissions of ^{228}Ac (Chu, Ekström and Firestone, 1999). Each brine sample was analyzed through 2 complete replicates of spiked and unspiked aliquots with at least one week between replicate analyses. When the two spiked replicates were within 10% of one another the analysis was considered to meet our criterion for reproducibility. If the two spiked replicates differed by more than than10%, then a third replicate analysis of both spiked and unspiked was performed.

Data Corrections And Calibrations For Radium Quantification

The gamma counter was calibrated daily by running the calibration and quality control programs with the sealed ^{137}Cs standard supplied with the Packard model 500C gamma counter. The gamma-emission spectra of freshly prepared, and aged (2 weeks), stoppered ^{226}Ra Rad Disks were determined for the energy range from 15 to1400 keV. From these spectra it was possible to determine peak widths, peak resolutions, and counting efficiencies for the 186-keV gamma emission from ^{226}Ra, and the 609-keV and 1120-keV gamma emissions from ^{214}Bi, a decay

product of ^{226}Ra (Chu, Ekström and Firestone, 1999). The counting efficiencies determined for the 609-keV and 1120-keV gamma emissions from ^{214}Bi, which bracketed the 900-1000 keV region, provided a good estimate of the counting efficiency in the 900-1000 keV window.

To determine the effectiveness of reducing the levels of ^{222}Rn and its radioactive-decay products from the Rad Disks by storage of the Rad Disks in a vacuum dessicator, and to determine the amount of interference from ^{226}Ra and its remaining radioactive-decay products in quantification of ^{228}Ac, the following experiment was performed. Twenty microliters of 1.85 x 10^4 Bq/mL $^{226}RaCl$ were added to 2.0 L of 2N HNO_3. Five hundred milliliter aliquots of this solution were then filtered through each of four Radium Rad Disks followed by rinsing with 2N HNO_3. The dried Rad Disks were placed in polystyrene gamma-counting tubes. Two tubes were left open to the air and two tubes were tightly stoppered. These were then counted in the gamma counter within 90 min of preparation with the counting windows set to 15-500 keV and 900-1000 keV. The stoppered samples were stored for 2 weeks on a shelf in the laboratory and the unstoppered samples were stored for 2 weeks in the vacuum desiccator as described above. They were then counted for 30 min with the counting windows set to 15-500 keV and 900-1000 keV. The effectiveness of removing ^{222}Rn was determined by comparing the results from these two pairs of samples. The correction for interference from ^{226}Ra decay products in quantification of ^{228}Ac was determined as the number of counts in the 900-1000 keV window from the vacuum-dessicator-aged Rad Disks divided by the number of counts in the 15-500 keV window from the same disks prior to aging. Since only ^{226}Ra and its decay products were present in these samples, and since the sample correction factors derived from gamma counts of the freshly isolated sample Rad disks where ^{226}Ra was the only emitting species, this ratio gives the correction for the contribution of ^{226}Ra decay products in the 900-1000 keV window independent of the amount of ^{228}Ra and its decay products that may be present in the samples. Counting efficiencies and extraneous counts at low count rates were determined by preparing additional Rad Disks as described above with varying levels of $^{226}RaCl$, and counting them in the 15-500 keV window prior to aging.

Determination Of Chloride Content Of Brines

The ion meter (Orion model 900A) was set up with a chloride electrode and a reference electrode filled with 1 M Na_2SO_4 reference electrode solution. Four chloride standard solutions (3 mM NaCl, 10 mM NaCl, 30 mM NaCl and 100 mM NaCl, each in 1 M $Na NO_3$) were used to calibrate the electrode at the beginning of the analysis. These same standards were used to check the instrument for calibration accuracy after each sample analysis. If the standards readings

were off by more than 10% on recheck the instrument was re-calibrated before continuing. Three successive aliquots of 20 µL each of brine were added to 20 mL of 1 M Na NO_3 and a meter reading was obtained after each addition. Then three successive aliquots of 1 M NaCl standard solution were added to the same sample and a meter reading was obtained after each addition.

Each meter reading was converted to moles per liter of chloride from the aliquot added. The procedure gave three replicate readings for each brine sample that were obtained by subtraction of the previous reading for each aliquot addition. Then, in the same manner, three internal standard readings were obtained from the three additions of the 1 M NaCl standard. The averaged values of the brine readings were then divided by the averaged values of the internal standard readings to correct for interferences from non-chloride brine components yielding the final result in moles per liter of chloride for the brine sample.

Determination Of Sulfate and Elemental Compositions Of Brines

Additional chemical analyzes were performed for anion and cation concentrations on 169 of the samples. These brine samples were from the first sampling phase, and only samples taken from individual wells were analyzed. Anions, including sulfate and chloride, were analyzed using an ion chromatograph (IC) equipped with a Dionex ionpac (R) AS10 high capacity separation column. Cations were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES).

Leaching Of Radioactivity From Scale And Sludge Samples

NORM Samples

The characteristics of three hydrocarbon production NORM samples collected in Mississippi were measured. The NORM 1 sample was a non-oily scale sample which had been exposed to the weather for several years. It was collected from the surface of the ground from the area around an oil well head that had ceased production several years earlier. The NORM 2 sample was an unweathered, non-oily scale sample that was collected from a section of hydrocarbon-production-facility transfer tubing. NORM 3 was an unweathered oily sludge sample that was collected from a NORM storage facility.

The leachability of radioactivity from these NORM samples alone and after mixing and incubating the samples with representative Mississippi "A horizon" top soils were characterized. Top soils were chosen because it was expected that these would have relatively high titers of microorganisms including those capable of sulfate reduction reactions and because this would re-create conditions similar to landspreading.

Soils

The soil samples used in the experiments were provided by Mr. Charlie Cooper of the U.S. Department of Agriculture(USDA), Agricultural Research Service/Sedimentation Research Laboratory in Oxford, MS. Soil characteristics were obtained from the National Cooperative Soil Survey (USDA-Natural Resources Conservation Service). The clay soil was from the Sharkey series, which consist of poorly and very poorly drained, very slowly permeable soils that formed in clayey alluvium on the flood plains and low terraces of the Mississippi River. The silt soil was from the Grenada series, which consist of very deep, moderately well drained soils that formed in loess, and are found in the southern Mississippi valley silty uplands. The sand soil was from the Ochlockonee series, which consist of very deep, well drained, moderately rapidly permeable soils that formed in loamy alluvium on flood plains.

Artificial Rainwater

The leaching studies were performed with artificial rainwater as the leachate. Artificial rainwater was produced by bubbling air through 20 L of deionized water in a 40 L carboy for at least 24 hrs with the aid of an aquarium pump. The pH of this water was 6.5 ± 0.1.

Measurement Of Radioactivity Derived From Solid Samples

The sources of radioactivity in the NORM samples are largely from decay of ^{226}Ra and ^{228}Ra and their radioactive decay products. These emitting species exhibit gamma emissions across the gamma spectrum (Chu, Ekström and Firestone, 1999). To optimize counting efficiency, samples were counted for 30 min in a Packard Auto-Gamma 500 C gamma counter equipped with a 7.6 cm NaI crystal with the counting window set wide open to 15-2000 keV. The wide open counting window allowed for detection of most gamma emitting species eliminating the need to determine the nature of the emitting species. Sample geometries were restricted to two types. When the sample was an extract there was very little material present in the sample. These were counted as solutions in 1.0 ml of HNO_3. When the samples were residues all measurements were made on 1.0 g dried samples. Since the goal was to compare relative radioactivities between samples having similar compositions, no attempts were made to correct for self-absorption of radioactivity from the samples.

To avoid the complications of differential extractions or retentions of the various radioactive decay products of the two radium isotopes, sample processing was performed such that extracted or retained radium was the source of greater than 90% of the radiation intensity. This was accomplished by always aging the samples to be counted in air-tight stoppered counter tubes for

two weeks prior to counting. Stoppering the counter tubes prevented the escape of radon gas, a decay product of both of the radium isotopes. Aging the samples stoppered for two weeks permitted the radioactive decay products of both radium isotopes to grow in and equilibrate while simultaneously allowing for greater than 90% of the decay products of the two radium isotopes that were in the extracts or that were retained in the samples to decay away. Thus, the radioactivity in the stoppered, aged tubes was due only to radium that was in the sample at the time of preparation. Because the samples were nearly equilibrated at the time they were counted all of the radioactive decay products of the two radium isotopes were present at near equilibrium with the parent radium isotopes. The only discrepancy in the preceding equilibration and decay procedure is ^{210}Pb, the sixth radioactive decay product of ^{226}Ra. ^{210}Pb has a half life of 22 yrs. The contributions to the gamma emissions due to this isotope were expected to be insignificant.

Statistical Analysis

All measurements throughout this study were performed in triplicate unless otherwise indicated. Statistical comparisons of two group means were examined using the Student t-test. Differences among many group means were analyzed using one-way ANOVA with Tukey's post hoc when statistical significance was observed.

NORM Sample Characterization

The NORM samples were air dried for three days by spreading the material in a thin layer (~ 3 mm) on paper in the laboratory at ambient temperature and humidity (23 ± 2° C and 45 ± 10% relative humidity). The samples were then pulverized by placing them in a stainless steel Waring® Blender cup and processing them at maximum speed for 2 min. Scale and sludge particles are readily pulverized by this procedure. The NORM 1 sample, which was collected from the surface of the ground, contained a significant proportion of gravel and soil. Scale particles from this sample were isolated by hand sorting prior to further processing. Weighed samples of the air dried material were then placed in the oven at 125° C for 16 hrs., followed by cooling and re-weighing to determine the content of water and other readily volatile substances in the samples. Longer drying times at each temperature were found to produce no additional weight loss.

Oven dried NORM samples (10 g) were extracted three times with toluene (100 mL each time) by mixing the sample with toluene, centrifuging the sample at 4° C in a Beckman Model J2-21 high speed centrifuge at 2400 x g for 10 min and then decanting the toluene phase. The insoluble fractions were redried in the oven at 125° C for 16 hours followed by cooling and re-weighing to determine the toluene soluble content (primarily oil and petroleum hydrocarbons).

The dried, toluene-extracted samples were extracted three times with concentrated HNO_3 (100 mL each time) followed by rinsing three times with deionized water (100 mL each time) as described for the toluene extractions. These were then redried in the oven at 125° C for 16 hours followed by cooling and re-weighing to determine the HNO_3 soluble content (largely carbonate salts, and native metals).

Soil Characterization

Soil samples were spread in a thin layer to air dry as described for the NORM samples. Plant debris was picked out by hand during this drying process. The soils were then pulverized as described for the NORM samples. Weighed samples of the air dried soils were then oven dried at 125 °C for 16 hours followed by cooling and re-weighing to determine their water content. These samples were then heated to 1800° C for 20 hr to oxidize and remove organic materials and other volatiles. The weight loss from this procedure was taken as the total organic content of the soils.

The water holding capacity of the soils was determined by soaking 100 g of air dried soil with deionized water and then draining the loosely covered samples for four days in 10 cm diameter Büchner funnels with Whatman #1 filter paper followed by re-weighing. The water content of these drained soils was then used as the standard for producing the moist soil condition. The pH values of the filtrates from this procedure were also determined.

The radioactivity recovery rate was determined for each soil sample. Artificial rainwater was added to 100 g of the air dried soil to achieve the moist soil condition as defined above. Then 90 μL of 1 x 10^4 Bq/mL of $^{226}RaCl_2$ was added to 1L of artificial rainwater and this was added to the moist soil sample. These were thoroughly mixed and allowed to sit for five hours followed by centrifuging the sample in a Beckman Model J2-21 high speed centrifuge at 10,000 x g for 10 minutes at room temperature and then decanting the supernatant. To remove the fine soil particulates from the supernatants they were then vacuum filtered through Whatman #1 filter paper followed by vacuum filtering twice through Whatman 0.45 μm cellulose nitrate membranes. Approximately 1L of filtrate was recovered by this procedure. The volume was carefully measured, and then the entire filtrate was evaporated to dryness by placing in the oven at 125° C. The solids from these filtrates were then redissolved in concentrated HNO_3 with the aid of a bath-type sonicator and transferred with three rinses into polystyrene gamma counting tubes. The tubes were then stoppered air tight and aged for two weeks followed by counting in the gamma counter. The results were adjusted for the fraction of the water that was not recovered. Sand soil samples (100 g) without added $^{226}RaCl_2$ were extracted through the same procedure as above to measure the amount of radioactivity that was extractable from the soil.

Control experiments involving centrifugation, filtering and evaporation of 1L solutions of $^{226}RaCl_2$ in artificial rainwater in the absence of soil demonstrated that 99 ± 2 % of the radioactivity was recovered following this procedure. Therefore, any ^{226}Ra not recovered from the soil incubation was likely the result of radium that had become complexed with the soil.

Leaching Of NORM Samples Alone

Pulverized air-dried NORM samples were slurried with artificial rainwater and packed into 0.9 x 35 cm glass columns until the height of the packed bed was 15 cm. Then artificial rainwater was allowed to percolate through the columns at ~ 0.15 ml per hour until 1L of effluent had been collected. The flow rates were adjusted by varying the hydrostatic pressure heads applied to the columns. The effluents were then dried, redissolved, and counted for radioactivity as described for the radioactivity recovery rate experiments.

Leaching Of NORM Samples When Mixed And Incubated With Moist Soils

Air dried NORM samples (10g) were combined with air dried soil samples (100 g) by mixing them together dry in the Waring® blender at maximum speed for two minutes. These were then transferred into 250-mL beakers and artificial rainwater was added to produce the moist soil condition determined as described above. These were then loosely covered with Parafilm® and incubated in the laboratory at room temperature for two weeks. Then, 1L of artificial rainwater was added and the aqueous phase was separated from the soil-NORM mixture and quantified for radioactivity as described for the radioactivity recovery experiments.

Solubilization Of Scale By Mixing And Incubation With Moist Soil

Air dried NORM 1 (10g) was mixed with air dried silt soil (100g) as described above. This mixture was divided into three equal portions, one was left dry and artificial rainwater was added to the other two to produce the moist soil condition as described above. One of the two moist portions was stoppered with a foam stopper and immediately autoclaved to sterilize it. After two weeks incubation the three samples were oven dried and repulverized. Samples (~1g) were taken, placed in weighed 12 x75 mm Pyrex® test tubes and weighed again. The soil and scale were separated by adding 3 ml of 1,1,2,2-tetrabromoethane, a liquid with a density of 2.966 g/ml at 20° C. This density is intermediate between the densities of soil and barite scale. The samples were mixed by vortexing and allowed to sit for 30 minutes. Then additional tetrabromoethane was pipetted between the floating soil and the scale at the bottom of the tube until all of the soil had been floated off and removed from the tube. The excess tetrabromoethane was then removed by pipette, and the residual tetrabromoethane was

evaporated off by placing in the oven at 250° C for 48 hrs. The outsides of the tubes were then carefully cleaned and the tubes were re-weighed to determine the amounts of the scale remaining in them.

Analytical Procedures Applied To Chemical Results

Calculation Of Barium Sulfate Saturation

Establishing the nature of spatial variation of radium and barium sulfate saturation is an important step for the description of any spatial continuity. First, the prediction of scale formation depends upon barium sulfate saturation and will be estimated using the saturation index defined by Matty *et al.* (1985). Fisher (1995, 1998) reported that barite ($BaSO_4$) is the host of most NORM in production equipment; in Texas calcite is much less common (Fisher, 1995). The first step in calculating barium sulfate saturation according to Oddo and Tomson (1994) and Matty *et al.* (1985) is finding the saturation ratio:

$$F_S = \frac{[Me][An]}{K_{sp}},$$

where *Me* is a specific cation concentration in molar units, *An* is a corresponding anion concentration in molar units, and K_{sp} is the solubility product (Matty *et al.*, 1985; Oddo and Tomson, 1994). Oddo and Tomson (1994) also describe activity as the product of the activity coefficient and the concentration, where the activity coefficient is a function of temperature (T), pressure (P), and ionic strength (S_i). It is useful to include the activity coefficients in the solubility coefficient term hence the change in subscripts from K_{sp} to K_C. This conditional solubility term can then be used in a predictive equation:

$$I_S = \log(F_S) = \frac{\log[Me][An]}{K_C(T,P,S_i)},$$

where *Me* is Ba^{2+}, *An* is $SO4^{2-}$, and K_c is the solubility product with respect to T, P, and S_i. If the saturation index is equal to zero, it is at equilibrium with respect to solid scale; if the saturation index is less than zero it is unsaturated and scale is not expected to form; if the saturation index is greater than zero, the sample is supersaturated and scale is likely to form.

A situation can arise where brines are supersaturated and scale does not form. This usually occurs with the introduction of chemical scale inhibitors commonly used by oil and gas

operators. These scale inhibitors according to Smith (1987) usually work by inhibiting crystal nuclei from adhering to nucleation sites. Therefore, wells treated with scale inhibitors could be supersaturated with respect to barium sulfate and not have a scaling problem. The crystal nuclei would be flushed through the production system and usually re-injected back into the formation in which they were derived.

A revised solution for the calculation of saturation indices, also presented by Oddo and Tomson (1994), uses empirical solubility data with the additional flexibility of varying pressure and temperature measurements. The basic equations are in the form:

$$pK_c = a + bT + cT^2 + dp + eS_i^{0.5} + fS_i gS_i^{0.5},$$

where pK_c is the negative log of the conditional solubility product. Using the complex formation between barium and sulfate, the mass-action stability constant, K_{st}, is given by:

$$K_{st} = \frac{[BaSO_4^0]}{[Ba^{2+}][SO_4^{2-}]},$$

where $BaSO_4^0$ refers to the complex in solution, not to the solid. The mass balance equation for total dissolved sulfates would be written as:

$$C_{SO_4} = [BaSO_4^0] + [CaSO_4^0] + [MgSO_4^0] + ... + [SO_4^{2-}],$$

and $C_{Ba} = [Ba^{2+}] + [BaSO_4^0]$ where C_x is total molar concentration of species x in solution. The mass-action stability constant equation and mass balance equation can then be solved as a quadratic equation for the free metal and sulfate concentrations in solution. The result of this quadratic equation along with numerical values for K_{st} and pK_c from literature, produce the final saturation index equation:

$$I_s = \log_{10}\{[Ba^{2+}][SO_4^{2-}]\} + 10.03 - 4.8\times10^{-3}T + 11.4\times10^{-6}T^2 - 4.8\times10^{-5}p - 2.62S_i^{0.5} + 0.89S_i - 2.0\times10^{-3}S_i^{0.5}T$$

where T is temperature (F°), p is total absolute pressure (psia), and S_i is ionic strength (M) (Oddo and Tomson, 1994). This equation was used for ambient conditions.

Additional saturation index calculations were performed using the geochemical software package SOLMINEQ.88. This software analyzes the input chemical data and uses Pitzer's equations for very saline waters to calculate its saturation index (Plummer *et al.*, 1988). Pitzer's equations are used to calculate the activity coefficient in highly concentrated electrolyte solutions. Like Oddo and Tomson's (1994) methods, a positive saturation index represents a supersaturated case for which the potential for precipitation exists, and a negative value represents undersaturation with respect to a particular mineral.

Identifying Homogeneous Subsets

Relatively homogeneous populations or groups of samples were identified within the dataset. Samples were identified into such groups on the basis of similar means and the results of linear regression. These groups were then used to create variograms using ^{226}Ra, Cl^- concentration, and $BaSO_4$ saturation. Barium was also selected for analysis when a three-dimensional plot using ^{226}Ra and Cl^- concentration revealed clustering of data by geologic groups.

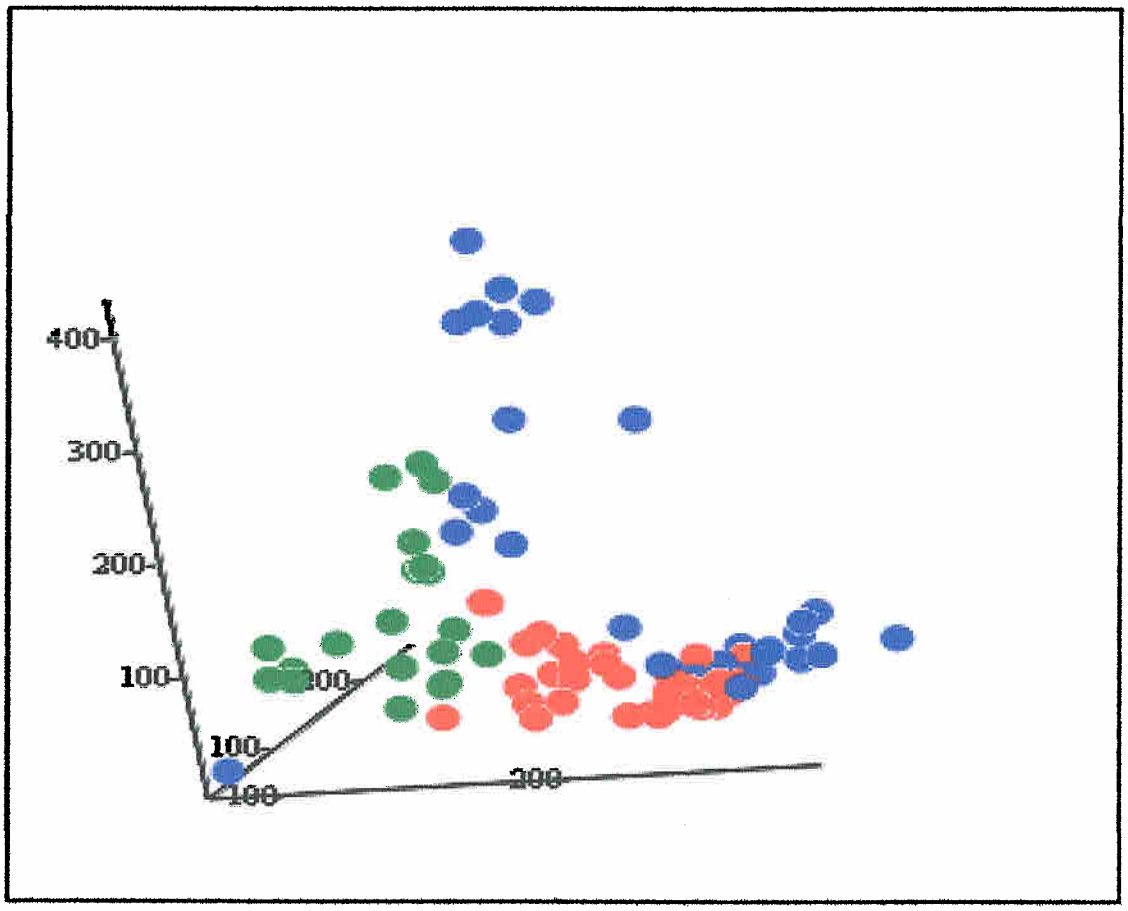
Identifying Spatial Continuity

Swan and Sandilands (1995) define a variogram or semivariogram as a graph that describes the properties of a regionalized variable, and therefore, examine for spatial continuity. Semivariance is:

$$\gamma_h = \frac{\sum_{i=1}^{n-h}(z_i - z_{i+h})^2}{2(n-h)},$$

where $_h$ is the semivariance for a distance h, n is the number of points in the specified separation distance, and z_i is the value of the variable at the ith point along the traverse. The semivariance is calculated for various distances and the semivariogram is constructed simply as a graph of γ_h against h. When h is zero, pairs of z values at a distance h apart are identical and the semivariance equals zero. As h increases the similarity between pairs of z values is likely to decrease and the semivariance therefore increases. This occurs until the semivariance ceases to increase at the variance (called the sill) of the dataset. When the variance between two points separated by a relative close distance is high, the variogram is displaying a nugget effect. A pure nugget effect would be a constant semivariance, the variance of the dataset, at all separation

distances. Usually a nugget effect is due to measurement errors, unsampled scales, non-ideal sample locations, or not enough sample locations.



(tds , cl , ba) , (tds1 , cl1 , ba1) , (tds2 , cl2 , ba2)

Figure 2 - Three dimensional plot of TDS (g/L), Cl^-(g/L), and Ba^{2+} showing distinct clustering of data. Groups plotted are Group 1 - blue (Washita-Fredericksburg, Paluxy, and Mooringsport Formations), Group 2 - red (Upper Tuscaloosa and Lower Tuscaloosa Formations), and Wilcox Trend samples - green.

A variogram created from data with spatial continuity will typically display a curve starting from zero semivariance at zero separation distance (no variance between a data point and itself) and will rise exponentially toward the sill. The semivariance is increasing as the distance between points is increasing. Once the distance between points is significantly large, one sample location would not be expected to be closely related to another, thus curve will flatten at the sill, and the semivariance is equal to the variance of the entire dataset.

Principal Component Analysis

To understand the nature of the fundamental relation between chemical variables principal component analysis was applied to the dataset. Jolliffe (1986) explains principal component analysis is used to reduce the complexity of the multidimensional nature of the data or the complex nature of relation. The method used for this analysis has the form of a series of individual measurements across a full set of variables (chemical constituents). First, a variance-covariance matrix is calculated for the available variables (note that variables with observations recording below detection limits were omitted). This matrix contains the fundamental information about the dataset and relation between variables. Because the variance-covariance matrix is symmetric, the eigenvalues are all real, and the eigenvectors are all mutually orthogonal (Jolliffe, 1986). The eigenvalues or principal components can be seen as an alternative method for describing the variation between measurements. The first principal axis will account for more of the total variance than any one of the original variables, and other principal axes will account for less of the total variance within the dataset. If only the first two or three largest or most significant axes are used to describe the variation within the dataset, the number of variables and axes necessary to describe this variation can be significantly reduced.

If brine samples from the same geologic formation have similar chemistry as represented by the full set of variables, it is very likely that this similarity will also be evident when the observations are plotted in the two- or three-dimensional space represented by the first two or three principal components. Because the chemical measurements (and units of measure) varied from one chemical to another, it is necessary to scale each of the variables before applying principal component analysis. In this analysis, each variable was normalized by applying a linear transformation such that the range of variation within each constituent was scaled to vary from 0 to 1. It is possible that the variation in brine chemistry within each geologic formation is insignificant compared to the variation between all samples. This case may result in transformed variables that do not cluster in either or both of the two- or three-dimensional principal component analyses. The results of principal component analysis as well as other methods are discussed in this section are presented in the following section with the results.

RESULTS AND DISCUSSION

Changes In Brines Upon Storage

The weights of the nonvolatile solutes from the acidified samples, after dilution corrections, were generally different from those from the unacidified samples. Often, additional solutes were dissolved with the acid treatment. This would cause an increase in the solute weights. Adding hydrochloric acid converts carbonate salts in solution to the corresponding chlorides. This generates carbonic acid and results in the effervescence of CO_2 gas. These changes could have the effect of either reducing or increasing the total solute weight. The largest observed changes in solute weights following acidification were -34.3 g/L and +25.0 g/L. The largest percentage changes were -10.9% and + 9.5%.

Radium Recovery On Rad Disks

When only ^{226}RaCl in 2N HNO_3 was applied to Rad Disks the cumulative recovery and counting efficiency for the 186 keV emission of freshly isolated ^{226}Ra was found to be 98.4 ± 2.7% (Table 1). Many of the solutes from the brines can produce substantial interference with recovery of Ra on the Rad Disks. Potassium, sodium, chloride and other potentially interfering monovalent ions from the brines were greatly reduced in concentration by bulk precipitation and collection of the multivalent cations as the insoluble carbonates leaving monovalent ions such as potassium, sodium, and chloride in solution. The slow rate of addition of Na_2CO_3 solution under constant vigorous stirring is necessary to minimize trapping of monovalent salts in the precipitates as they form. This insures optimal and reproducible separation. Recovery of radium by the Radium Rad Disks was nearly zero if the carbonate precipitation step was not performed. The recovery of radium from sample to sample remains highly variable due to the different compositions of the samples and hence the different levels of interfering substances that are not removed by the carbonate-precipitation step. For the 60 samples analyzed at the time of this writing radium recoveries have ranged from 10% to 85%, with an average of 47%. Because of the large variation in recovery from sample to sample, it was necessary to run an internal standard for each sample (^{226}Ra spike).

The 60 samples analyzed contained radium ranging from a high of 120 Bq/L (50.3 Bq/100g of dissolved solutes) to a low of 1.1 Bq/L (0.9 Bq/100g of dissolved solutes). The isotope distribution in the high sample was 34.7 ± 0.6 Bq/L (8.50 ± 0.14 pmole/L) of ^{226}Ra and 85 ± 52 Bq/L (74 ± 45 fmole/L) of ^{228}Ra. The low sample was below the detection limit for ^{226}Ra and 1.1 ± 0.5 Bq/L (0.94 ± 0.39 fmole/L) of ^{228}Ra. The average values for the 60 samples were 188.2 g/L solute, 12.6 Bq/L (3.1 pmole/L) of ^{226}Ra, and 15.1 Bq/L (13.1 fmole/L) of ^{228}Ra.

Data Corrections For Radium Isotope Determination In Brines

Freshly isolated ^{228}Ra has no significant gamma emissions and, therefore, will not interfere with quantification of ^{226}Ra by gamma counting. Both of these radium isotopes, however, generate radioactive-decay products that emit gamma radiation. The method described here takes advantage of this fact for the quantification of ^{228}Ra by counting the 911-keV and 969-keV gamma emissions of ^{228}Ac following aging of the Rad Disks. Aging the Rad Disks in the vacuum desiccator under conditions in which some of the ^{222}Rn would emanate from the disks was found to reduce the levels of interfering decay products of ^{226}Ra by 33 $\pm$ 1%. However, ^{214}Bi produces a gamma emission at 934 keV that increases the activity detected in the 900-1000 keV window used to quantify ^{228}Ac (Chu, Ekström and Firestone, 1999). The interference from remaining ^{214}Bi and other emissions in the 900-1000 keV counting window after vacuum-dessicator aging of the samples was determined to be 9.6% $\pm$ 0.3% of the counts for the freshly-prepared Rad disks in the 15-500 keV counting window. After subtracting the background this number of counts was subtracted from the counts in the 900-1000 keV window before further analysis. It is estimated that for samples with an isotope activity ratio of greater than 10 ($^{226}Ra/^{228}Ra$) the activity of ^{228}Ra will be effectively masked within the error of the measurement due to the presence of the residual 934-keV emission of ^{214}Bi.

Analysis of the spectra of unaged and aged Rad Disks prepared with known amounts of $^{226}RaCl$ allowed determination of peak widths, peak resolution and counter efficiencies at different energies and it allowed determination of counter precision and accuracy at different activity levels (Table 1). Peak widths at one-half-peak height were found to be125-130 keV. Assuming the peaks were statistically normal permitted corrections of data for the 911-keV and 969-keV peak tails that were not included in the 900-1000 keV counting window.

The counting window (900-1000 keV), chosen for quantification of the 911-keV and 969-keV emissions of ^{228}Ac, was intentionally narrow to minimize interferences from nearby emissions of ^{226}Ra decay products, most notably the 768-keV, 786-keV, 806-keV, 1052-keV and 1120-keV emissions of ^{214}Bi and the 786-keV and 839-keV emissions of ^{214}Pb (Chu, Ekström and Firestone, 1999). Because the emissions are broadened into peaks with width at one-half peak height of 125-130 keV when detected with the NaI gamma detector, and assuming that the shapes of these peaks are statistically normal, then approximately 2% of a peak with maximum at 770 KeV would overlap into the 900-1000 KeV window. Fortunately, with the exception of the 1120-KeV emission of ^{214}Bi none of the emission transitions that result in gamma energies from ^{214}Bi or ^{214}Pb that fall within 130 KeV of the 900-1000 KeV window occur at intensities greater than 5% of the disintegrations of that isotope. Because of their low intensities and

extensive spectral overlap they generally contribute to elevation of the apparent spectral baseline throughout this energy range. Their contributions to the 900-1000 KeV window are cumulatively corrected for with the subtraction of 9.6% of the 186-KeV emission of ^{226}Ra from the unaged sample Rad Disk.

The counting efficiency of the Packard 500 C gamma counter was found to decline rapidly with increasing energy. The combined recovery efficiency for recovering ^{226}RaCl from 2N HNO_3 solution on Rad Disks and the counting efficiency for the 186-keV emission of ^{226}Ra in the Packard NaI detector Gamma Counter was determined to be 98.4% ± 2.7% (Table 1). After aging some of these same samples were then used to determine the counting efficiency for the 609-keV emission of ^{214}Bi (2.8% ± 0.4%), and the counting efficiency for the 1120-keV emission of ^{214}Bi (11.9% ± 0.5%). Extrapolation between the later two values provided an estimate of the counting efficiency in the 900-1000 keV range of 12.2% ± 0.5%.

Leaching Of Radioactivity From Sale And Sludge Samples

The two scale samples (NORM 1 and NORM 2) had very little water content, very little toluene soluble content and relatively little HNO_3 soluble content. The sludge sample (NORM 3) had much larger content of all of these components. The HNO_3 treatment resulted in extraction of 7% of the radioactivity from NORM 2 while it did not extract any radioactivity from NORM 1 or NORM 3. Toluene treatment did not extract any radioactivity from any of the samples.

Table 1 - Recovery and counting efficiency of ^{226} RaCl from 2N HNO_3 on Rad Disks

^{226} Ra added Bq	^{226} Ra measured Bq*	Measured (%)* Added
0	0	-
9.25	8.92 ± 0.27	96.4 ± 2.9
92.5	89.2 ± 2.5	96.4 ± 2.8
223	225 ± 7	101 ± 3.1
334	333 ± 6	99.6 ± 1.8
	Cumulative recovery average	98.4 ± 2.7

* Values are mean ± standard deviation for three determinations

The clay soil had the largest water content, the largest water holding capacity and the largest organic content with the silt soil intermediate and the sand soil lowest in each of these

parameters. The pH of the water drained from each of the soils was slightly alkaline, and the endogenous radiation intensity of each of the soils was within the range expected for uncontaminated soils (Table 2) (Kathren, 1998). The radioactivity recovery rate was highest for the sand soil with the silt soil intermediate and the clay soil lowest. The radioactivity recovery rate for each of the soils was low with the maximum recovery of radioactivity at 1.83 ± 0.15% for the sand soil. Since the soils alone had small amounts of radioactivity, the sand soil was carried through the same procedure as the soils plus added $^{226}RaCl_2$ to determine how much of the endogenous soil radioactivity could be extracted. Table 3 shows that the radioactivity extracted from the sand soil alone was 3.9% of the radioactivity extracted from the sand soil plus added $^{226}RaCl_2$. This endogenous soil radioactivity may have been due to a combination of radioactive elements including ^{40}K, ^{238}U, ^{232}Th, and radioactive decay products from the latter two (Kathren, 1998).

Percolation of artificial rainwater through the NORM samples did not extract any measurable radioactivity from NORM 1, while this treatment extracted 0.02% ± 0.01% of the radioactivity from NORM 2 and 0.11 % ± 0.04% of the radioactivity from NORM 3. All of the soil incubation conditions resulted in greater extraction of soluble radioactivity than were observed for percolation of artificial rainwater through the isolated NORM samples. The amounts of radioactivity extracted, however, were still very low for all of the soil incubation conditions, and there was no significant effect of soil type on the leaching of radioactivity from the NORM samples. When $^{226}RaCl_2$ was added to a mixture of sand soil (100 g) and NORM 3 (1 g) the radioactivity recovery rate was significantly lower (0.68 ± 0.14%) than for the sand soil alone in spite of the fact that the added NORM sample contributed 56% additional radioactivity over that of the added $^{226}RaCl_2$ (Table 3).

When NORM 1 and silt soil mixtures were separated by differential density with tetrabromoethane 95.7% ± 0.6% of the scale was recovered from the portion that was left dry, 84.1% ± 3.3% of the scale was recovered from the moist/sterile incubation portion, and 55.5 % ± 0.3% of the scale was recovered from the moist/septic incubation portion (Table 4).

Table 2 - pH and radiation intensity of soils

Measurement	Clay soil (Mean ± S.D*)	Silt Soil (Mean ± S.D.*)	Sand Soil (Mean ± S.D.*)
pH	7.74 ± 0.04	7.43 ± 0.01	7.03 ± 0.06
Intensity (cpm/g)	7.18 ± 0.62	6.35 ± 0.92	4.61 ± 1.06

* S.D.= standard deviation

Table 3 - Radioactivity recovery characteristics of sand soil		
Sample composition*	Radiation intensity of the extract (cpm**) (Mean ± S.D***.)	% total counts extracted
Sand	12 ± 4	2.6
Sand + $^{226}RaCl^2$	308 ± 25	1.8
Sand + $^{226}RaCl^2$ + NORM 3	112 ± 23	0.4

*100 g of sand soil, 90 µL of 1 x 10^4 Bq/mL of $^{226}RaCl_2$, 1 g of NORM 3, moist soil condition plus 1 L of artificial rainwater, incubation and extraction as described under Materials and Methods. The count rate for the added ^{226}Ra with the equipment and condition used for these experiments was 16560 ± 80 cpm. The NORM 3 sample contributed an additional 9370 ± 570 cpm. The sand soil sample contributed an additional 460 ± 100 cpm.

** cpm = counts per minute

*** S. D. = standard deviation

Table 4 - Differential density separation of soil and scale*		
Incubation condition	Scale recovery (Mean ± S.D.)	Comparative recovery
Dry	95.7% ± 1.2%	
		Dry minus Moist (sterile) 11.6 %
Moist / sterile	84.1% ± 3.3%	
		Moist /sterile minus Moist / septic 28.6 %
Moist / septic	55.5% ± 4.0%	

*100 g of the air dried silt soil and 10 grams of air dried NORM 1 were pulverized and mixed thoroughly. The mixture was divided into three equal portions, one portion was left dry and water was added to the other two portions to achieve the moist soil condition described in the methods section. One of the moist portions was immediately autoclaved to sterilize it, the other portion was left septic. After two weeks incubation the samples were oven dried at 125°C, repulverized, and the soil and scale separated by differential density using tetrabromoethane as described in the methods section.

Validation Of The Radium Isotope Analysis Method For Brines

The data in Table 1 show that the gamma counter quantification of ^{226}Ra is both accurate and precise over the concentration range normally encountered in the brines. This demonstrates that spiking of the samples with $^{226}RaCl$ is a valid means of obtaining an internal recovery standard. Spectral analysis of stoppered, aged Rad Disks prepared with known amounts of

^{226}RaCl permits calibration of the gamma counter for the 900-1000 keV energy range used for quantification of ^{228}Ac, and for correction of peak tails from the 911 and 969 keV emissions of ^{228}Ac that overlap the boundaries and fall outside of this window. Comparison of the counts in the 900-1000 keV window for freshly prepared versus vacuum desiccator aged Rad Disks with known amounts of ^{226}RaCl allows determination of the correction factor for the activity that appears in the 900-1000 keV window due to the radioactive decay products of ^{226}Ra.

Brine Stability

Brine samples were generally stored for several weeks before final analysis was completed. Upon storage most of the brines generated precipitates that could be redissolved by the addition of ~1 M HCl. These precipitates were probably formed as a result of a combination of factors including temperature and pressure differences from those of the brine origins, reactions due to mixing of brines from different geological reservoirs, and gradual production of insoluble carbonates from reaction with dissolved CO_2. Prior to sample collection the investigators had no control over any changes of this nature or of dilution or concentration changes due to condensation or evaporation that may have taken place in the field. Acidified, filtered brine samples have been stored for more than one year with no noticeable formation of precipitates or other changes. The authors recommend the addition of ~1 M HCl as a preservative for brines that are to be stored.

Radium Rad Disk Performance

Radium was collected on Radium Rad Disks by vacuum filtering the samples through the disks. The Rad Disks are designed to specifically adsorb radium from aqueous samples and have been used for analysis of the radium content of drinking water and other water samples (Smith et al., 1998). Several salts have been shown to interfere with radium binding to the Rad Disks. Potassium and barium are the components likely to be present in the brines that are capable of producing the highest levels of interference with radium uptake by the Radium Rad Disks (Smith et al., 1998). Potassium, at 10 g/L, and barium, at 0.1 g/L, have been shown to reduce radium uptake by Radium Rad Disks to less than 50%. High concentrations of sodium, calcium, magnesium, and other solutes also interfere (Smith et al., 1998). The carbonate-precipitation step greatly reduced the levels of potassium in the samples and made it possible for the Radium Rad Disks to effectively complex radium from the samples. If this step was not added the recovery of radium on the Rad Disks was near zero.

Radium Isotope Discrimination

Aging the Rad Disks in a desiccator under vacuum with activated charcoal and $CaSO_4$ for 2 weeks resulted in a 33% ± 1% reduction in the presence of radioactive-decay products of ^{226}Ra on the Rad Disks compared to Rad Disks that were sealed in polystyrene counting tubes immediately after preparation. In retrospect a 36-hr or 48-hr incubation period would have been sufficient to allow ^{228}Ac to grow in and equilibrate, the shorter incubation time would have further reduced interference from radioactive-decay products of ^{226}Ra. The shorter incubation is recommended with the caution that the timing of this incubation must be precise (± 2 hr).

The freshly collected Rad Disks were counted with the gamma counter window set to the 15-500 keV range. This range resulted in the inclusion of a significant quantity of extraneous counts due to low energy noise that was not adequately corrected for by subtracting the blank. It was, therefore, necessary to correct the data for this problem mathematically. In retrospect, setting the counter window to a narrower range, excluding the low-energy end of the range, would have yielded accurate counts without the need for applying a correction factor.

When the isolated radium samples have been allowed to age the only significant gamma emissions in the 900-1000 keV range for either isotope are the 911-keV and 969-keV emissions of ^{228}Ac and the 934-keV emission of ^{214}Bi and other ^{226}Ra-related sources such as the 768-keV, 786-keV, 806-keV, 1052-keV and 1120-keV emissions of ^{214}Bi and the 786-keV and 839-keV emissions of ^{214}Pb. Contributions to the emissions in the 900-1000 keV range from ^{214}Bi and other ^{226}Ra-related sources were corrected for by subtracting 9.6% of the 15-500 keV emission of the unaged Rad Disk sample from the 900-1000 keV emission of the same sample after vacuum-dessicator aging. By counting these different energy ranges for freshly-prepared and aged Rad Disks and applying the appropriate corrections it is possible to quantify both of the radium isotopes from the same isolated radium sample without further isolation steps using commonly available gamma-counting equipment.

The counting efficiency of the Packard 500C gamma counter in the energy range (900-1000 keV) employed for quantification of ^{228}Ra was relatively low (12.2% versus ≥98.4% for the 186 keV range). This resulted in proportionately low count rates for ^{228}Ra relative to those for ^{226}Ra with consequently larger counting errors.

Quantification Of Radioactivity Derived From Solid Samples

The radioactivity detection protocols that were used for the leaching measurements were intended to provide reproducible estimates of the relative radiation intensities in the samples. As much as possible, sample geometries were held constant. The aging of samples in air-tight stoppered counting tubes prior to counting allowed standardization of the radioactive contents that were being counted. Radium is continuously producing short lived radioactive decay

products. These are different elements having different chemistries and different solubility properties from the parent radium. In addition, the first decay product of ^{226}Ra is ^{222}Rn, which is volatile and may leave the sample. Aging of the samples in tightly stoppered containers had the effect of allowing any short lived radioisotopes that might have been extracted disproportionately to the parent radium to decay away, and for the radioactive decay products of the extracted radium to grow in and come to near equilibrium. The only significant radioactivity in the aged samples was, therefore, that which resulted from the extracted radium.

Solid NORM Sample Characteristics

The HNO_3 treatment did not extract any radioactivity from the weathered scale sample (NORM 1) but it did extract 7.1% of the radioactivity from the non-weathered scale sample (NORM 2). In addition artificial rainwater percolated through the weathered scale sample did not extract any measurable radioactivity, while 0.02% of the radioactivity from the non-weathered scale sample was extracted by this treatment. NORM 1 and NORM 2 were different scale samples collected from different locations, and their compositions are not likely to be the same. However, these results indicate that it is possible to remove a small amount of the radioactivity from scale samples by weathering them, but once this component is removed the remaining radioactivity is highly resistant to solubilization. The highly insoluble radioactivity is most likely present as radium sulfate. Radium co-deposited with the barium in barite probably has a solubility coefficient similar to that of barite (~1.6×10^{-10} M at low ionic strength, Oddo, 1999). The radioactivity that can be extracted with HNO_3 or artificial rainwater is probably radium carbonate. There was a small amount of effervescence of CO_2 gas observed upon the first addition of HNO_3 to the NORM samples.

It is interesting to note that HNO_3 treatment resulted in the extraction of nearly the same proportion of material from the two scale samples. However, HNO_3 treatment only resulted in extraction of radioactivity from the non-weathered scale sample. This indicates that there are non-radioactive components of the scale samples that can be extracted with strong acid, but not with weak acid such as rainwater. It has previously been noted that scale samples from Mississippi hydrocarbon production may contain significant quantities of trace metal inclusions (Saunders and Rowan, 1990). These metal inclusions may account for much of the material that is extractable with HNO_3, but which are not extractable with rainwater.

The sludge sample was nearly 10% oil and once the oil was removed by extraction with toluene greater than 35% of the remaining material was HNO_3 soluble. This indicates that the oil effectively protected the sludge particles from exposure to and dissolution by water. However, the radiation in the sludge particles remained insoluble through these extractions indicating that it was probably present as $RaSO_4$. Most scale formation occurs before the produced fluids have

had significant exposure to the atmosphere. It is possible that sludge particles grow in storage tanks as atmospheric CO_2 dissolves and reacts with other solutes to form only slightly soluble carbonates. As these carbonates form they may condense out on colloidal barite particles causing these to grow large enough to settle to the tank bottoms. Brine samples stored in the laboratory generate precipitates over time (Matthews, *et al.*, 2000). This scenario could explain why the sludge particles have a larger proportion of HNO_3 soluble content (probably carbonates) than scale.

Recovery Of Soluble Radium From Soils

The radium recovery experiments showed that less than 2% of ^{226}Ra from $^{226}RaCl_2$ remained in the aqueous phase after mixing the solution with top soils. Furthermore, when $^{226}RaCl_2$ solution was added to a mixture of the sand soil and NORM 3 (Table 3) even less of the radioactivity remained in the aqueous phase. These findings demonstrate that radium will complex with soil components and that the presence of sludge or scale particles in the soil will enhance the abilities of the mixture to complex radium and take it out of solution. It is well documented that radium has affinity for, and will adsorb to alkaline earth sulfates such as barite (Huck, McCymont, Nesbitt, Anderson and Kratochvil, 1989). From the data reported here for recovery of radium from soils it is estimated that soil partition coefficients for soluble radium will fall in the 1×10^{-2} M range. These levels are consistent with published values for radium partitioning with non-contaminated soils (Frissel and Koster, 1990).

Actions Of Soil Microorganisms On Scale And Sludge

Top soils are expected to contain high concentrations of microorganisms and these are expected to be capable of numerous processes for solubilizing inorganic minerals. Among the processes relevant to solubilization of radium from scale and sludge particles are chelation and sulfate reduction. The release of metal chelating agents by microorganisms is a well documented process by which microorganisms extract needed trace metals from the substrates they are growing in (Barton and Hemming, 1993). Many soil microorganisms are capable of reducing sulfates to sulfites and sulfides. Sulfites and sulfides of the alkaline earth elements are generally much more soluble than the sulfates (CRC Handbook of Chemistry and Physics, 1971). Sulfate reduction processes are used industrially to process barite, celestite and other alkaline earth minerals (Brobst, 1983; Ober, 1991). An additional action that soil microorganisms have on scale and sludge wastes is that they will break down the organic components of the petroleum further enhancing access of water to the inorganic components and enhancing their solubilization (Roberts, Quinby, Duggan and Yuan, 1998).

Leaching Of Radium From Scale And Sludge Samples

Only small amounts of radium could be washed out of the NORM samples by slowly percolating artificial rainwater through the pulverized samples. The maximum extraction observed was 0.11% ± 0.04% for the tank sludge sample (NORM 3). The data show that incubation of the scale and sludge samples with moist top soils for two weeks resulted in increased amounts of radium that could be washed out of the mixtures compared with the amount of radium that could be washed out of the scale or sludge samples alone. The maximum proportion of radioactivity that was washed out from the soil-NORM mixtures in these experiments was 0.36% ± 0.13% for the NORM 3-silt soil mixture. This is still a very small amount. On first examination this increase may seem trivially small, however, when the abilities of soils to complex soluble radium are considered, the indication is that substantial amounts of radium may have been released from the NORM samples through incubation with moist top soils.

Effects Of Soil Incubation On Leaching Of Radioactivity From Scale And Sludge Samples

The data from Table 3 demonstrate that greater than 98% of soluble radium can be complexed by soil. The observation that radium extracted from the NORM samples was somewhat enhanced by incubation with soils even though the soils and the soil-NORM mixtures were found to be able to complex most of the soluble radium added to them indicates that the release of radium from the NORM samples by incubation with soils is probably much larger than is indicated by the amount of radium extracted. The large values for the soil-radium partition coefficients relative to the equivalent values for radium complexation with barite (approximately eight orders of magnitude different) can be interpreted to mean that radium complexed with soil will be much more mobile and biologically available than radium complexed with barite. In addition, the contribution of soluble radium from equilibrium with the undissolved barite in a soil-barite mixture will be negligible, and any radium extracted will represent only the radium that is in equilibrium with the soil (Matthews, 1993). Based on these conservative approximations, it can be estimated from the leaching studies that an average in the range of 20% of the radium was solubilized from the NORM samples by incubation with moist top soil for two weeks.

Physical Separation Of Scale From Soil

The data from Table 4 demonstrate that there was a 28.6% lower recovery of scale from the tetrabromoethane separation procedure from the moist/septic soil incubation condition as compared with the moist sterile incubation condition. We interpret this loss to be due to

solubilization of scale through the actions of soil microorganisms. It is assumed that the 4.3% weight loss from scale from the dry mixture was probably due to the fact that NORM 1 contained a small amount of soil adhering to the scale particles, and this soil that came with the scale became dislodged and separated as the result of the experimental manipulations. The additional 11.6% loss of recovered scale from the moist/sterile incubation relative to the dry incubation may have been due, in part, to tiny scale particles adhering to soil as the result of interactions between the scale and soil facilitated by wetting. Thus some of the undissolved scale could have been floated off by adhering to soil. A second possibility for the loss of scale in the sterile incubation could have been due to insufficient sterilization. Some soil microorganisms may have survived the sterilization procedure.

Results Of Analytical Procedures Applied To Chemical Dataset

General Statewide Trends

Radium (^{226}Ra and ^{228}Ra) activities in brines are distributed throughout the state in a wide range of values, from 25 pCi/L, to values as high as 2000 pCi/L, but there does not appear to be any trend in the variation across the basins. By contrast, a regional trend in another constituent is evident, elevated chloride values do exist in the Mississippi Interior Salt Basin. Saunders and Swann locate the salt basin in Mississippi from the Pickens-Gilberton fault zone in the north to the Wiggins Arch in the south (Saunders and Swann, 1989). Numerous Jurassic salt domes are located in this area making these brines more chloride rich. Within the brine samples in this research, mean chloride values in the Interior Salt Basin are 104.1g/L compared to 56.6g/L in sampled wells outside the Interior Salt Basin. Testing to see if the means of the two groups are similar (using a two sample *t*-test) yields an observed level of significance, or *P*-value of 1.74×10^{-14}, indicating chloride concentration of the two groups are distinctly different.
The correlation between major constituents in the database was calculated for the main analysis data set. Most samples were used, 184 of 195 total, which included samples from the Black Warrior Basin, Mississippi Interior Salt Basin, and Wilcox Trend. Some samples were removed because they were untested or below detection limits with respect to one or more constituents. The results of this analysis reveal that several constituents are moderately to well correlated. A sample correlation coefficient, r, of 1 or -1, depending on a positive or negative correlation, would represent perfect correlation between two variables. A correlation coefficient of 0 would represent two uncorrelated variables. The total dissolved soilds (TDS) has a positive correlation with Cl, $r = 0.78$, while $BaSO_4$ saturation displays a more moderate correlation with Cl, $r = 0.44$. ^{226}Ra and ^{228}Ra also have a moderate correlation with one another, $r = 0.54$. The correlation between the major constituents and SO_4 concentration was sought, but first, the samples which had values of sulfate below detection had to be removed. This decreased the Main analysis data

set size for calculating the correlation coefficient from 195 samples to 91 samples. The results reveal that SO_4 has a low to moderate correlation with $BaSO_4$ saturation, ^{226}Ra activity, and ^{228}Ra activity with *r* values of 0.41, 0.36, and 0.34 respectively.

Homogeneous Data Sets By Geologic Formation

Relatively homogeneous subsets of data were needed to consider the data spatially. The similarity of means for two or more populations was used to identify these homogeneous datasets. The subsets or groups of data are important to combine similar data with respect to not only brine chemistry, but also the geology and stratigraphy of the system to completely and accurately describe NORM in Mississippi. A two sample *t*-tests, which test the hypothesis that the means of the two populations are equal was conducted for the major constituents in the Main analysis dataset. First, data from each brine sample was separated by geologic formation. Two sample *t*-tests were run for TDS, ^{226}Ra, ^{228}Ra, Cl^- concentration, and Ba^{2+} (Table 5 - 9). These *t*-tests compared the means of each formation to all other formations. Tables 5 through 9 are results of *t*-tests with values of 1 or 0. A value of 1 indicates the means of the two formations are similar with a 95% confidence, while a value of 0 indicates the means are not the same. The results of these tests reveal that many of the chemical constituents contained in the brines do, in fact, have similar means or are derived from populations with the same means at the 95% confidence level. Table 10 summarizes the results from the *t*-tests by adding the 1's and 0's from Table 5 through 9. At this point, a numerical value between zero and five exists for every pair of formations. A value of five exists if all of the major constituents tested (TDS, ^{226}Ra, ^{228}Ra, Cl^- concentration, and Ba^{2+}), have similar means with a 95% confidence. Areas outlined in blue have values of four or five and were considered for further analysis. Final homogeneous groups (subsets) by geologic formation where chosen from formations outlined in blue in Table 10. These formations outlined in blue will be referred to as the Mesozoic subset.

The continuous and complete stratigraphy of Mississippi is not represented by the samples comprising the Main analysis data set, so it was important to locate the Mesozoic subset stratigraphically to see if any of the formations were directly adjacent to one another. Adjacent formations with similar geology would be expected to have similar brine chemistry. It was important to create groups based on brine chemistry as well as formation geology. This important step was used to create the final homogeneous groups. By following this process, groups of roughly uniform characteristics were established. Group 1 consists of the geologic formations Washita-Fredericksburg, Paluxy, and Mooringsport and Group 2 is composed of Upper Tuscaloosa and Lower Tuscaloosa samples. Samples from the Eutaw Formation, which constitute what is called Group 3, were also used due to the relatively large amount of data. Once these three groups were created from formation geology, analysis of variance was applied

using the major constituents (^{226}Ra, $BaSO_4$ saturation, Ba^{2+}, ^{228}Ra, SO_4^{2-}, TDS, Cl^- concentration) to see if these Final homogeneous groups did indeed have similar means. A summary of the ANOVA analysis for major chemical constituents is located in Table 11. Table 11 was used to finalize the groups created from formation geology which will be used to test for spatial continuity. *Accept* indicates there is a 95% probability that the means in that group are similar, and *reject* indicates that the means are not similar with a 95% probability.

Group 1 consists of 31 samples coming from 16 different fields, and displayed similar means with respect to ^{226}Ra, $BaSO_4$ saturation, Ba^{2+}, ^{228}Ra, SO_4, and TDS. Similar means are reported in Group 1 for six out of the seven major database constituents tested. Group 2 consists of 35 samples from 14 fields having similar means for five out of seven major constituents. Group 3 the Eutaw Formation samples consists of 34 samples coming from 11 fields.

Homogeneous Data Sets By Field Of Production

In order to create homogeneous populations by field, all Main analysis dataset wells were plotted. Groups of fields were chosen based on the number of samples within the field and its proximity to other fields. Four groups were selected for preliminary analysis: Group A, Group B, Group C, and Group D. Group A consists of Davis, Frances, and Quitman Fields. Heidelberg Field (Group B) was sampled three different times, and therefore, the samples were compared. Group C consist of Laurel, Reedy Creek, Eucutta, Sandersville, West Yellow Creek, and Pool Creek Fields. Group D consists of Martinville and Puckett Fields. Once again, ANOVA was used to see if the groups had similar means. The results of this analysis are presented in an ANOVA summary Table 11. Table 11 was used to select the final groups created from producing field to test for spatial continuity. *Accept* indicates there is a 95% probability that the means in that group are similar, and *reject* indicates that the means are not similar with a 95% probability. Only groups with at least 5 out of the 7 major constituents with similar means were considered for analysis.

Two of the four groups were selected based on analysis of variance results: Group B - Heidelberg Field, Group D - Puckett and Martinville Fields. Wilcox Trend samples were also selected for analysis due to the relatively large number of samples in the southwest corner of the state, and the wells from this area are all producing from the Wilcox formation. This would seem to be an ideal situation for looking for spatial continuity. Heidelberg Field consisted of 32 samples producing from seven different formations, and displayed similar means with respect to six out of seven of the major chemical constituents tested. Puckett and Martinville Fields consist of 13 samples from seven formations having similar means for all seven major constituents. The Wilcox Trend samples consist of 20 samples coming from 16 fields. A summary of the ANOVA analysis for major chemical constituents is located in Table 11.

Table 5 - A summary of t-tests of TDS by geologic formation*

	Mean		Wilcox			Selma		Upper	Lower						Cotton
Basins (# of samples)	**Pci/L**	****MISB**	**Trend**	**Sparta**	**Wilcox**	**Chalk**	**Eutaw**	**Tuscaloosa**	**Tuscaloosa**	**Wash. -Fred.**	**Paluxy**	**Morringsport**	**Rodessa**	**Hosston**	**Valley**
Black Warrior (9)	79	0	0	1	0	0	0	0	0	0	0	0	0	0	1
**MISB (137)	189		0	0	0	0	0	1	0	1	0	1	1	0	1
Wilcox Trend (23)	134			1	1	1	0	0	0	0	0	0	0	0	1
Formations and Groups (# of samples)															
Sparta (3)	100				1	0	0	0	0	0	0	0	0	0	1
Wilcox (20)	136					1	0	0	0	0	0	0	0	0	1
Selma Chalk (10)	146						1	0	0	0	0	1	1	0	1
Eutaw (34)	157							0	0	0	0	1	1	0	1
Upper Tuscaloosa (3)	182								0	1	0	1	1	0	1
Lower Tuscaloosa (30)	205									1	1	1	1	1	1
Washita-Fredrisburg (16)	189										0	1	1	0	1
Paluxy (12)	219											1	1	1	1
Moringsport (3)	215												1	1	1
Rodessa (13)	192													1	1
Hosston (7)	269														1
Cotton Valley(3)	219														
Parkwood - Pennington (6)	91														

*A value of 1 expresses the means of the two formations are the same with 95% confidence, and a value of 0 expresses the means are not the same.

**MISB = Mississippi Interior Salt Basin

Table 6 - A summary of t-tests of ^{226}Ra by geologic formation*

	Mean		Wilcox			Selma		Upper	Lower						Cotton
Basins (# of samples)	**Pci/L**	****MISB**	**Trend**	**Sparta**	**Wilcox**	**Chalk**	**Eutaw**	**Tuscaloosa**	**Tuscaloosa**	**Wash. -Fred.**	**Paluxy**	**Morringsport**	**Rodessa**	**Hosston**	**Valley**
Black Warrior (9)	356	1	1	1	1	1	1	1	1	1	1	1	1	1	1
**MISB (137)	401		1	0	1	0	1	1	0	1	1	1	1	1	1
Wilcox Trend (23)	346			0	1	1	0	1	1	1	1	1	1	1	1
Formations and Groups (# of samples)															
Sparta (3)	190				0	1	0	0	0	0	0	0	0	0	1
Wilcox (20)	363					0	1	1	1	1	1	1	1	1	1
Selma Chalk (10)	230						0	0	1	0	0	1	0	1	1
Eutaw (34)	428							1	0	1	1	1	1	1	1
Upper Tuscaloosa (5)	478								1	1	1	1	1	1	1
Lower Tuscaloosa (30)	319									1	0	1	1	1	1
Washita-Fredrisburg (16)	433										1	1	1	1	1
Paluxy (12)	518											1	1	1	1
Mooringsport (3)	577												1	1	1
Rodessa (13)	511													1	1
Hosston (7)	449														1
Cotton Valley(3)	320														
Parkwood - Pennington (6)	452														

*A value of 1 expresses the means of the two formations are the same with 95% confidence, and a value of 0 expresses the means are not the same.

**MISB = Mississippi Interior Salt Basin

*Table 7 - A summary of t-tests of ^{228}Ra by geologic formation**

	Mean		Wilcox			Selma		Upper	Lower						Cotton
Basins (# of samples)	**Pci/L**	****MISB**	**Trend**	**Sparta**	**Wilcox**	**Chalk**	**Eutaw**	**Tuscaloosa**	**Tuscaloosa**	**Wash. -Fred.**	**Paluxy**	**Morringsport**	**Rodessa**	**Hosston**	**Valley**
Black Warrior (9)	265	1	1	1	0	1	1	1	1	1	1	1	1	1	1
**MISB (137)	359		1	1	0	0	1	1	1	1	1	1	1	1	1
Wilcox Trend (23)	439			0	1	0	1	1	0	1	1	1	1	1	1
Formations and Groups (# of samples)															
Sparta (3)	190				0	1	0	1	1	1	1	1	1	1	1
Wilcox (20)	466					0	1	1	0	1	1	1	1	1	1
Selma Chalk (10)	118						0	0	0	0	0	1	0	0	0
Eutaw (34)	443							1	0	1	1	1	1	1	1
Upper Tuscaloosa (5)	376								1	1	1	1	1	1	1
Lower Tuscaloosa (30)	292									1	1	1	1	1	1
Washita-Fredrisburg (16)	453										1	1	1	1	1
Paluxy (12)	371											1	1	1	1
Moringsport (3)	828												1	1	1
Rodessa (13)	368													1	1
Hosston (7)	322														1
Cotton Valley(3)	389														
Parkwood - Pennington (6)	358														

*A value of 1 expresses the means of the two formations are the same with 95% confidence, and a value of 0 expresses the means are not the same.

**MISB = Mississippi Interior Salt Basin

Table 8 - A summary of t-tests of Cl^- by geologic formation*

	Mean		Wilcox			Selma		Upper	Lower						Cotton
Basins (# of samples)	**Pci/L**	****MISB**	**Trend**	**Sparta**	**Wilcox**	**Chalk**	**Eutaw**	**Tuscaloosa**	**Tuscaloosa**	**Wash. -Fred.**	**Paluxy**	**Morringsport**	**Rodessa**	**Hosston**	**Valley**
Black Warrior (9)	41.6	0	0	1	0	0	0	0	0	1	1	0	0	0	1
**MISB (137)	97.88		0	0	0	0	0	1	1	1	0	0	1	0	1
Wilcox Trend (23)	62.47			1	0	0	0	0	0	1	0	0	0	1	1
Formations and Groups (# of samples)															
Sparta (3)	21.15				1	0	0	0	0	0	0	0	0	0	1
Wilcox (20)	66.44					0	0	0	0	0	0	0	0	0	1
Selma Chalk (10)	52.58						0	0	0	0	0	0	0	0	1
Eutaw (34)	85.11							1	0	0	0	0	1	0	1
Upper Tuscaloosa (5)	109.27								1	0	1	0	1	1	1
Lower Tuscaloosa (30)	106.19									1	1	0	1	1	1
Washita-Fredrisburg (16)	117.13										1	0	1	1	1
Paluxy (12)	124.94											1	1	0	1
Moringsport (3)	149.23												0	1	1
Rodessa (13)	103.77													1	1
Hosston (7)	161.35														1
Cotton Valley(3)	151.27														
Parkwood - Pennington (6)	45.62														

*A value of 1 expresses the means of the two formations are the same with 95% confidence, and a value of 0 expresses the means are not the same.

**MISB = Mississippi Interior Salt Basin

Table 9 - A summary of t-tests of Ba^{2+} by geologic formation*

	Mean		Wilcox			Selma		Upper	Lower						Cotton
Basins (# of samples)	**Pci/L**	****MISB**	**Trend**	**Sparta**	**Wilcox**	**Chalk**	**Eutaw**	**Tuscaloosa**	**Tuscaloosa**	**Wash. -Fred.**	**Paluxy**	**Morringsport**	**Rodessa**	**Hosston**	**Valley**
Black Warrior (9)	112	1	1	0	1	0	0	0	0	1	1	1	0	1	1
**MISB (137)	54		0	1	0	0	0	1	0	1	1	1	1	1	1
Wilcox Trend (23)	115			0	1	0	0	0	0	1	1	1	0	1	0
Formations and Groups (# of samples)															
Sparta (3)	48				1	0	1	1	1	0	1	1	1	1	1
Wilcox (20)	123					0	0	0	0	1	1	1	0	1	0
Selma Chalk (10)	16						1	1	1	0	0	1	1	1	1
Eutaw (34)	30							1	1	0	1	1	1	1	1
Upper Tuscaloosa (3)	31								1	0	1	1	1	1	1
Lower Tuscaloosa (30)	31									0	1	1	1	1	1
Washita-Fredrisburg (16)	129										1	1	0	1	0
Paluxy (12)	127											1	1	1	1
Moringsport (3)	139												1	1	1
Rodessa (13)	41													1	1
Hosston (7)	51														1
Cotton Valley(3)	33														
Parkwood - Pennington (6)	128														

*A value of 1 expresses the means of the two formations are the same with 95% confidence, and a value of 0 expresses the means are not the same.

**MISB = Mississippi Interior Salt Basin

*Table 10 - A summary of t-tests by formation, Ba^{2+}, Cl^-, ^{226}Ra, ^{228}Ra, and TDS**

		Wilcox			Selma		Upper	Lower						Cotton
Basins (# of samples)	****MISB**	**Trend**	**Sparta**	**Wilcox**	**Chalk**	**Eutaw**	**Tuscaloosa**	**Tuscaloosa**	**Wash. - Fred.**	**Paluxy**	**Morringsport**	**Rodessa**	**Hosston**	**Valley**
Black Warrior (9)	3	3	4	2	2	2	2	2	4	4	3	2	3	5
**MISB (137)		2	2	1	0	2	5	2	5	3	4	5	3	5
Wilcox Trend (23)			2	4	2	1	2	1	4	3	3	2	4	4
Formations and Groups (# of samples)														
Sparta (3)				2	2	1	2	2	1	2	2	2	2	5
Wilcox (20)					1	2	2	1	3	3	3	2	3	4
Selma Chalk (10)						2	1	2	0	0	4	2	2	4
Eutaw (34)							4	1	2	3	4	5	3	5
Upper Tuscaloosa (5)								4	3	4	4	5	4	5
Lower Tuscaloosa (30)									4	4	4	5	5	5
Washita-Fredrisburg (16)										4	4	4	4	4
Paluxy (12)											5	5	4	5
Moringsport (3)												4	5	5
Rodessa (13)													5	5
Hosston (7)														5
Cotton Valley(3)														
Parkwood - Pennington (6)														

*The numbers corresponds to the addition of 1's and 0's from other tests. A value of 5 says for all of the above constituents tested, their means are the same at a 95% confidence level. Areas in blue area areas with high values. Final groups by geologic formation were picked from these areas.

**MISB = Mississippi Interior Salt Basin

Table 11 - ANOVA summaries of populations by geologic formation and producing field*							
	P-value ^{226}Ra	P-value $BaSO_4$	P-value Ba	P-value ^{228}Ra	P-value SO_4	P-value TDS	P-value Cl
Total							
Formation	Reject	Reject	Reject	Reject	Reject	Reject	Reject
Field	Reject	Reject	Reject	Reject	Reject	Reject	Reject
Subgroups Formation							
Wash. - Fred.	Accept	Accept	Accept	Accept	Accept	Accept	Reject
U. Tusc. - L. Tusc.	Reject	Accept	Accept	Reject	Accept	Accept	Accept
Subgroups - Fields							
Group A	Accept	Reject	Reject	Accept	Accept	Reject	Accept
Group B	Accept	Accept	Accept	Accept	N/A	Accept	Accept
Group C	Accept	Reject	Reject	Accept	Accept	Reject	Accept
Group D	Accept	Accept	Accept	Accept	Accept	Accept	

* This table was used to select the final groups to test for spatial continuity. Accept says there is a 95% probability that the means in that group are the same, and reject says that the means are not the same with a 95% probability. The field subgroups are defined in the following text.

^{226}Ra vs. Cl^-

Several relationships have been examined based on previous published work. The relation between ^{226}Ra and chloride concentration is strong along the Gulf Coast as reported by Kraemer and Reid (1984) and a relation does exists in Texas as reported by Fisher, and therefore is significant for this study (Fisher, 1995; Kraemer and Reid, 1984). Samples with elevated levels of ^{226}Ra (>100pCi/L) also displayed elevated levels of chloride (>20g/L). Figure 3 shows four quadrants, two white and two shaded. Ninety-four percent of samples follow the trend identified by Fisher and lie in the shaded area having elevated levels of both ^{226}Ra and Cl^- or neither (Fisher, 1998). Twelve out of 207 samples fall in the white quadrants having only

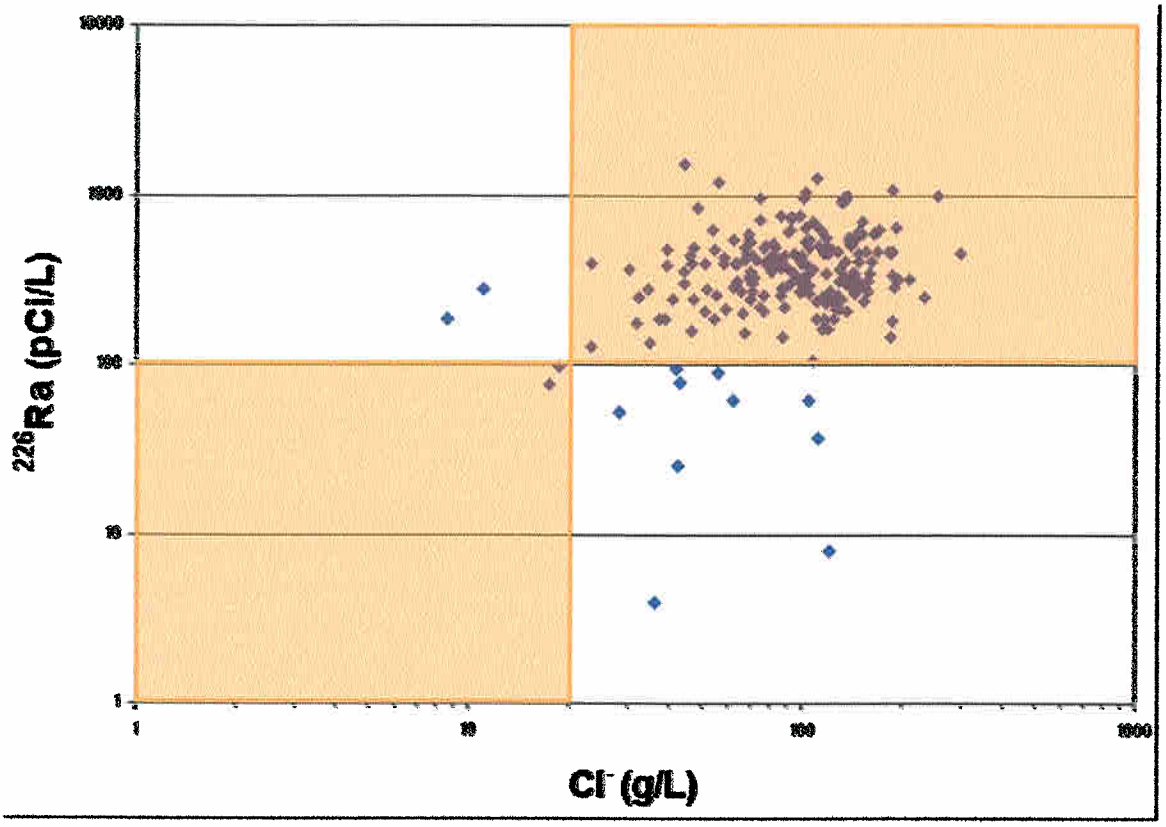


Figure 3 - The relation between ^{226}Ra and Cl^- concentration (g/L) for well producing in Mississippi. Four quadrants, two shaded and two not, show 12 out of 207 samples fall in the shaded quadrant having only elevated levels of either ^{226}Ra or Cl^-, and therefore do not follow the trend of elevated ^{226}Ra (100pCi/L) all have high Cl^- concentration (>20g/L); 94.2% of samples follow the trend and lie in the blue area having elevated levels of both ^{226}Ra and Cl^- or neither.

elevated levels of either ^{226}Ra or Cl^-, and therefore do not follow this trend. The relationship between ^{226}Ra and Cl^- implies there is an association between salinity and NORM occurrence.

^{226}Ra vs. ^{228}Ra

A high coefficient of determination ($R^2 = 0.96$) between ^{226}Ra and ^{228}Ra was found by Fisher indicating the results of one isotope can be extrapolated to find the other (Fisher, 1995; 1998). Hayter (2000) defines R^2, or the coefficient of determination, as the proportion of the total variability in a dependent variable accounted for by the regression line. Higher values of R^2 usually indicate that the data points are closer to the regression line. The results of linear regression analysis performed on the first set of data for Mississippi, 212 samples taken between the years 1998 to 2000, produces an R^2 value of 0.54, significantly different from the Texas study (Figure 4). Regression analysis performed on the samples taken in the second sampling group (collected in 2002) has a slightly higher R^2 value, 0.71 (Figure 5). This dataset only consists of 27 samples approximately 10% of the entire dataset. With the two datasets combined the results display a $R^2 = 0.40$, but this is still significantly different from Fisher's work (Figure 6). This difference in R^2 values is possibly due to the fact that the two isotopes come from two different decay series (^{238}U and ^{232}Th) with different half-lives, therefore one would not expect the two isotopes to decay in a linear manner. Calculations for both ^{226}Ra and ^{228}Ra were done by taking the average of two measurements made in the laboratory. Error analysis revealed that the average percent error associated with ^{226}Ra and ^{228}Ra measurements was 42% and 35% respectively. Such a large error in these measurements may account for the lack of correlation between the two isotopes. This finding is important because both ^{226}Ra and ^{228}Ra will remain independent variables retained in further analysis. Had they been as strongly correlated as Fisher found, it would have been more appropriate to retain only one of the isotopes in analysis.

Data Trends In Formation Geology

While analyzing other relationships in the data such as pH and ^{226}Ra, some clustering of the data based on location and/or geology was observed. Such clustering would suggest the significance of geology on controlling brine chemistry. In an effort to characterize such clustering, three-dimensional plots were created using the most significant variables in the database. A plot of ^{226}Ra, ^{228}Ra and Cl^- concentration separated by formation clearly displays the clustering of data (Figure 7). This clustering by producing formation indicates that chemicals associated with NORM in brines are not an entirely random process and that there are some geologic controls.

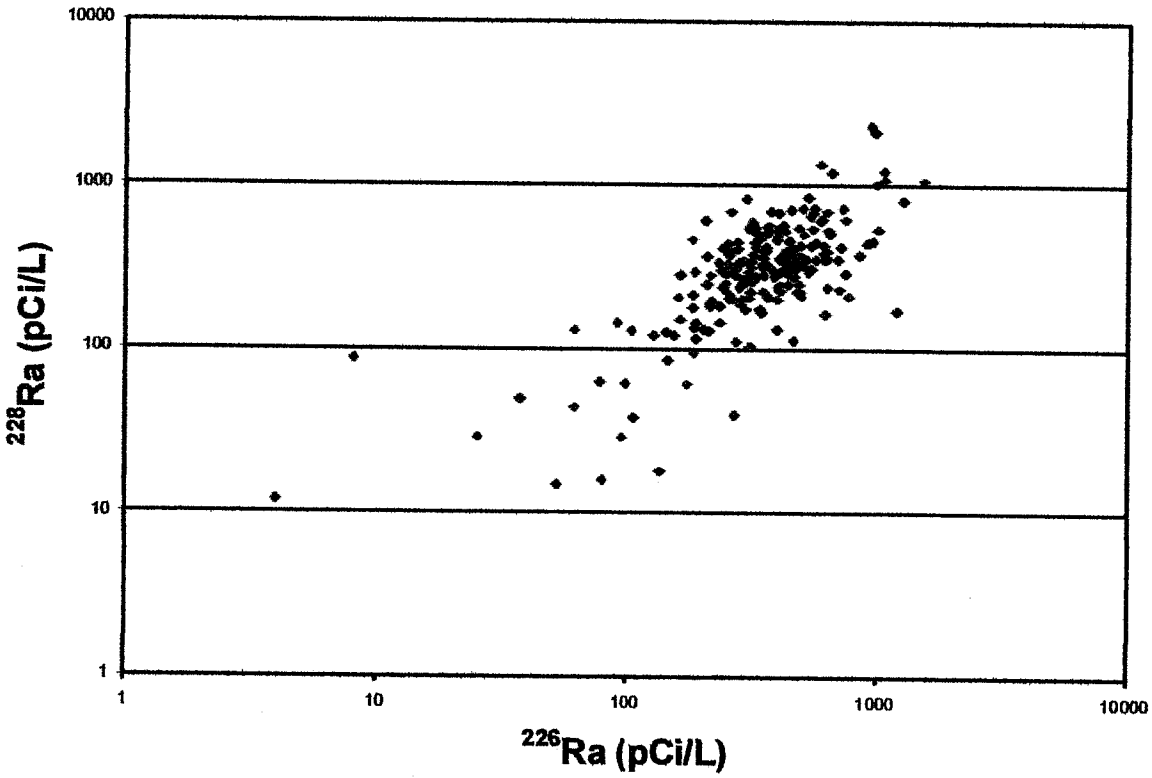


Figure 4 - The relation between ^{226}Ra (pCi/L) and ^{228}Ra (pCi/L) for wells producing in Mississippi and sampled from 1998 through 2000. The coefficient of determination, R^2, in this case is 0.54.

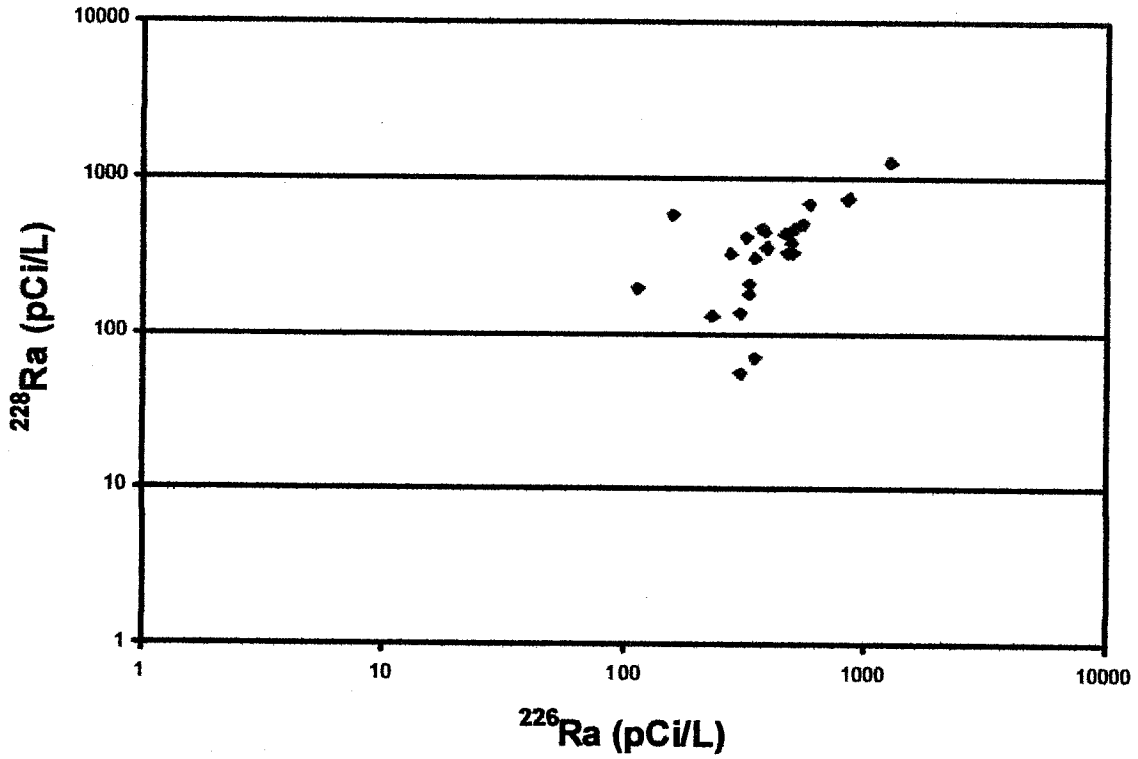


Figure 5 - The relation between ^{226}Ra (pCi/L) and ^{228}Ra (pCi/L) for wells producing in Mississippi and sampled in 2002. The coefficient of determination, R^2, in this case is 0.71.

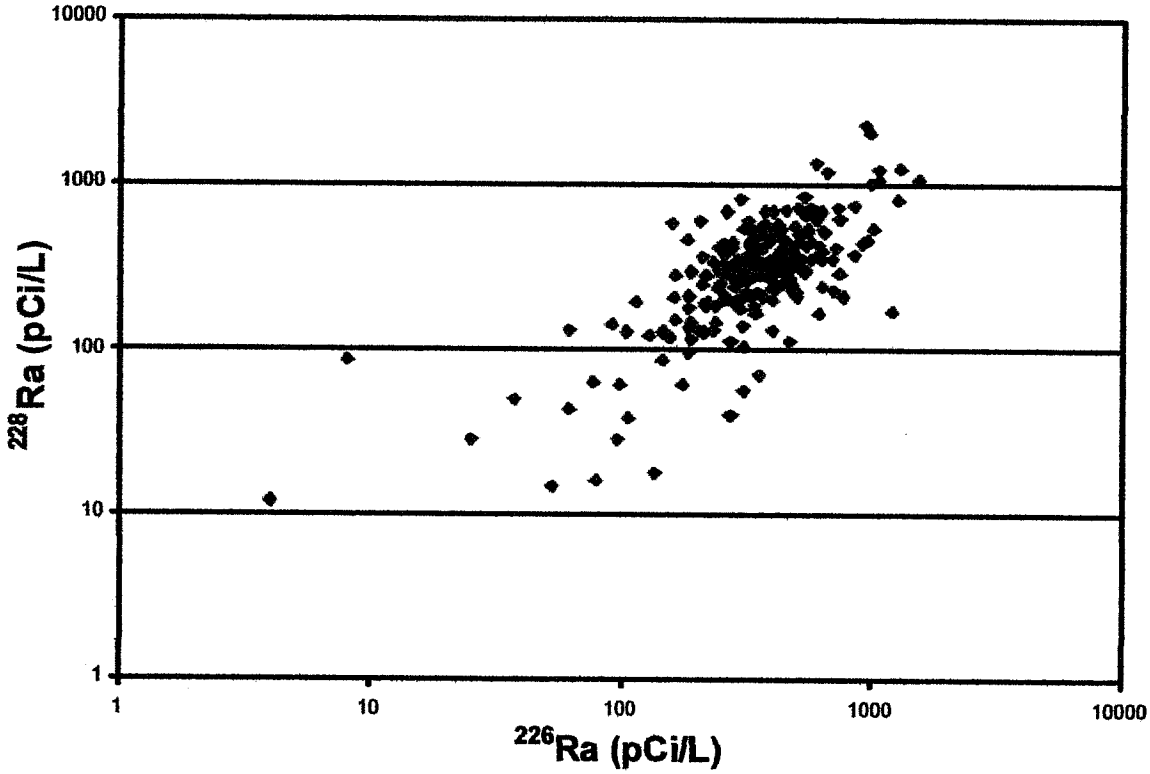


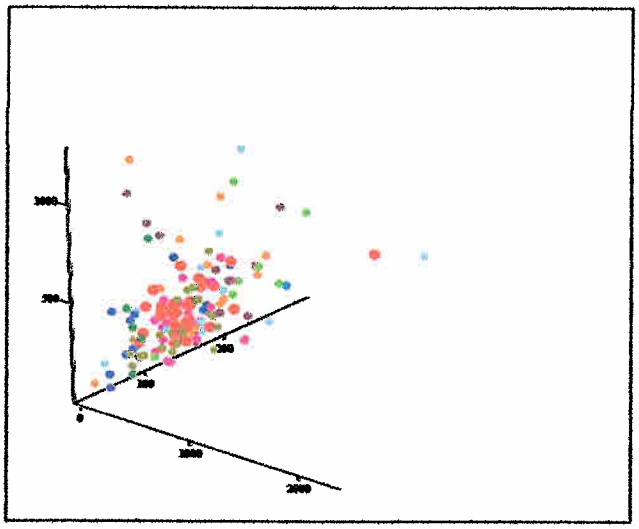
Figure 6 - The relation between ^{226}Ra (pCi/L) and ^{228}Ra (pCi/L) for wells producing in Mississippi, data from two sampling periods were combined. The coefficient of determination, R^2, in this case is 0.71.

Box plots (Figure 8) were also created showing the concentration increase of Cl^- and TDS with depth in order to establish which chemical constituents are most closely associated with the formation of NORM. In Mississippi 93.2% of samples have both Cl^- levels greater than 20g/L and ^{226}Ra activities greater than 100pCi/L, and 85.7% of samples have both TDS greater than 35g/L and ^{226}Ra greater than 200pCi/L. With elevated levels of ^{226}Ra in some part increasing the likelihood of NORM, these plots illustrate once again that there is some geologic and or stratigraphic controls to the system. A boxplot of ^{226}Ra values separated by formation geology can also be used to illustrate the large variation of ^{226}Ra within each geologic formation with only a relatively small amount of variation across all formations. The mean values of ^{226}Ra are similar across all formations.

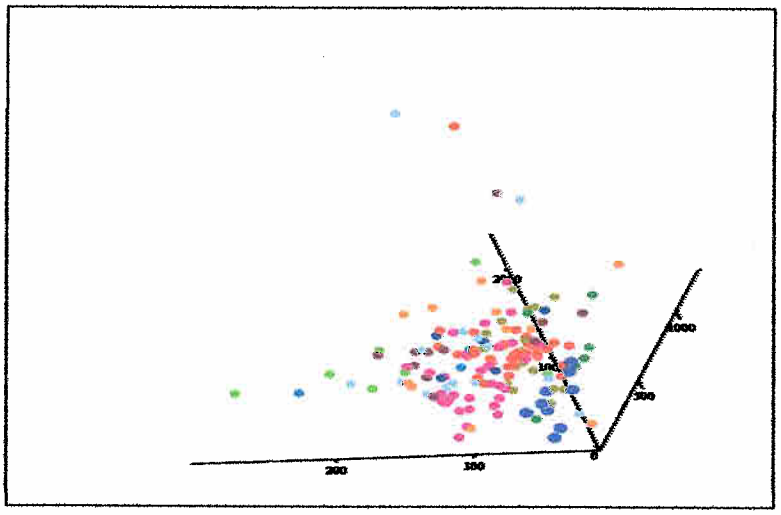
All of the wells sampled in Mississippi are producing from clastic or carbonate sedimentary formations. Brines used for analysis were produced from 18 different, primarily clastic, geologic formations. Of these 18, two formations, the Smackover and Selma Chalk, are carbonate formations. Twelve brine samples were collected from these two carbonate formations. Analyses were conducted to determine if water chemistry in the clastic formations differed significantly from the carbonate formations. Two sample *t*-tests, using major database constituents TDS, ^{226}Ra, ^{228}Ra, Cl, Ba^{2+}, Ca^{2+}, and $BaSO_4$ saturation, were applied to see if the means of the two groups are similar with a 95% confidence. The results of the tests suggest that for many of the major database constituents the mean values are distinctly different. ^{226}Ra, ^{228}Ra, Cl^-, Ba^{2+}, and Ca^{2+} have different means (all with $P < 0.05$). Although most of the major constituents display a difference in mean values, TDS and $BaSO_4$ saturation exhibit similar means. These results suggest that one should expect different brine chemistry when dealing with brines produced from clastic and carbonate formations.

Cl^- Concentration And Depth Of Production

The relation between depth of production and Cl^- concentration was also examined. In the Lower Cretaceous formations of the Mississippi Interior Salt Basin, where a large data set exists, the relation between the depth of production and Cl^- concentration was examined. Linear regression yielded an R^2 value of 0.04 for this entire set of data (Figure 9). In looking at Figure 9, notice the significant difference in the trend of data points producing below 11,000 ft. These data points producing below 11,000 ft were isolated from the rest of the set and regression was applied again only on samples from producing above 11,000 ft. There is a substantial difference in correlation between wells producing to a depth of 11,000 ft with the deeper wells omitted, $r = 0.6$ (Figure 10), suggesting there is a moderate relation between Cl^- concentration and depth of production. Other significant database constituents such as ^{226}Ra and TDS show little to no correlation with depth of production, r values are 6.1×10^{-3} and 0.24 respectively. Unlike Cl^-



(r6a,r8a,cla),(r6b,r8b,clb),(r6c,r8c,clc),(r6d,r8d,cld),(r6f,r8f,clf),(r6g,r8g,clg),(r6h,r8h,clh),(r6i,r8i,cli),(r6k,r8k,clk),(r6l,r8l,cll),(r6m,r8m,clm)



(r6a ,r8a ,cla),(r6b ,r8b ,clb),(r6c ,r8c ,clc),(r6d ,r8d ,cld),(r6f ,r8f ,clf),(r6g ,r8g ,clg),(r6h ,r8h ,clh),(r6i ,r8i ,cli),(r6k ,r8k ,clk),(r6l ,r8l ,cll),(r6m ,r8m ,clm)

Figure 7 - Two views of a 3D plot of ^{226} Ra (x-axis), ^{228} Ra (y-axis), and Cl- concentration (z-axis). Samples from the same formation are shown with the same color. Eutaw Formation samples (red) and Selma Chalk (blue) are clustered, suggesting chemicals associated with NORM are not an entirely random process and there are some geological controls.

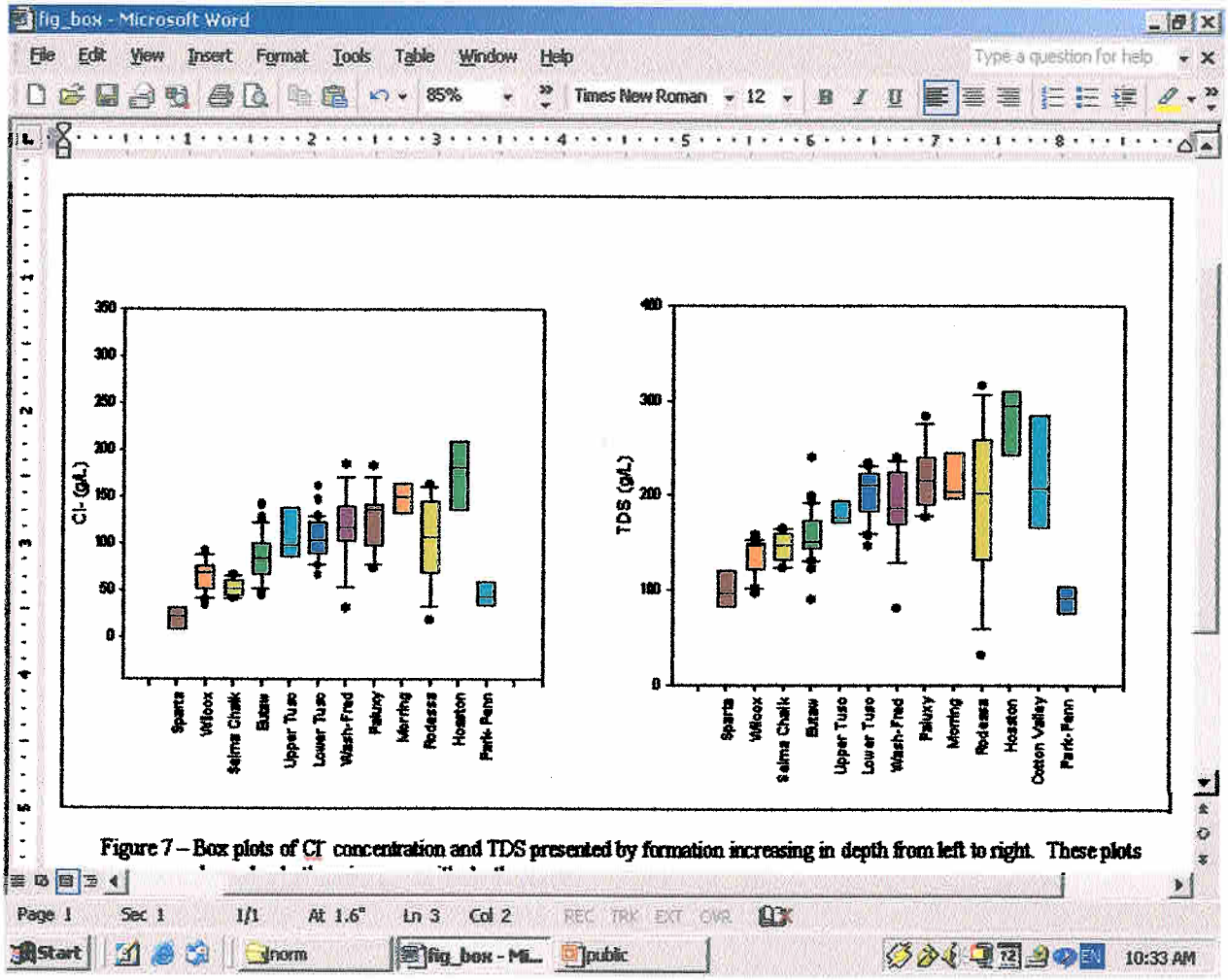


Figure 7 – Box plots of Cl⁻ concentration and TDS presented by formation increasing in depth from left to right. These plots

Figure 8 - Boxplots of Cl^- concentration and TDS presented by formation increasing in depth from left to right. These plots show clearly the increase with depth.

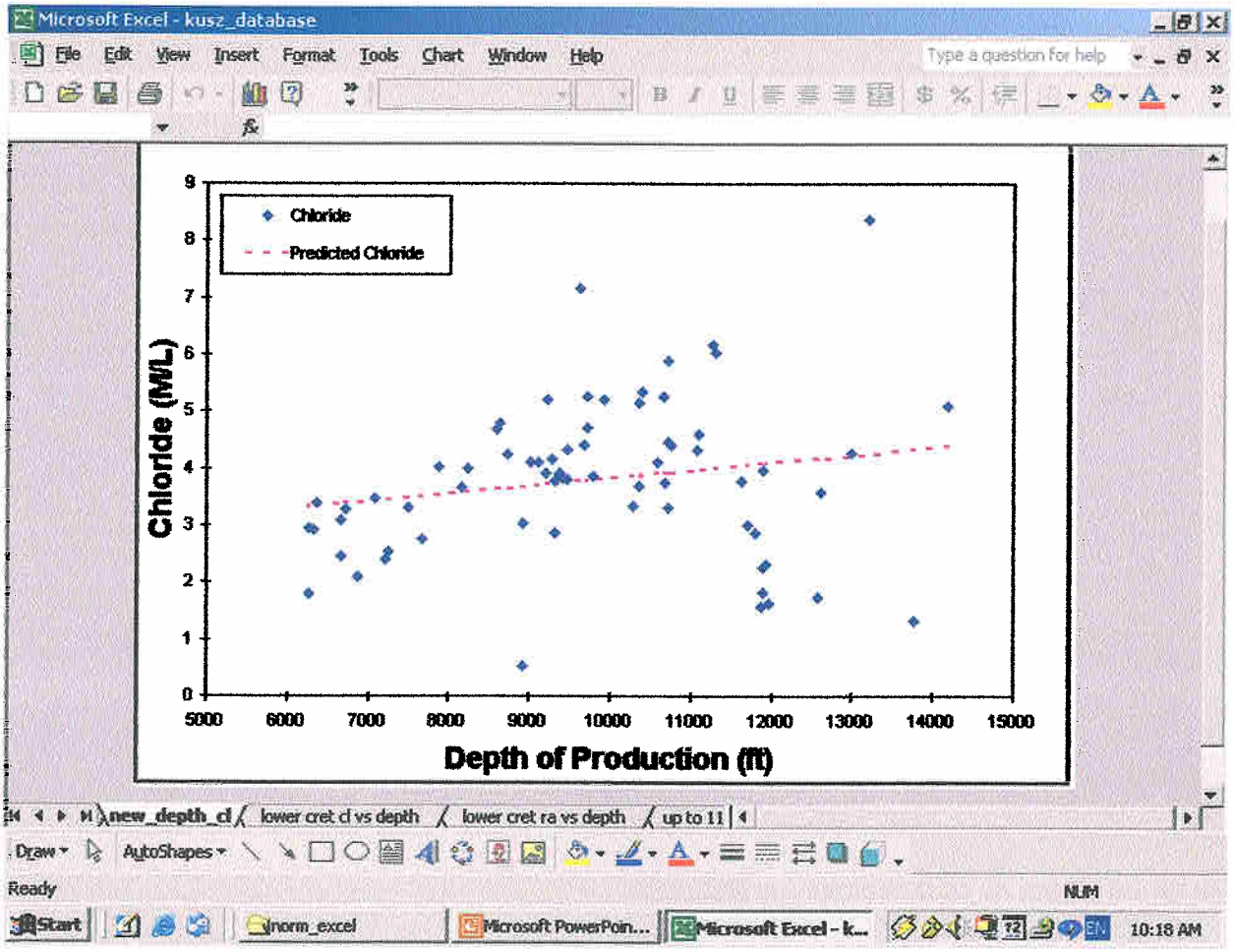


Figure 9 - The relation ($R^2 = 0.04$) between chloride concentration and depth of production for wells producing from Lower Cretaceous age sediments within the Mississippi Interior Salt Basin.

neither has the distinct difference of data values at a particular depth and therefore, was not separated for analysis. This suggests that some brine chemical components such as Cl^- are related to production depth while others do not, helping further describe brines in Mississippi.

Trends Using Structural Geology

Faults identified by structural geology studies were used to separate production data within a field to see if populations of data were distinctly different. Heidelburg and Tinsley Fields were identified for this analysis. These fields were chose due to the relatively large number of sample locations and the presence of faults dividing the fields. Tinsley Field consists of 14 samples separated into two groups, *i.e.* the east group and west group. The grouping is based on a system of faults running northwest/southeast to north/south (Figure 11). Two sample *t*-test were conducted to examine whether the two populations had similar means using the major chemical constituents in the database: ^{226}Ra, TDS, Cl^-, SO_4^{2-}, and Ba^{2+}. Results from all of theses tests indicate the two groups (east and west) have similar means with a 95% confidence and therefore cannot be considered as separate groups (*P* values = 0.15, 0.99, 0.42, 0.31, and 0.87, respectively). Figure 9 shows the wells sampled from Tinsley Field having a definite north/south trend. Regression analysis was performed using the major constituents in the database, as previously mentioned, and the y-component of the sample location. This procedure would indicate any linear relationship between the data and location within the field. Results from the regression produces R^2 values for TDS, Cl^-, and SO_4^{2-} of 0.0035, 0.041, and 0.033, respectively. Regression performed for ^{226}Ra and Ba^{2+} show a substantially higher R^2 value, *i.e.* 0.268 and 0.239 respectively. Although these R^2 values are not necessarily high, they do indicate there is some correlation between ^{226}Ra, Ba^{2+}, and the location of production within Tinsley Field.

A similar analysis was conducted in Heidelberg Field, and, as in Tinsley Field, the samples were divided into an east and west group. The east group samples were taken from wells that are producing directly adjacent to a fault located in the eastern portion of Heidelberg field (Figure 12). The western group samples are located approximately two miles from this fault. These two groups were compared using two sample *t*-tests and the same chemical constituents as Tinsley field, ^{226}Ra, TDS, Cl^-, SO_4^{2-}, and Ba^{2+}. Like the results obtained in Tinsley Field, most of the constituents tested did display similar means with a 95% confidence and therefore cannot be considered as separate populations (*P* values = 0.59, 0.08, 0.32, 0.04, and 0.29, respectively). One constituent, SO_4^{2-} did have a significant difference in the means. Twenty-one of the 30 samples were below the detection limit, so due to the low number of points analyzed and the results of the other *t*-tests, this result does not change the overall outcome of the analysis.

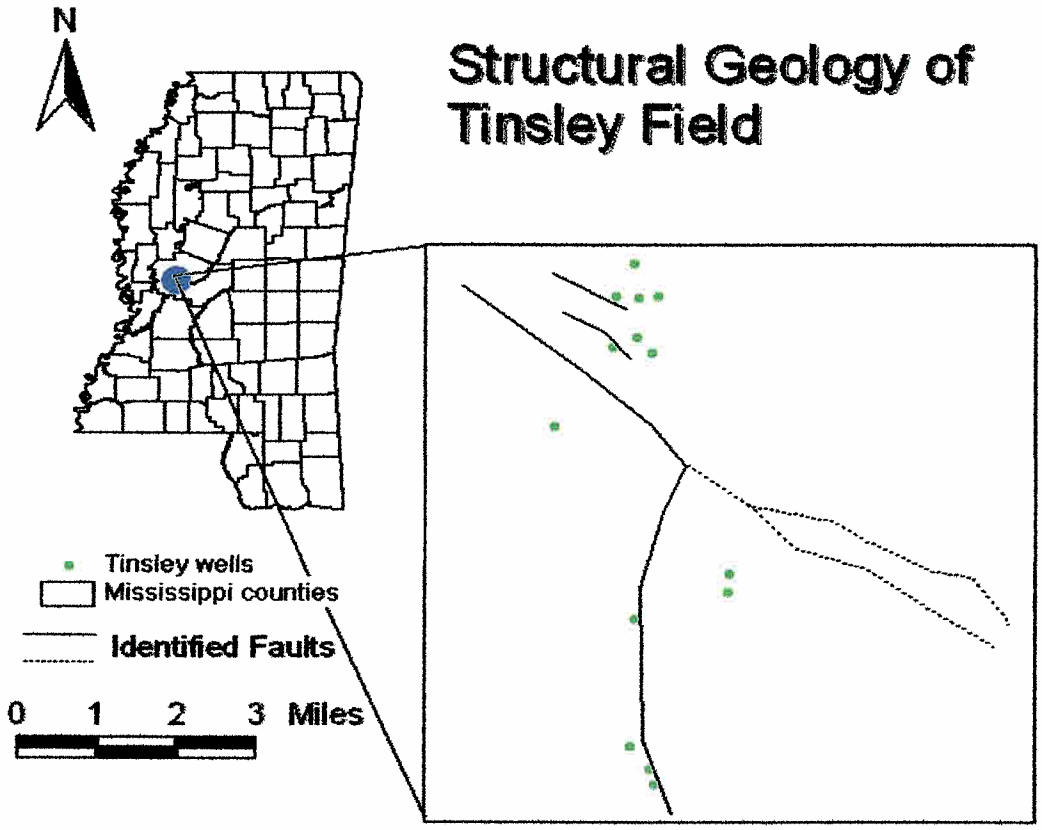


Figure 10 - The Tinsley Field data set consists of 14 samples separated into two groups, east group and west group, divided by a system of faults trending north to northwest (modified from Mississippi Geological Society, 1957).

d

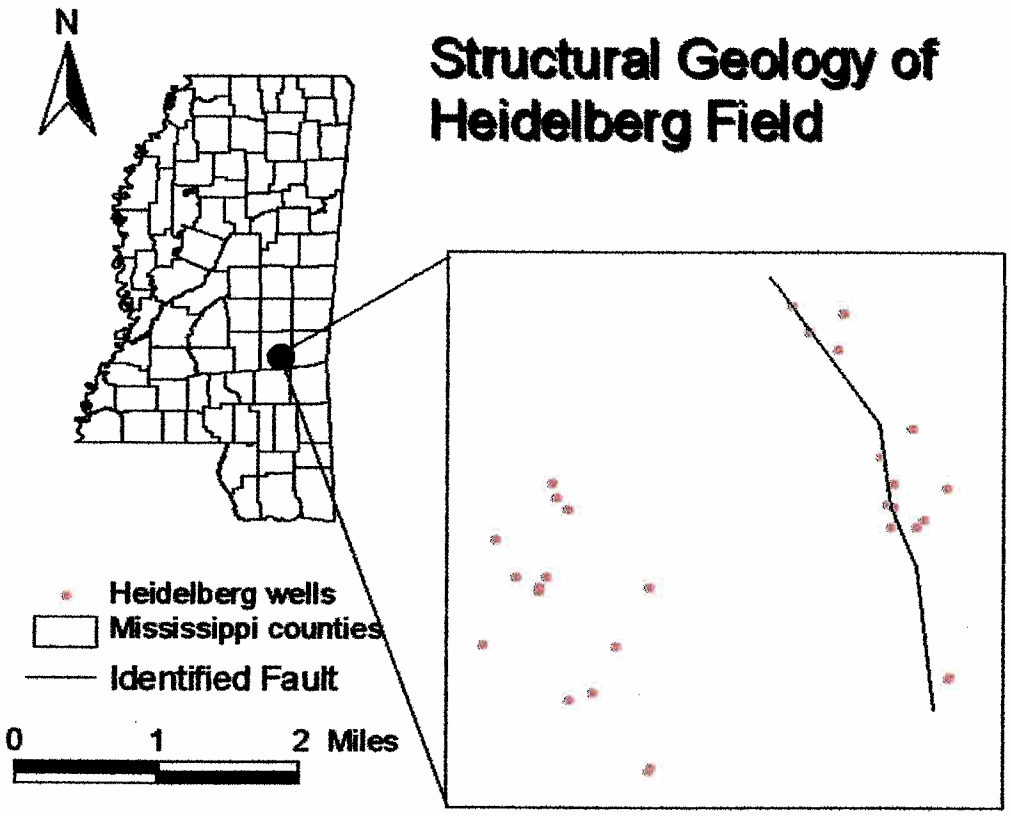


Figure 11 - The Heidelberg Field data set consists of 28 samples separated into two groups, east group and west group, divided by a fault trending north to northwest (modified from Mississippi Geological Society, 1957).

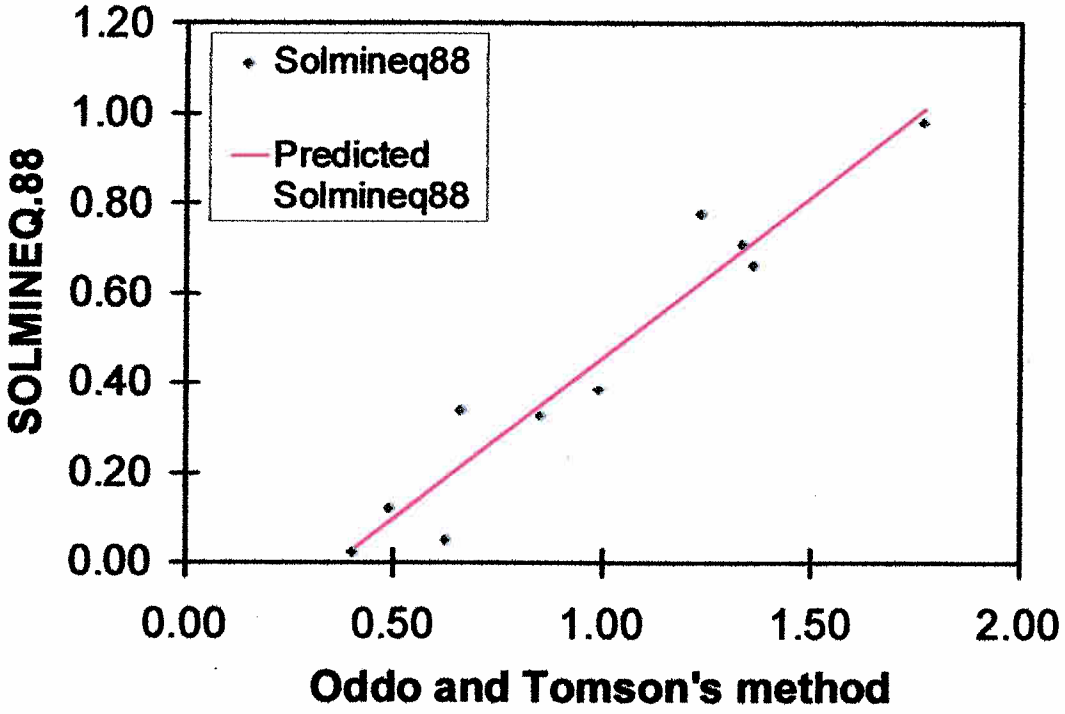


Figure 12 - The relation ($R^2 = 0.93$) between Oddo and Tomson's method for calculating $BaSO_4$ saturation and SOMINEQ.88 using Pitzer's equations.

Due to the combination of results from Tinsley and Heidelberg Fields, samples cannot be segregated or distinguished based solely upon their location relative to structural features, mainly faults, within a field. In Tinsley Field, there does seem to be only a weak correlation between location within the field and some elements, ^{226}Ra and Ba^{2+}. There seems to be no trend suggesting the relation between faulting and brine chemistry.

Comparison Of $BaSO_4$ Saturation Calculations

The $BaSO_4$ saturation was calculated using two methods, Oddo and Tomson's (1994) saturation index equation for common sulfate mineral scales and using SOLMINEQ.88, a geochemical software package. Oddo and Tomson's method was the primary method for calculating saturation, while SOLMINEQ.88 had a limited value as an alternative method to test the results of Oddo and Tomson's method. To compare the results of the two methods, a subset of ten samples, five samples with the lowest values of Ba^{2+} and five samples with the lowest values of SO_4^{2-}, were compared by the two methods (Figure 13). Regression analysis was conducted to identify if the two methods were correlated. A $R^2 = 0.93$ was calculated suggesting the methods for estimating saturation are well correlated but note that the slope of the regression line is not 1. The regression line is instead 0.61, which indicates that the SOMINEQ.88 program using Pitzer's equations is on average 61% lower than Oddo and Tomson's method. Both methods produce $BaSO_4$ saturation values greater than 0 for all samples, suggesting the sample is supersaturated with respect to $BaSO_4$ and precipitation is likely, but Oddo and Tomson's method is more than double the SOLMINEQ.88 value.

Variograms Using ^{226}Ra, Cl, Ba And $BaSO_4$ Saturation

Using the relatively homogeneous groups identified in the formation analysis and in the field-by-field analysis, variograms or semivariograms were created using radium activity, chloride concentration, barium, and barium sulfate saturation. If a spatial relationship were to exist, wells located adjacent to one another should be more similar, or have a smaller variance than wells located some distance apart. If spatial continuity exists, variograms can be used to make predictions at unknown locations by using data from known data points. Variograms were created using homogeneous populations previously described in the methodology section:

- Producing Formations
  - Group 1 - Washita-Fredericksburg, Paluxy, and Mooringsport,
  - Group 2 - Upper Tuscaloosa and Lower Tuscaloosa,
  - Group 3 - Eutaw,

- Field of Production / Trend
  - Heidelberg,
  - Puckett
  - Martinville, and the
  - Wilcox Trend.

Looking at the variograms created using populations developed by formation, there is little to no spatial relationship when analyzing ^{226}Ra activity and Cl^- concentration. Figure 14, a variogram using ^{226}Ra and Group 1 shows a typical example of these variograms. A dataset with spatial continuity would yield a variogram substantially different from that found for ^{226}Ra. In fact, the results depicted in Figure 14 suggest wells located farther away are more alike than wells close together. The variability between two the samples is high, suggesting a lack of spatial continuity. This variogram structure could be attributed to measurement errors, estimation errors, non-ideal sample locations, or an insufficient number of samples. When variograms were created using Ba^{2+} and $BaSO_4$ saturation some spatial continuity was evident. Figures 15 and 16, Group 1 and Group 2 respectively, are variograms using Ba^{2+} and $BaSO_4$ saturation displaying a more typical variogram structure for data with spatial continuity. These graphs show some spatial continuity with an increase in variability as the distance between samples increases.

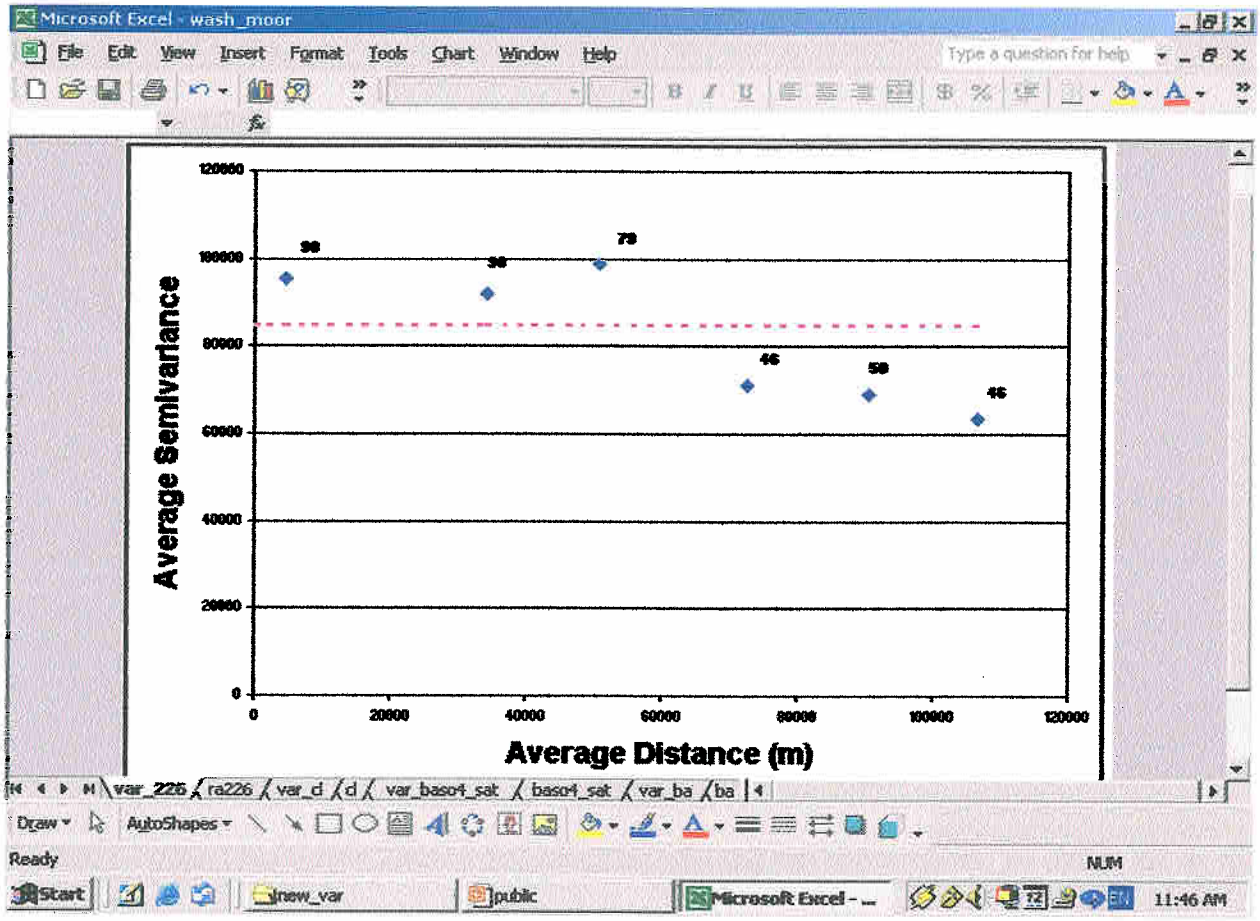


Figure 13 - A variogram of ^{226}Ra and Group 1 - Washita-Fredericksburg, Paluxy, and Mooringsport Formations displaying the typical structure of variograms created using ^{226}Ra and Cl^- concentration and groups created by formation geology. The graph shows points at various distances and the semivariance at those points. The number of pairs of points is also displayed next to each data point. The variability between two samples is high, suggesting a lack of spatial continuity.

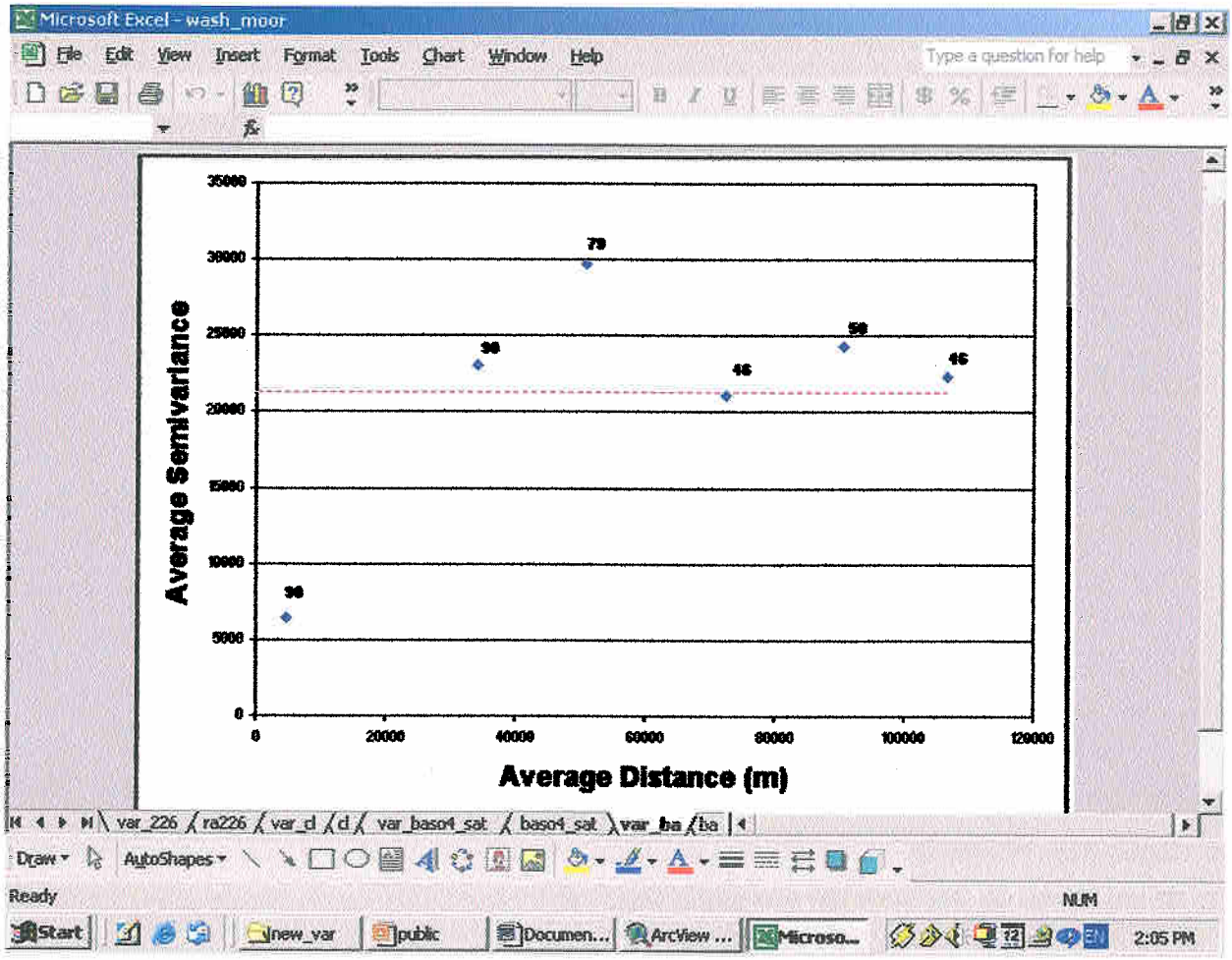


Figure 14 - A variogram of Ba^{2+} and Group 1 - Washita-Fredericksburg, Paluxy, and Mooringsport Formations displaying a more ideal variogram with variability increasing with distance. This graph suggests there is significant spatial continuity between Group 1 and Ba^{2+}.

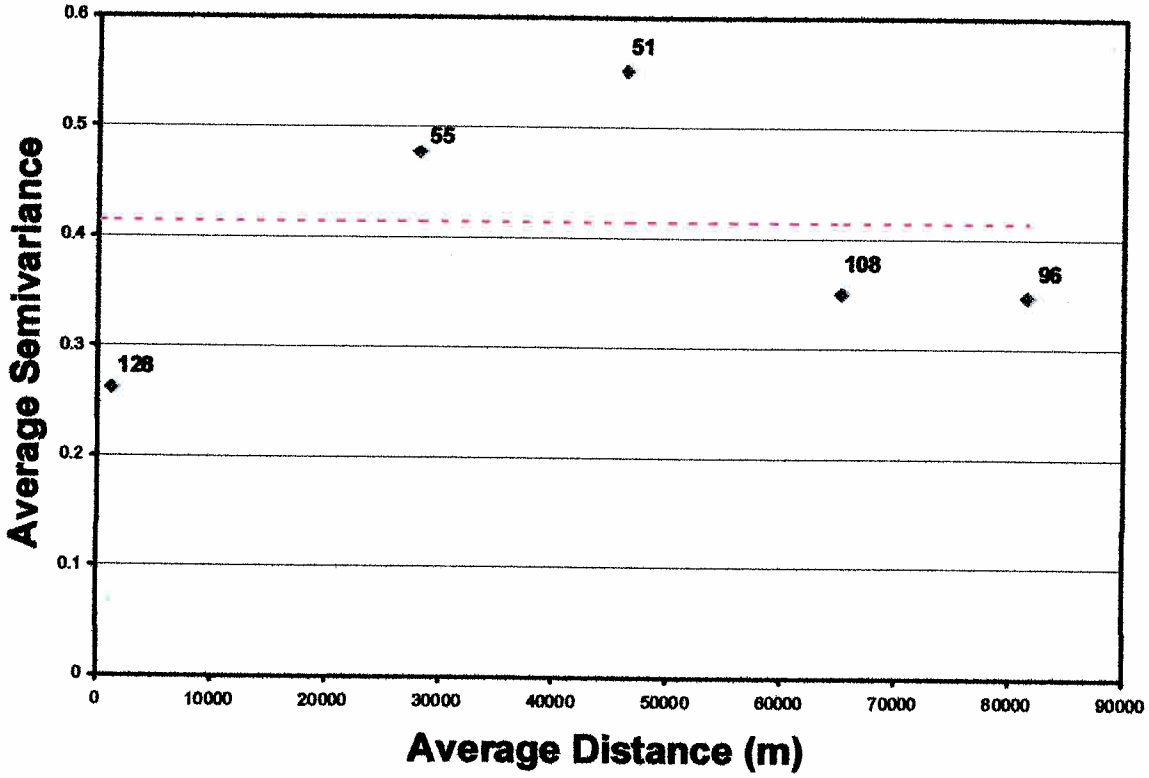


Figure 15 - A variogram of $BaSO_4$ saturation and Group 2 - Upper Tuscaloosa and Lower Tuscaloosa Formations displaying a more ideal variogram with variability increasing with distance. This graph suggests there is some spatial continuity between Group 2 and $BaSO_4$ saturation.

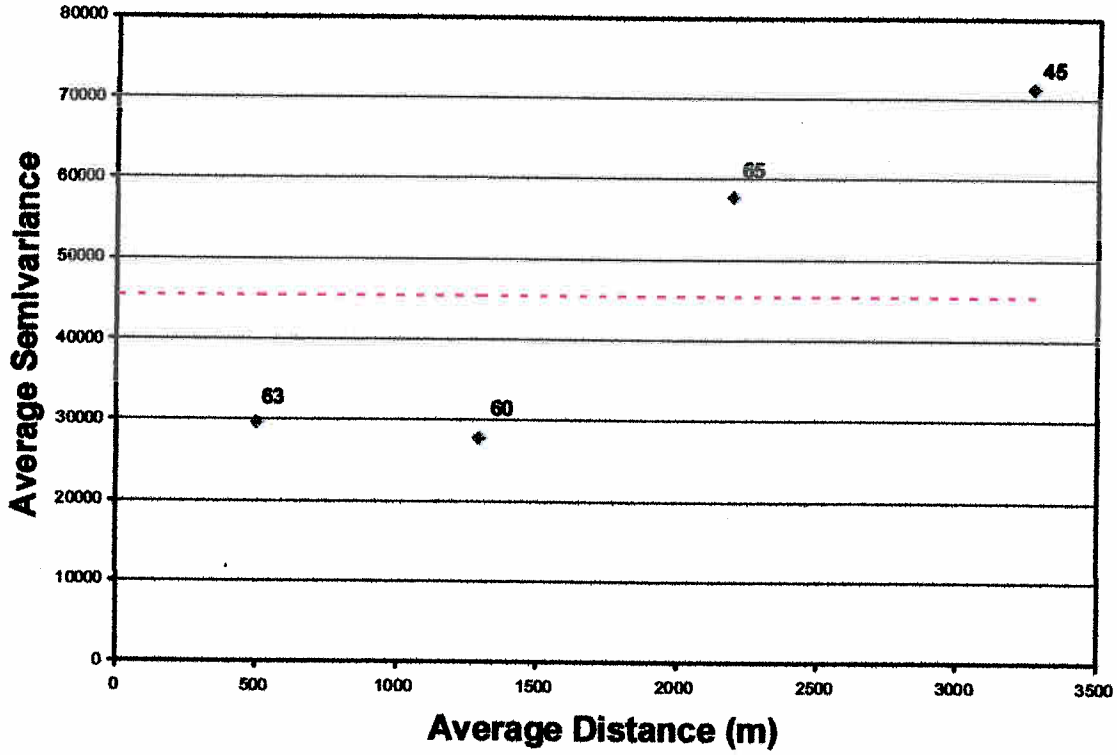


Figure 16 - A variogram of ^{226}Ra in Heidelberg Field displaying a more ideal variogram with variability increasing with distance. This graph suggests there is some spatial continuity in Heidelberg Field and ^{226}Ra.

The results for variograms created using ^{226}Ra, Cl concentration, and $BaSO_4$ saturation and producing field including the Wilcox Trend group, as a whole, show better spatial continuity than the producing formation groups. Ba^{2+} was also analyzed, and unlike the groups created from geologic formations, there seems to be some spatial continuity within the Heidelberg Field. Variograms created for Heidelberg Field using ^{226}Ra, Cl, and $BaSO_4$ saturation display some spatial continuity (Figures 17, 18, and 19). Although the spatial continuity results are better from field of production, namely Heidelberg Field, than producing formation, most of the variograms still show little to no spatial continuity. Figure 20, for example, is a variogram of the Wilcox Trend using Cl. This example illustrates well how many of the variograms created for field of production exhibit little to no spatial continuity. Samples adjacent to one another display the same variability as samples separated by a large distance.

When spatial continuity exists, other geostatistical methods can be employed to make predictions based on known observations. Results from analysis using formation geology and field of production suggest wells located relatively close to one another have little to no statistical relation. Only wells of the Heidelberg Field displayed spatial continuity. The sampling within Heidelberg Field was on a much more detailed scale than most other sampling around the state. The implications for regulatory agencies and operators are that ^{226}Ra activity, Cl concentration, Ba^{2+} concentration, and $BaSO_4$ saturation will be random, both statewide and across fields. Only detailed investigations within individual fields may produce trends that can by used in order to make predictions with that particular field.

With the exception of Ba^{2+} using Group 1 (Washita-Fredericksburg, Paluxy, Mooringsport), $BaSO_4$ saturation using Group 2 (Upper Tuscaloosa and Lower Tuscaloosa), and ^{226}Ra, Cl, and $BaSO_4$ saturation in the Heidelberg Field, variograms using the major constituents and populations created from geologic formation and field of production show little to no spatial relationships. Fisher reported that due to the relatively short half-lives, geological speaking, of ^{226}Ra and ^{228}Ra and the typical flow rates of basinal brines before (cm/yr) and after (m/yr) production begins, the radium originating from uranium and thorium in the formation must be generated relatively close to the producing well (Fisher, 1995). Therefore, significant changes in radium activity may correspond to lithologic changes in formation geology. The subset of data whose constituents produced the most spatial continuity was Heidelberg Field. The sampling in this particular field was one of the most extensive and on a much more detailed scale than most other groups. This may suggest that spatial continuity may exist only on a very small scale, or on a scale much smaller than was used for most of the sampled wells.

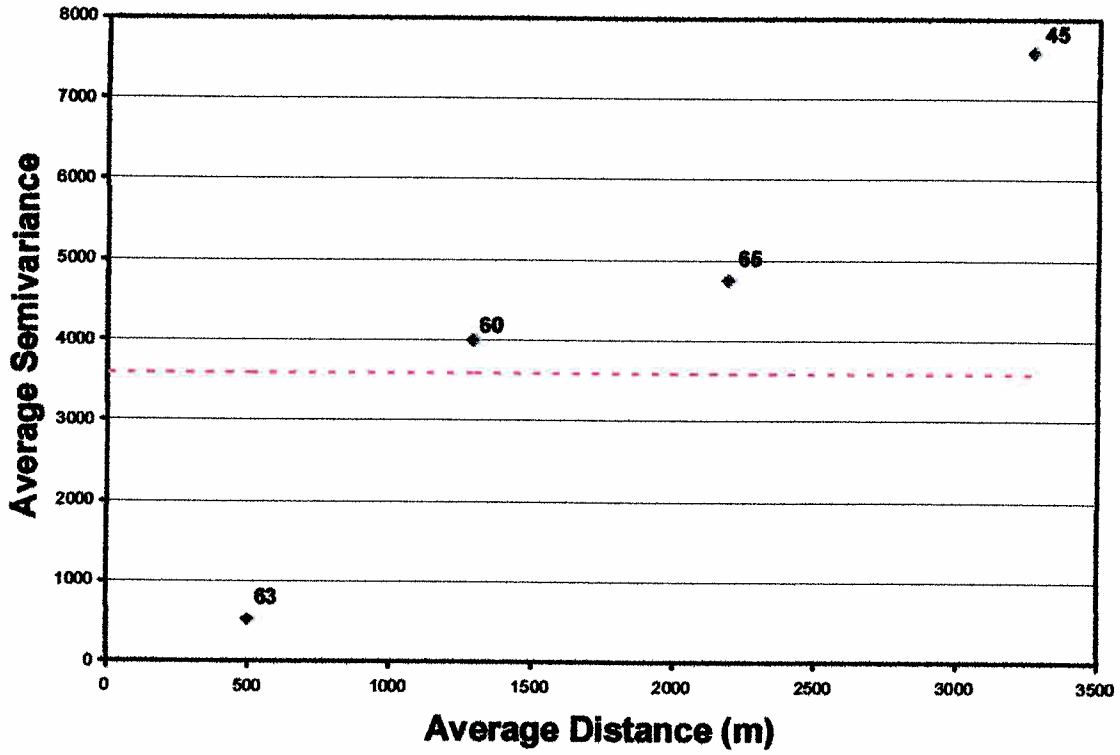


Figure 17 - A variogram of Cl^- concentration in Heidelberg Field displaying a more ideal variogram with variability increasing with distance. This graph suggests there is some spatial continuity in Heidelberg Field and Cl^- concentration.

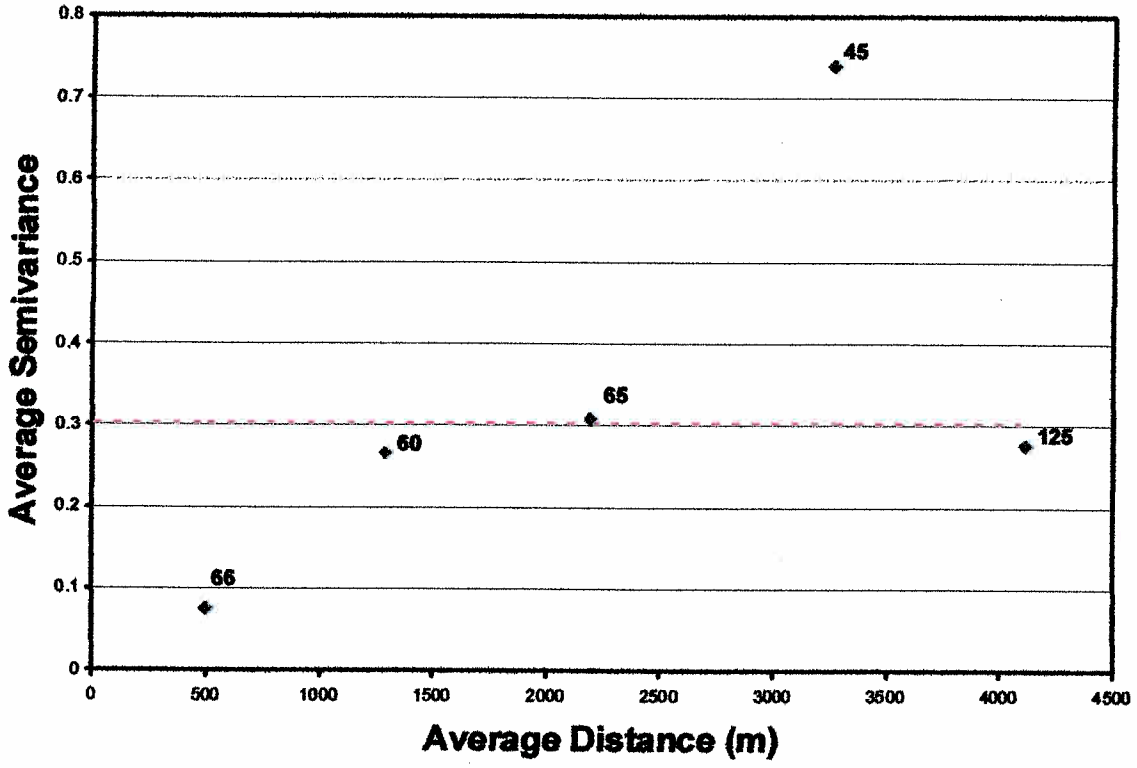


Figure 18 - A variogram of $BaSO_4$ saturation in Heidelberg Field displaying a more ideal variogram with variability increasing with distance. This graph suggests there is significant spatial continuity in Heidelberg Field and $BaSO_4$ saturation.

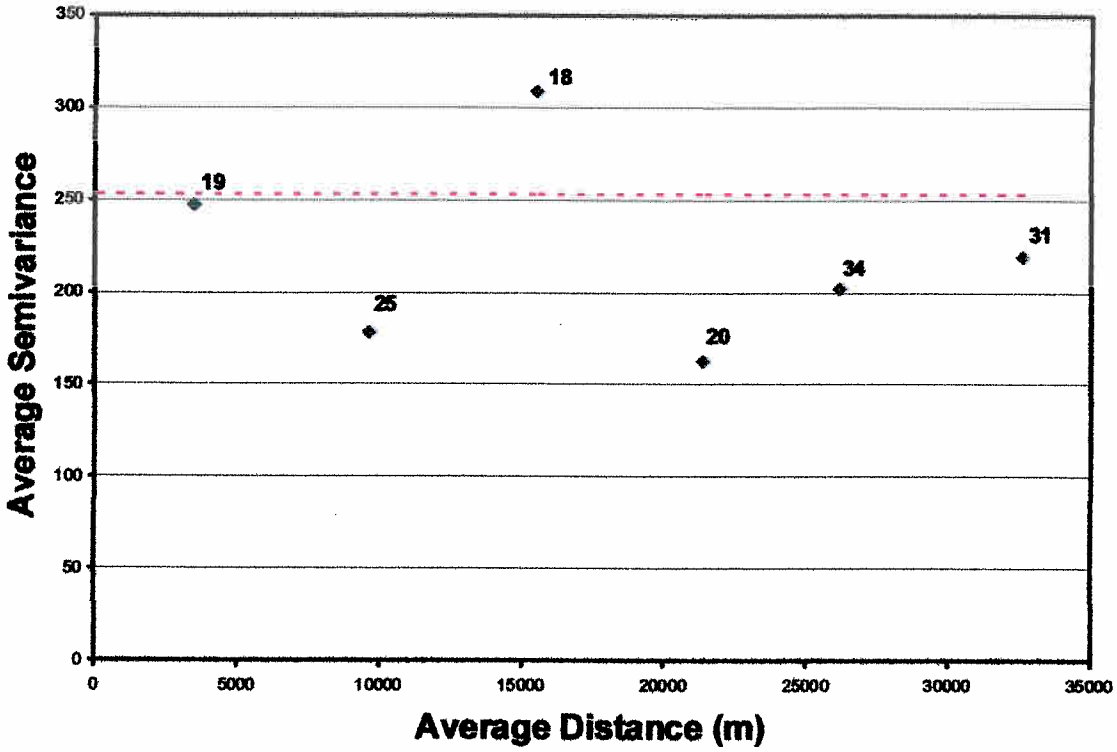


Figure 19 - A variogram of Cl^- concentration and Wilcox Trend samples displaying the typical structure of variograms created using field of production. Little to no spatial continuity exists in most cases.

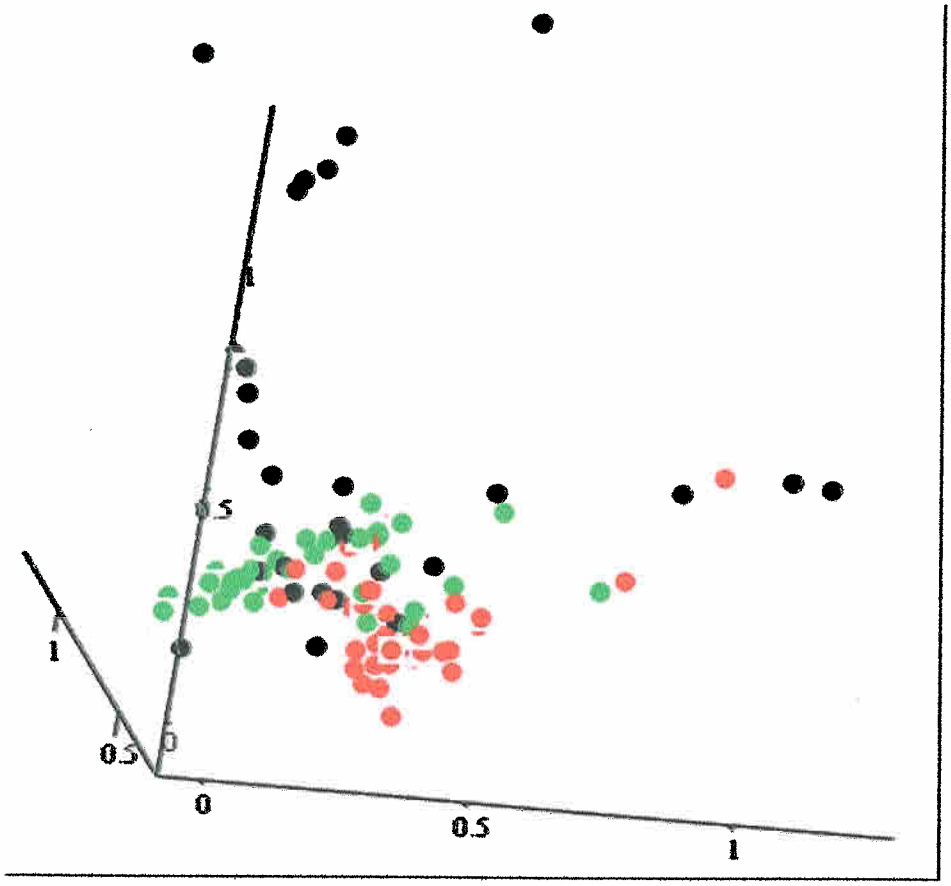


Figure 20 - A three dimensional plot showing the geologic formation groups plotted in the three principal directions as determined by PCA. Looking at the three groups together, it is obvious that the brine samples do cluster together to some extent.

The measured ^{226}Ra was calculated by taking the average of two measurements made in the laboratory. Error analysis revealed that the average normalized error associated with these ^{226}Ra measurements was 0.42 or 42%. Such a large error in ^{226}Ra might account for most of the groups not displaying spatial continuity. On the other hand, very little spatial continuity exists between any groups and Cl^- or Ba^{2+}, and error analysis reveals these constituents have a relatively small amount of error. An average normalized error of 0.02 or 2% was calculated for Cl^-, and a percent difference of 0.0081 or 0.81% was calculated for ten duplicate samples measured for Ba^{2+}. These results emphasize the significance of sampling interval or sampling scale.

Results From Principal Component Analysis

The brine chemistry measurements that were used in the principal component analysis (PCA) included TDS, ^{226}Ra, ^{228}Ra, Cl^-, Ba^{2+}, and $BaSO_4$ saturation. The samples included in this PCA application were from the three groups representing different geologic formations. The variance-covariance matrix that resulted from the PCA application involving the 114 brine samples was

$$V := \begin{pmatrix} 0.03111012 & -0.000565203 & 0.005018482 & 0.015732594 & -0.003633812 & 0.023747484 \\ -0.000565203 & 0.031383941 & 0.014119225 & 0.003192571 & 0.013330664 & -0.002635206 \\ 0.005018482 & 0.014119225 & 0.019929146 & 0.003889411 & -0.004167257 & -0.004170371 \\ 0.015732594 & 0.003192571 & 0.003889411 & 0.026081135 & -0.004692252 & 0.011727511 \\ -0.003633812 & 0.013330664 & -0.004167257 & -0.004692252 & 0.044946458 & 0.008242602 \\ 0.023747484 & -0.002635206 & -0.004170371 & 0.011727511 & 0.008242602 & 0.048485765 \end{pmatrix}$$

$[V] =$

The eigenvalues associated with this matrix are the principal components in this case, which were

$$b = \begin{pmatrix} 0.011 \\ 5.747 \times 10^{-3} \\ 0.016 \\ 0.042 \\ 0.055 \\ 0.073 \end{pmatrix}.$$

using the order of variables listed above. The first three principal components (the largest values shown as the bottom three values in the vector above) were selected for further consideration. Together these three components account for 83.8 % of the total variation within the data set. Using the components of the eigenvectors associated with each of these principal components, we mapped all 114 samples into the space defined by the three principal directions. Using a different symbol for each geologic formation group, it was possible to determine if brine samples from the same group were clustered together in this sample space. Looking at the three groups together, it is obvious that the brine samples cluster together to some extent, but the clusters are not distinct or not separated from one other. The fact that the samples cluster within this space suggests that geologic origin of the brine samples play a significant role in controlling or affecting the chemical results found.

Elements Of Best Practice For Management Of NORM

Important considerations related to the handling of NORM and NORM-contaminated equipment include, 1) the unintentional environmental release of NORM into the environment, 2) the reasonable and adequate protection of workers handling NORM-contaminated equipment, 3) working in a NORM-contaminated environment, and 4) the protection of the general public from accidental or unwarranted exposure and/or ingestion of these NORM-containing materials. The elements of best practice described below seek to minimize human exposure and / or block potential pathways to environmental contamination. These practices should not be construed as an exhaustive listing of best management practices, but only a beginning around which a more complete management plan can be built. In addition to these suggested best practices there are several mandatory and/or suggested regulatory requirements which should be considered. Examples include rules promulgated by the Mississippi State Oil & Gas Board (2001), and the Federal Government (Occupational Safety Hazard Administration). Many of these other regulatory requirements lie outside the scope of this discussion and as such are not specifically discussed.

Wellsite Work - Well Workovers

The following practices are suggested to minimize the amount of radioactive scales introduced into the environment by workovers and maintenance work centered around the well head..

1) It is suggested as a component of best practices that either tarpaulin or plastic sheeting be placed in the area(s) directly surrounding the wellhead and in those areas where the equipment, tubing, sucker rods, etc. may be placed or temporarily stored. The placement

of sheeting and/or tarpaulin should underly those areas where scale may become dislodged from the equipment being removed from the well and/or wellsite facility. Covering the work area allows the dislodged scale to be retained and disposed of rather than allowing it to be introduced into the environment near the well head.

When the workover is completed, the plastic or tarpaulin should then be carefully folded or rolled up as to not allow the scale accumulated on it to end up on the ground in the work area. It is also suggested that the amount of radiation which may or may not be emanating from the materials contained within the sheeting or tarpaulin be recorded.

Once the tarpaulin/plastic sheeting has been folded or rolled up it should be transferred into suitable storage barrels, sealed, and then transported to the site designated for NORM storage pursuant to State Oil & Gas Board Rule 69 (Mississippi State Oil & Gas Board, 2001). Alternatively, the NORM contained within the barrels may be shipped directly from the wellsite to an approved facility for permanent disposal (permits are required from the Mississippi State Oil & Gas Board and other agencies).

Transportation Of NORM-Contaminated Tubulars, Sucker Rods, And Other Equipment

Suggested best practices as related to the transportation of NORM-contaminated equipment include the components discussed below. The desired end result, as noted earlier, is to reduce the potential for introducing radium-enriched scale into the environment.

2) Prior to the loading or placement of equipment on/in floats for transport, the float should be lined with one continuous sheet of plastic film. This lining of the float will allow equipment loaded on to the float to be sealed as a unit. This sealing will allow any scale which may become dislodged from the equipment to be retained. Sealing may be generally accomplished the use of any high-quality duct tape.

3) To reduce the opportunity for scale to be widely dispersed from tubulars, it is suggested that tubular ends be sealed for transport. Sealing of the ends of the tubular so any NORM contaminants, e.g. pipe scale that may become dislodged, will be prevented from exiting the equipment and becoming scattered on field and public roads. Dislodged scales on the graveled road surfaces will become ground to dust-sized particles by traffic and could become airborne. These airborne particles could be easily inhaled and become lodged in lung tissue, allowing the alpha and beta radiation from the radium enriched scale to directly affect tissue. Sealing may consist of plastic film and duct tape.

If the transport distance is relatively short it is unlikely that additional protection of the NORM-contaminated equipment is required. Highway speeds, however, should be kept to a minimum to maintain the integrity of the sealed plastic sheeting containing the

NORM contaminated equipment. If the equipment is to be transported any significant distance then the sealing procedure described in Suggested Practice 1 should be used. Some containers (roll-off boxes) generally include a tarpaulin cover which may be utilized to cover the equipment being transported.

Equipment Maintenance And Closed Vessel Issues

It is important to note here that closed vessels may include heater treaters, separators, stock tanks, vacuum trucks, barrels or any other sealed containers containing NORM materials or NORM contaminated equipment such as tools, clothing, gloves, and discarded plastic sheeting. During the production of hydrocarbons, sediment, sludge, and precipitates accumulate in equipment such as treating, transfer and storage equipment, *e.g.* stock tanks. It also accumulates in separators and heater treaters and other vessels. When tanks or other equipment require the removal of these particulates, there is always the hazard associated with explosions resulting from the hydrocarbons formerly stored in the vessels. Proper training in working in this dangerous environment should include, among others, principals of tank ventilation, and familiarity with self-contained breathing units which are necessary when working in the closed vessel environment. Hydrogen sulfide (H_2S) is also a significant safety consideration as only small concentrations can prove fatal.

Radon gas is a colorless, odorless, and non-flammable gas that is generated as radium (contained in fluids or solids within tank sludges) progresses through its natural radioactive decay process. Even though radon gas does not pose any explosion threat if it is present in any concentration it is considered a potential carcinogen which is a health risk of consequence. The following practices are intended to protect workers from NORM-related accumulations of radon that could be found in confined spaces such as described above.

4) In order to minimize exposure to any radon gas (also hydrocarbon vapors) which may have accumulated in an enclosed vessel the vessel should be well ventilated prior to entry.

5) Entry should be allowed only by workers using self contained breathing units and wearing protective clothing.

Closed Barrels/Containers With NORM-Enriched Contents

NORM containing materials are commonly stored in barrels with removable lids either onsite or at a disposal facility. If it is necessary to remove these lids to inspect the container's contents it is suggested that the following practices be followed.

6) Adequate ventilation needs to be provided within the working area. It is suggested that containers not be opened within a closed facility, *e.g.* an interior warehousing area.

7) Worker(s) should first remove the containers lid and allow the container to come in contact with the exterior air for a minimum of 10 minutes to allow the dispersion of any radon gas which may have been generated and accumulated within the headspace of the container.

8) Worker(s) should always avoid the direct inhalation within the area of the headspace of the container so as not to inhale any residual radon gas which may be confined within the container.

9) Once the inspection is completed the containers lid should be replaced and throughly secured to prevent any leakage of liquids which may contain NORM (such as sludges).

Protective Measures For Worker Clothing

Inhalation and ingestion are the most important pathways by which radium-enriched minerals enter the body. Any measures which minimize exposure via these pathways are useful to protect worker health and safety.

10) Clothing, including foot coverings, coveralls, work gloves and any other protective items which may have come in contact with NORM-containing materials should be surveyed with a radiation meter to determine levels of radiation. If the presence of NORM-enriched particulates are suggested, the clothing should be disposed of completely and not reused. The clothing can be placed in barrels along with other NORM-related wastes and stored or permanently disposed of at a NORM facility.

Dust Control

Pursuant to the Mississippi State Oil and Gas Board Rule 68 (Mississippi State Oil & Gas Board, 2001), oil and gas operators may landspread NORM-containing scales and other waste. If this method is utilized, there would be the potential to generate dust which may include particles of NORM bearing materials. As noted in Rule 68 workers are to be equipped with dust control devices. The use of these devises would assure the minimization of potential inhalation of such materials and its ingestion into the respiratory tracts of those workers which would generate an obvious health risk.

11) It is also advisable, especially during dry conditions, that workers wear dust protection breathing masks to filter out any NORM contaminates which may have become airborne. This is particularly applicable under conditions which would necessarily create dust such as with landspreading activities.

12) If fugitive dust is present at landspreading operations, then the use of water should be required to minimize airborne dispersion.

During the field sampling phase of this project, it was noted that operators have the practice of spreading gravel around wellheads/wellsites where workovers had recently occurred for several reasons. It was related that after a period of several months that this gravel at the workover locations would then be leveled, bringing the wellsite back to its original level grade. The gravel materials which are commonly placed around the wellhead are moved with a box blade/tractor onto the location/access road. If the materials that were once around the wellhead contained NORM, they now have been moved from a localized area and dispersed to other parts of the wellhead location and access road. Moving the NORM-containing gravel around the well head area creates a larger area of NORM contamination than existed. Dispersal of the scale over a significant area offers multiple pathways for the radioactive scale to enter the environment and should be discouraged. Another complication exists when vehicular traffic on access roads may generate dusts containing NORM-enriched particulates. The generation of this dust then may be inhaled or ingested by the occupant(s) of the vehicle(s) as well as any bystanders.

13) It is suggested that as an element of best practice that this method of "cleaning" a location cease and that any NORM contaminated materials be removed from the location prior to the addition of any additional site materials/gravel.

In-Field Storage Facilities

Pursuant to Rule 69 of the Mississippi State Oil and Gas Board, NORM contaminated equipment, tubulars, etc. and NORM which has been captured and stored in containers (barrels) may be stored within the geographically defined limits of an oil and/or gas field. As suggested here, there are several best practice recommendations relating to those facilities and to NORM storage containers.

14) A recommended best practice procedure is that any metal containers containing NORM materials with liquids or high moisture content should have their interiors coated with a rust resistant material. This recommendation is particularly important for those

storage containers which are anticipated to be stored for an extended period of time prior to permanent disposal.

It was noted during field sampling that NORM storage facilities are in compliance with existing rules regarding fencing and posting of warnings. We would, however, suggest some practices that could enhance the ability of the storage facilities to isolate the NORM-bearing solids and liquids from the environment.

The facilities typically have washed gravel pads on which the barrels or equipment are stored. There appears to be little or no use of barriers to prevent fugitive NORM-enriched liquids or solids from being entrained in surface water from the facility or being introduced into the groundwater system through surface infiltration.

15) It is suggested that the potential for waste isolation could be improved by constructing one or more barriers to retard any potential for NORM-enriched liquids escaping through the floor of facilities. This goal could be accomplished by the use of compacted clay liners and/or the use of synthetic liners below the washed gravel surface. The use of concrete pads rather than simple washed gravel surfaces would also be a viable alternative that would allow easy maintenance and clean up.

16) It is suggested that the owner of the facilities take appropriate measures to prevent surface erosion at NORM storage facilities.

17) The storage area could be bermed to prevent any runoff of NORM liquids/suspended solids. The operator would be able to, from time to time, remove any liquids which may have accumulated in the bermed storage area by a vacuum truck and disposed of in a manner consistent with existing state laws and regulations.

Storage Facilities Siting Issues

Lastly, it has been noted that in Rule 69 (see also Rule 68) promulgated by the Mississippi State Oil and Gas Board that the location of such NORM storage facilities are restricted to areas within the geographical limits of an oil and gas field (Special Field rules adopted by the Mississippi State Oil and Gas Board). In addition to these rules we suggest the that following criteria also be considered.

18) Long-term NORM storage facilities should be located as far as physically possible from any dwelling;

19) These facilities should also be located as far as possible from any areas in which livestock, poultry, etc. may be housed or contained. As a result of the geographic distribution of oil and gas producing areas in relation to aquiculture, at least within Mississippi, this issue is currently a mute point, but may be of importance in the future.

20) NORM storage facilities should not be located adjacent to any stream (including ephemeral), river, or other body of water. If any accidental or otherwise unintended release of NORM materials should occur it is likely that transport away from the site of storage would be fluid induced (i.e. surface water movement) and therefore the reason for this recommendation.

Rule 68 suggests that the disposal of NORM through landspreading shall be allowed only in those areas where published literature or site-specific determinations indicate that the ground water is equal to or greater than five feet below the bottom of the disposal area. Water tables may vary greatly over relatively short distances and also vary from season to season.

21) It is suggested that before burial is contemplated, that the depth to ground water be determined by published information and also by actual measurement of the potentiometric surface at the proposed burial site over a period of time. A minimum one year time period would allow seasonal variations to be determined.

22) Further it is suggested that as an additional measure of safety, the depth to the ground water table be increased from five feet to ten feet.

23) Lastly, if at all possible, NORM storage facilities should not be located within the outline of the 100 year flood plain. If located within the 100 year flood plain it would increase the likelihood of transport and dispersal of NORM contaminates away from the facility and their reintroduction and dispersal into the environment.

With the implementation of some or all of the preceding suggested practices outlined above, many of which are already employed by oil and gas operators within the state and industry overall, it is anticipated that the additional incremental expense associated with these practices will be of lesser significance.

CONCLUSIONS

1) - The findings from the leaching studies indicate that within a relatively short time following landspreading significant amounts of the scale and sludge will have become solubilized through the actions of soil microorganisms. The radium will become biologically available and can work its way into the food chain. Due to its relatively strong affinity for soil it will only slowly migrate away from the application site through hydrostatic processes. However, this migration rate will be enhanced by its uptake into plants, and its subsequent introduction into the food chain and through processes of erosion. In general these processes are dispersive in their overall effect. It is possible, however, that some plant species may be able to concentrate radium in their tissues.

2) - The amounts of radium found in brines from Mississippi hydrocarbon production are generally very low. When handled according to regulations and the suggested practices contained herein, these should pose little or no threat to human health or the environment.

3) - NORM remediation of an oil and gas facility can become very costly. If all, or a significant portion of the suggested practices are employed, then the overall need for site remediation should be significantly reduced. A program of waste isolation management could result in a reduction or lack of required remediation measures required for the unconditional release of the property after oil and/or gas production has ceased at the site. This further minimizes the potential liability to the following: the operator of the property, the working interest owners of the property, as well as others who may have had subsidiary activities on or within the confines of the property.

4) - Adequate NORM/OSHA training of workers should result in the minimization of negative environmental and personnel related impacts and potential liabilities.

5) - There is a clear statewide trend of elevated levels of chloride in the Mississippi Interior Salt Basin. Mean chloride values in the Interior Salt Basin are 104.1g/L compared to 56.6g/L in other wells sampled around the state. A two-sample *t*-test confirms the means of the two groups are not similar.

6) - Several database constituents display correlation statewide. The TDS and $BaSO_4$ saturation are correlated to moderately correlated with Cl^- with correlation coefficients, *r*, of 0.78 and 0.44, respectively. ^{226}Ra and ^{228}Ra are moderately correlated with an $r = 0.54$, and SO_4^{2-} is moderately to weakly correlated with $BaSO_4$ saturation, ^{226}Ra, and ^{228}Ra with $r = 0.41$, 0.36, and 0.34, respectively.

7) - As in Fisher's work Texas brines, wells that contain elevated levels of chloride do usually have high levels of ^{226}Ra - 93.2% of Mississippi samples have >100pCi/L ^{226}Ra and >20g/L Cl^-.

8) - The ^{226}Ra and ^{228}Ra isotopes appear to be moderately correlated (r = 0.63) in Mississippi wells compared to Fisher's results showing strong correlation (r = 0.98) from Texas wells.

9) - Clustering of data using Cl^-, ^{226}Ra, and ^{228}Ra suggests that chemicals associated with NORM formation are not entirely randomly distributed and that there are some geologic controls.

10) - As in the Texas brines, wells that contain elevated levels of TDS do usually have high levels of ^{226}Ra - 85.7% of Mississippi samples have >200pCi/L ^{226}Ra and >35g/L TDS. Box plots suggest Cl^- concentration and TDS both increase with depth in Mississippi wells.

11) - The ^{226}Ra isotope displays large variation within geologic formations, but only small variations across all formations. Very similar mean values exist for all formations.

12) - Means of ^{226}Ra, ^{228}Ra, Cl, Ba^{2+}, and Ca^{2+} for samples taken from carbonate formations differ significantly from clastic formations. Two sample t-tests yield P values < 0.05, suggesting carbonate and clastic formation water chemistries are different.

13) - Lower Cretaceous wells producing above 11,000 ft in the Mississippi Interior Salt Basin have a substantially higher correlation (R^2 = 0.36) with respect to Cl^- concentration than the entire dataset (R^2 = 0.04), therefore depth of production is evidently a factor in controlling brine chemistry. Both ^{226}Ra and TDS do not display the same trend.

14) - Subdividing samples within the Heidelberg Field and Tinsley Field by structural geology (major faults) does not produce distinctly different populations within these fields. The major constituents (^{226}Ra, TDS, Cl, SO_4^{2-} and Ba^{2+}) subdivide by structural feature and have similar means, therefore cannot be considered as separate groups. Tinsley Field has a definite north south trend and displays moderate correlation between ^{226}Ra, Ba^{2+} and the northing direction, r = 0.52 and r = 0.49 respectively.

15) - With a few exceptions, there seems to be little or no spatial continuity between producing formations and the variables ^{226}Ra, Cl^-, Ba^{2+}, and $BaSO_4$ saturation at the sampling scale used for this project. The two most notable exceptions are Ba^{2+} for the samples of Group1 and $BaSO_4$ saturation for the samples of Group 2.

16) - Heidelberg Field displays some spatial continuity with the variables ^{226}Ra, Cl^-, and $BaSO_4$ saturation. Although spatial continuity exists within this one field, there is little to no spatial continuity evident in the other subsets created by field of production.

17 - The application of principal component analysis demonstrated that brine samples do cluster by geologic formation to some extent, when the samples are considered in the sample space defined by the directions of the first three principal components of the data set. The fact that the samples cluster within this space suggest that geologic origin of the brine samples play a significant role in controlling or affecting the chemical results found. The extent or cause of this clustering might be considered in future research, but it does demonstrate that geologic origin of the samples in this research controlled the results that were found.

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LIST OF ACRONYMS AND ABBREVIATIONS

API - American Petroleum Institute

ANOVA - analysis of variance

GIS - geographic information system

MMRI - the Mississippi Mineral Resources Institute, University of Mississippi

NOAA - National Oceanic and Atmospheric Administration

NORM - Naturally occurring radioactive materials

PCA - principal component analysis

SOLMINEQ.88 - Software package from the USGS as described in Plummer *et. al.*, 1988

TDS - total dissolved solids

TENORM - Technically-enhanced radioactive materials

USDA - United States Department of Agriculture

USDOE - United States Department of Energy

USGS - United States Geological Survey