ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

ANL/EES-TM--259

ANL/EES-TM-259

DE85 001439

**RADIOACTIVE WASTE ISOLATION IN SALT:
PEER REVIEW OF THE OFFICE OF NUCLEAR WASTE ISOLATION'S REPORT
ON THE ORGANIC GEOCHEMISTRY OF DEEP GROUNDWATERS
FROM THE PALO DURO BASIN, TEXAS**

by

D.F. Fenster, D.G. Brookins,* W. Harrison,
M.G. Seitz,[†] A. Lerman,** and V.C. Stamoudis

Energy and Environmental Systems Division
Geoscience and Engineering Group

August 1984

work sponsored by
U.S. DEPARTMENT OF ENERGY
Salt Repository Project Office
Office of Civilian Radioactive Waste Management

*University of New Mexico
[†]Chemical Technology Division, ANL
**Northwestern University

NOTICE
PORTIONS OF THIS REPORT ARE ILLEGIBLE.

It has been reproduced from the best
available copy to permit the broadest
possible availability.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Department of Energy
Chicago Operations Office
Salt Repository Project Office
505 King Avenue
Columbus, Ohio 43201-2693

NOTICE TO READERS

At the request of the Salt Repository Project Office, Argonne National Laboratory carried out a review of a Battelle report: "The Organic Geochemistry of Deep Groundwaters from the Palo Duro Basin, Texas," by J.L. Means.* The report describes the organic geochemistry of groundwater samples from the Palo Duro Basin, with analyses and identification of the primary organic constituents. Results from the report are important in assessing radionuclide transport rates in groundwater and indicating the possible existence and location of petroleum deposits in the Palo Duro Basin. Argonne was asked to consider the appropriateness of the methodology, the conclusions based on data presented, and the adequacy of correlation and integration between geochemical interpretation and knowledge of the geologic setting.

The Argonne review comments have been provided to the author. These comments, along with other reviews, will greatly aid in the preparation of a revised document of greater clarity and applicability to the program.

Thomas A. Baillie
for Jo Ann Sherwin
Chief
Site Evaluation
Salt Repository Project Office

*A microfiche copy of the reviewed report is attached to the inside back cover of this report.

FOREWORD

Documents are being submitted to the Salt Repository Project Office (SRPO) of the U.S. Department of Energy (DOE) by Battelle Memorial Institute's Office of Nuclear Waste Isolation (ONWI) to satisfy milestones of the Salt Repository Project of the Civilian Radioactive Waste Management Program. Some of these documents are being reviewed by multidisciplinary groups of peers to ensure DOE of their adequacy and credibility. Adequacy of documents refers to their ability to meet specified legal or regulatory requirements. Credibility of documents refers to the validity of the assumptions, methods, and conclusions, as well as to the completeness of coverage.

Since late 1982, Argonne National Laboratory has been under contract to DOE to conduct multidisciplinary peer reviews of program plans and reports covering research and development activities related to siting and constructing a mined repository in salt for high-level radioactive waste. This report summarizes Argonne's review of ONWI's final report entitled *The Organic Geochemistry of Deep Ground Waters from the Palo Duro Basin, Texas*, dated September 1983. Argonne was requested to review this report on October 27, 1983 (see App. A).

The review procedure involved obtaining written comments on the report from two extramural and four Argonne experts in relevant research areas. The peer review panel met at Argonne on November 10, 1983, and reviewer comments were integrated into this report by the review session chairman, with the assistance of Argonne's core peer review staff. All of the peer review panelists concurred in the way in which their comments were represented in this report (see App. B). A draft of this report was sent to SRPO on November 18, 1983.

PREVIOUSLY PUBLISHED REPORTS IN THE SERIES

"RADIOACTIVE WASTE ISOLATION IN SALT"

- ANL/EES-TM-242** Peer Review of the Office of Nuclear Waste Isolation's Geochemical Program Plan (Feb. 1984)
- ANL/EES-TM-243** Peer Review of the Office of Nuclear Waste Isolation's Socioeconomic Program Plan (Feb. 1984) (revised July 1984)
- ANL/EES-TM-246** Peer Review of the Office of Nuclear Waste Isolation's Plans for Repository Performance Assessment (May 1984)
- ANL/EES-TM-254** Peer Review of the Office of Nuclear Waste Isolation's Reports on Preferred Repository Sites within the Palo Duro Basin, Texas (April 1984)
- ANL/EES-TM-256** Special Advisory Report on the Status of the Office of Nuclear Waste Isolation's Plans for Repository Performance Assessment (Oct. 1983)
- ANL/EES-TM-258** Peer Review of the Office of Nuclear Waste Isolation's Plan to Decommission and Reclaim Exploratory Shafts and Related Facilities (July 1984)

CONTENTS

PEER REVIEW PANEL MEMBERS	viii
SUMMARY OF RECOMMENDATIONS	1
1 INTRODUCTION	3
2 PURPOSE	4
2.1 Stated Objective	4
2.2 Role of the Report in the Salt Repository Project	4
3 TECHNICAL CONTENT	6
3.1 Compatibility with Related Publications	6
3.2 Sample Collection	6
3.3 Analytical Methods	7
3.4 Geochemical Interpretations	8
4 ADDITIONAL CONCERNS	10
5 PAGE-BY-PAGE COMMENTARY	12
REFERENCES	14
APPENDIX A: U.S. Department of Energy Letter Requesting Peer Review	15
APPENDIX B: Concurrence Sheet	19
APPENDIX C: Credentials of Peer Review Panel Members	23

* * *

A microfiche copy of the following unpublished report is attached to the inside back cover of this report: J.L. Means, *The Organic Geochemistry of Deep Ground Waters from the Palo Duro Basin, Texas*, Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio (Sept. 1983).

PEER REVIEW PANEL MEMBERS

Prof. Douglas G. Brookins
Department of Geology
University of New Mexico
Albuquerque, New Mexico

***Mr. David F. Fenster**
Geoscience and Engineering Group
Energy and Environmental Systems Division
Argonne National Laboratory

†Dr. Wyman Harrison
Associate Director for Geoscience and Engineering
Energy and Environmental Systems Division
Argonne National Laboratory

Prof. Abraham Lerman
Department of Geological Sciences
Northwestern University
Evanston, Illinois

****Dr. Martin G. Seitz**
Geochemistry Group
Chemical Technology Division
Argonne National Laboratory

Dr. Vassilis C. Stamoudis
Geochemistry Section
Geoscience and Engineering Group
Energy and Environmental Systems Division
Argonne National Laboratory

The credentials of panel members are summarized in App. C.

***Review session chairman and member of core peer review staff.**

†Review panel chairman and member of core peer review staff.

****Assistant review session chairman.**

**RADIOACTIVE WASTE ISOLATION IN SALT:
PEER REVIEW OF THE OFFICE OF NUCLEAR WASTE ISOLATION'S REPORT
ON THE ORGANIC GEOCHEMISTRY OF DEEP GROUNDWATERS
FROM THE PALO DURO BASIN, TEXAS**

by

D.F. Fenster, D.G. Brookins, W. Harrison,
M.G. Seitz, A. Lerman, and V.C. Stamoudis

SUMMARY OF RECOMMENDATIONS

The following recommendations for improving the Office of Nuclear Waste Isolation's final report entitled *The Organic Geochemistry of Deep Ground Waters from the Palo Duro Basin, Texas* have been abstracted from the body of this review report. In general, the ONWI report should be modified to conform to one of the following three alternatives so that the text is consistent with the report title and with the objectives of the project as stated in the introduction.

1. Change the title to *Determination of Short-Chain Aliphatic Acids and Total Organic Carbon Content in Nine Deep Groundwater Samples from the Palo Duro Basin, Texas*, and rewrite the objectives to match the present scope of work. Delete any material that does not pertain to analytical chemistry. This option would require minimal revision of the text.
2. Change the title as above but revise the text more extensively. Treat the correlations between geochemical and geologic/hydrogeologic data in more detail. Review the present level of knowledge with respect to the two major waste management concerns relating to organic geochemistry -- radionuclide mobility in the presence of certain organic compounds and presence of organic compounds as indicators of petroleum resource potential. Discuss geochemical interpretations in more depth.
3. Leave the title as it is and revise the report extensively so as to discuss geochemical interpretations in light of available geologic and hydrogeologic data from the Palo Duro Basin. This option would require additional chemical analyses and studies of the complexing properties of the organic compounds in the groundwater. The relationship between the presence or absence of aliphatic acids and potential petroleum resources would have to be documented.

The following recommendations apply to one or more of the options listed above.

1. Fully characterize additional deep groundwater samples using state-of-the-art methods.

2. Restate the study objectives so that they correspond to the actual work performed, and revise the report title accordingly. The revised objectives, along with an explanation of scope, should clarify why the analytical methods described in the report were used.
3. Incorporate discussions on the sampling of water wells and the effects of sample filtration on analytical results. Give reasons for selecting specific filter pore sizes.
4. In future analyses, include stable carbon and hydrogen isotope data, which are useful in characterizing organic compounds typically found in oil fields. Isotope ratios such as $\text{Sr}^{87}/\text{Sr}^{86}$ can often be correlated with organic material derived from petroleum.
5. In Fig. 4-3 eliminate the solid curve and add error bars to show the standard deviation associated with each data point. Because the present curve is based on only nine samples, it is not defensible.
6. Address inconsistencies in the available data. Differences between analytical results presented in the reviewed report and those reported in previous related publications should not be ignored.
7. Use the services of a technical editor to improve the readability and clarity of the report.

1 INTRODUCTION

The U.S. Nuclear Regulatory Commission (1982) states in Sec. 6.2 that organic compounds in groundwater must be identified as part of characterization of sites for repositories for high-level radioactive waste. The need to be knowledgeable about the organic geochemistry of deep groundwaters in particular arises from two major concerns. First, such knowledge is important from the perspective of assessing repository performance because certain organic substances may form soluble complexes with radionuclides, thereby increasing radionuclide transport rates from the repository to the accessible environment. On the other hand, certain organic compounds (e.g., oxalic acid) may retard radionuclide migration from the near-field repository environment by increasing the adsorption of radioactive ions by clay minerals (Means, 1982a). Second, the presence of certain organic compounds in deep groundwaters may indicate that the potential repository site or nearby areas contain previously undiscovered petroleum resources. Such knowledge might prevent locating a repository where future resource developers might inadvertently disturb the site.

Argonne's peer review of the Office of Nuclear Waste Isolation's (ONWI's) final report entitled *The Geochemistry of Deep Ground Waters from the Palo Duro Basin, Texas* involved obtaining written critiques of the report from two extramural and four Argonne experts in relevant research areas. Panelists did not contact ONWI personnel, and none of the panelists have been involved in any programs sponsored by the U.S. Department of Energy (DOE) or directed by ONWI such that their participation in the review could be construed as a conflict of interest.

Although no specific guidance was provided to Argonne by DOE on how to conduct the review, the following questions were prepared by DOE to assist in the review process (see App. A):

1. Does the study satisfy its stated purpose?
2. Are the methods used appropriate or are there other methods that should have been used?
3. Are the conclusions valid and based on the data presented?
4. Is there adequate correlation and integration between the geochemical interpretations and what is known about the geologic setting?

2 PURPOSE

2.1 STATED OBJECTIVE

As stated in the introduction, the objective of the ONWI report is "to identify organic compounds in ground water from the Palo Duro Basin in the Texas Panhandle." This objective should be narrowed to more accurately reflect the actual scope of work, that is, identification of short-chain aliphatic acids in nine groundwater samples from the basin.

The title should also be revised to reflect the contents of the report. Because the report barely discusses the interaction of the chemical components with the geosphere or with the conceptual repository environment and because it discusses analytical organic chemistry while barely mentioning geochemistry, a more appropriate title might be *Determination of Short-Chain Aliphatic Acids and Total Organic Carbon Content in Nine Deep Groundwater Samples from the Palo Duro Basin, Texas*.

The two major concerns related to the organic geochemistry of groundwater and radioactive waste isolation mentioned in Sec. 1 of this peer review report are also mentioned in the ONWI report but are not discussed in detail (pp. 1 and 21). Although not part of the stated objective, these concerns are introduced in Sec. 1.1 (Objective). Such prominence implies that these issues will be addressed and that some conclusions may be drawn. At a minimum, the reader would expect to be informed about the status of research with respect to these issues and about the relevance of the organic compounds identified in the nine groundwater samples. Are these two concerns the subject of ongoing research? Will a more complete discussion, based on analyses of additional samples, be forthcoming in a subsequent report?

Section 1.1 (Objective) should also explain why certain organic compounds were selected for analysis and relate the methods used to the stated objective. The author presents a rapid, though effective, analysis of the major short-chain aliphatic acids present in nine groundwater samples. From a review of state-of-the-art analytical techniques used at Argonne and the methods described in previous ONWI studies (Means, 1982a, b), it is apparent that less sophisticated analytical techniques were used for some unexplained reason (see Sec. 3.3 of this report). The author should relate the analytical techniques used either to constraints in time or budget or to a decision to limit the inquiry to the group of low-molecular-weight organic compounds analyzed.

2.2 ROLE OF THE REPORT IN THE SALT REPOSITORY PROJECT

The reviewed report does not present a complete analysis of the organic constituents of groundwater in the Palo Duro Basin, it does not effectively relate the analytical results to the geochemistry of deep groundwater, and it does not discuss the implications of the analytical results with respect to the two major waste isolation concerns. Indeed, the designation "final report" is somewhat misleading and might be more appropriate for Means (1982a) or Means (1982b). However, with minor modifications and a change in title, the report could serve as a status or technical report

providing data related to the geochemical analysis of deep groundwaters in the Palo Duro Basin. It will prove most effective if it clearly relates its limited objectives to the objectives of the Salt Repository Project.

3 TECHNICAL CONTENT

3.1 COMPATIBILITY WITH RELATED PUBLICATIONS

The ONWI report is potentially important in that it identifies several organic compounds in, as well as the total organic carbon (TOC) contents of, nine groundwater samples obtained from DOE-sponsored wells, the locations of which are shown in Fig. 2-1. A subsequent draft could go a step further and explain any differences between data presented in the reviewed report and data presented in earlier related reports. For example, Means et al. (1983) present analyses from the fourth and fifth production zones of S&W Sawyer Well No. 1. Do previously published data support, supplement, or contradict the current data? This point is discussed further in Sec. 4 of this report.

3.2 SAMPLE COLLECTION

Section 2 (Sample Collection) is generally clearly written but would benefit from additional editing (see Secs. 4 and 5 of this report). One aspect that should be considered in a subsequent draft is the number of samples (nine) relative to the report title. While nine samples appear to be adequate to provide useful information on the types and relative amounts of organic compounds present in deep groundwaters, nine samples are far too few to fully characterize the groundwaters contained in the thick geologic section within the large area shown in Fig. 2-1, especially since brine compositions vary widely in bedded salt basins (Stewart and Potter, 1979; Bassett et al., 1981; Molecke, 1983).

Section 2.2 (Sample Acquisition and Treatment) outlines the procedures followed before and after April 1983. This section should state whether samples were obtained from open-hole intervals isolated by inflated packers or from cased boreholes. It should also state whether blanks were bottled in the field for laboratory testing. Given that samples obtained prior to April 1983 were not filtered and those obtained after April 1983 were filtered in the field, the text should state what effect, if any, filtering has had on the analysis of organic compounds. For example, filtering may introduce a bias in the TOC data by removing organic-rich particulates. Analyses of short-chain aliphatic acids should not be affected by filtering.

All of the groundwater samples with the "weakest mass balances" as described on page 17 and in Table 4-3 were collected prior to April 1983 and, thus, had not been filtered. The report does not address the possible effects of filtering on these analyses. Comparing analyses from filtered versus unfiltered samples is relevant to assessing the adequacy of using a mass-balance argument to account for TOC not associated with aliphatic acids, as opposed to performing additional analyses. Finally, the author might discuss precautions taken to avoid sample contamination during the filtration process.

On page 4, the report states that groundwater samples were filtered through millipore 0.45 μm or nuclepore 0.4 μm polycarbonate membranes. Workers in the Nevada Nuclear Waste Isolation Program use 0.05 μm pore filters (e.g., Daniels et al., 1982). Experience at Argonne (e.g., Steindler et al., 1983) indicates that filters with micropores

can drastically change the inorganic as well as the organic constituents of the filtrate. A subsequent draft of the report should discuss choice of filter pore size as it affects analytical results. Also, any filterable organic-rich particulate should be characterized to some extent because it is part of the organic content of the groundwater.

The last paragraph in Sec. 2 mentions thiocyanate tracer levels (also see Table 2-1). A subsequent draft should explain the purpose of analyzing tracer levels, the source of the tracer, and the history of its introduction into the groundwater system.

3.3 ANALYTICAL METHODS

As discussed in Sec. 2.1 of this report, the analytical methods described in the ONWI report are suitable for rapid analysis of short-chain aliphatic acids. However, given the report's title and stated objective, the analytical methods are inadequate. Organic compounds other than short-chain aliphatic acids could be present in any of the nine groundwater samples. The discussion of gel filtration chromatography (GFC) and the chromatographs (elution profiles) in Fig. 4-1 indicates that humic substances and fulvic acids may be present in some of the samples. No attempt has apparently been made to characterize the high-molecular-weight fraction shown on elution profiles of samples from the fourth and fifth production zones of S&W Sawyer Well No. 1 and the second production zone of Mansfield Well No. 1 (pp. 11-14 and Fig. 4-1).

The gas chromatography (GC) analysis presented in Sec. 3.3 is adequate only for the two major short-chain aliphatic acids analyzed -- acetate and propionate. The analysis should have been designed to have a detection limit more sensitive than 1 mg/L because most of the acids reported are present in concentrations of 1 mg/L or less. A longer packed column using a temperature program would have improved detection considerably. If an extraction step using larger volumes of the original sample had been included in the analytical method, if this step had been followed by methylation of the acids, and if state-of-the-art capillary-column GC methods had been used, the limit of detection could have been approximately 1 μ g/L. Such a level of detection is one thousand times more sensitive than the one used. A variety of other aliphatic acids and other organic compounds, if present, could have been identified with a 1 μ g/L detection limit. Although the author states that his study identified the major organic compounds present in the groundwater samples, it is conceivable that important higher-molecular-weight compounds in smaller concentrations could have been identified.

Argonne peer review panelists raised several questions about the analytical methods used by the author. Were blanks used for GFC and GC analyses as they were for TOC analysis? Why were temperature ranges instead of constant temperatures reported for the GC analysis? Why were these less sophisticated analytical methods used? The author has used state-of-the-art GC methods in similar studies (Means, 1982a; Means et al., 1983). Why were the analyses described in the report focused on short-chain aliphatic acids? Did time or cost constraints prevent a more comprehensive analysis than the one used? Although the author assumes that the aliphatic acids analyzed are present in the form of anions in the original sample, he does not explain how this was determined. The ONWI report could be improved considerably if the methods chosen were matched to carefully delineated objectives and the stated scope.

Analytical methods that have been useful for characterizing organic compounds found in oil fields include stable isotope studies (Carothers and Kharaka, 1978). It may be desirable to obtain data on stable carbon and hydrogen isotopes from samples obtained in later studies. Isotope ratios such as $\text{Sr}^{87}/\text{Sr}^{86}$ often correlate with petroleum-derived organic material and may be useful for interpretation.

Incorporation of standard deviation and mass balance is an excellent technical practice and permits a more thorough review of the data than would otherwise be possible. The author is to be commended in this regard, and the panelists encourage continuation of the practice.

3.4 GEOCHEMICAL INTERPRETATIONS

Although chemical analysis is the stated purpose of the ONWI report, the title and the early mention of the two major concerns related to organic geochemistry and repository performance indicate that the report will also touch on the geochemistry of the analyzed organic compounds.

Whereas the author's conclusions with regard to identification of the major components of his nine samples appear to be valid, his comparison of the organic chemical constituents of the Palo Duro Basin with those reported by Carothers and Kharaka (1978) is less persuasive. The weakness of the comparison may be partly due to the much larger number of samples used by Carothers and Kharaka (1978, Fig. 2, p. 2448). In their work, some 50 data points were used to plot aliphatic anion content against temperature. The author's statement that Palo Duro Basin groundwaters are compositionally similar to Carothers and Kharaka's zone 2 waters is not compelling because the Palo Duro groundwaters appear to be low in total anion content relative to other Texas or California groundwaters and because the Palo Duro groundwater temperatures are lower (Carothers and Kharaka, 1978). In fact, the author does not provide complete compositional analyses for his groundwater samples. Are the differences between the Palo Duro groundwaters studied by the author and those studied by Carothers and Kharaka related to the lack of petroleum potential in the Palo Duro Basin? Have different geochemical processes been operative in each basin, or are some of the compositional differences related to age (Carothers and Kharaka, 1978, Fig. 5)?

If a different mechanism accounts for the lack of biodegradation of acetate in Palo Duro Basin waters (p. 21), does this lack of correspondence affect the usefulness of these data for assessing petroleum potential? Alternatively, can the mechanisms for acetate-propionate segregation be identified, and will these mechanisms be useful in assessing petroleum potential through analysis of organic compounds? On the basis of the data presented in this report, the reader does not know whether a specific aliphatic acid anion content indicates areas where the potential for finding economic deposits of petroleum is negligible. The author should explain why using this indicator to screen out areas from further consideration as repository sites is not mentioned.

The attempt to correlate analytical results with available geologic or hydrogeologic data is weak. Although there is a high TOC peak in the strata penetrated by many wells at depths of 5000-7000 ft (1500-2300 m), TOC values show wide variation

(Dutton et al., 1982, Fig. 45, pp. 61-63). The interpretation with regard to short-chain aliphatic acid concentrations and depth does not integrate available knowledge of the geology and hydrology of the Palo Duro Basin, the locations of producing oil and gas wells, or the locations of trends with potential for containing petroleum reserves. For example, groundwater samples obtained from S&W Zeeck Well No. 1 and S&W Sawyer Well No. 1 are located within a zone mapped as $\geq 0.5\%$ TOC in the Lower Permian Wolfcamp (Dutton et al., 1982, Fig. 47). However, a sample from the second production zone of the S&W Mansfield Well No. 1, also drawn from the Lower Permian Wolfcamp, had a TOC content of 60.7 mg/L (see Table 4-1). Was the author's sample obtained from the porous carbonate interval, which is more than 200 ft (61 m) thick (Dutton et al., 1982, Fig. 53)? Does the high acetate content (219 mg/L) shown by the data presented in Fig. 4-3 of the ONWI report correlate with specific source rocks? No attempt was made to correlate data from groundwater TOC analyses with TOC analyses from well cuttings obtained from the same depth intervals. Little correlation was found between TOC values for groundwater and rock in Dutton et al. (1982). Also, no mention is made of petroleum production from the zones sampled during this study. No comparisons were made among sample locations, producing oil and gas well locations, and analytical results. The report does not discuss the deep groundwater regime, nor does it discuss any relationship, however speculative, between hydraulic gradients and transport of petroleum-derived organic compounds.

Argonne peer review panelists have little confidence in the curve shown in Fig. 4-3 because the shape of the curve is based on data from only nine samples. As drawn, the curve places relatively greater weight on the sample from the S&W Zeeck Well No. 1 and much less weight on the sample from the first production zone of the S&W Mansfield Well No. 1. No explanation is offered as to why this latter sample is so different from the others.

The ONWI report is potentially important for the characterization of deep groundwater in the Palo Duro Basin. However, the author does not provide criteria for distinguishing areas within the basin of high and low petroleum potential. Perhaps he should focus more narrowly on his central effort, the analysis of TOC, acetate, and propionate concentrations in several deep groundwater samples. In any case, the report would be improved by rewriting the introductory section to include comments concerning ONWI's ongoing organic geochemical work and the objectives for future work.

4 ADDITIONAL CONCERNS

The ONWI report should address inconsistencies in the data base generated by the author and his coworkers. Data presented in the report are not consistent with relevant data in cited references. For example, nine groundwater samples from the fourth and fifth production zones for S&W Sawyer Well No. 1 have mean TOC content values of 34.4 mg/L and 57.0 mg/L, respectively (see Table 4-1). However, Means et al. (1983, Table 1) indicate that six groundwater samples from the fourth and fifth production zones for S&W Sawyer Well No. 1 have mean TOC content values of 20.6 mg/L and 47.6 mg/L, respectively. The difference in the number of analyses cannot explain these discrepancies. The standard deviations shown in Table 4-1 are too small to accommodate the large increases in TOC values that apparently result from the three additional analyses.

The GFC data in Fig. 4-1 for the fourth and fifth production zones for the S&W Sawyer Well No. 1 are different from similar data shown in Fig. 4 of Means et al. (1983). Specifically, a peak from a groundwater sample from the fifth production zone is prominent in Fig. 4 of Means et al. (1983) but is missing at 280 mL in Fig. 4-1. Also, the elution profile for a groundwater sample from the fourth production zone is completely different in the ONWI report from the one shown in Fig. 4 of Means et al. (1983). What is the explanation for these differences? What do they imply?

The ONWI report does not explain the results of the mass-balance calculations discussed on page 17 and shown in Table 4-3. The author uses the term "weak mass balance" to indicate that the short-chain aliphatic acids are only a small fraction of TOC. He does not discuss the analysis showing that acetate concentration as carbon can be expressed as 262% of TOC of the sample from S&W Mansfield Well No. 2.

The following examples demonstrate the need for technical editing. The last sentence of the abstract should not say what is discussed in the report but should summarize what is said. The final sentence in the report is ambiguous. Two symbols, 1 and 2, are used to represent liter. Error bars representing the standard deviations listed in Table 4-2 should be shown in Fig. 4-3. The authors should include references to support the statement that the broad peaks in many of the GFC elution profiles from 260 mL to 500 mL elution volumes likely represent inorganic solutes (p. 14). The long-term leaching experiments at Battelle mentioned on page 4 must be referenced or the results included. Other more detailed editorial comments are included in Sec. 5.

The summary section should be rewritten to be in accord with the stated objective of the report. Because paragraph two introduces new interpretations not discussed in the text, it does not belong in the summary. The statements in the third paragraph that aliphatic acid anions peak at depths of 5000-7000 ft (1550-2300 m) and that the highest aliphatic acid concentrations occur in the Lower Permian Wolfcamp are based on only one sample and should be deleted. The last paragraph does not summarize data presented in the report. The two major concerns stated in the introduction, which are not addressed in the body of the report, are merely restated here. The report should indicate if there are sufficient data available to address these concerns or if these concerns will be addressed in a subsequent report.

Overall, the ONWI report represents a worthwhile effort. Greater attention to detail should resolve discrepancies and enhance the credibility of the report. If allowed to stand as a "final report," it should summarize the previous work by the author and his colleagues, especially with regard to radionuclide mobility as a function of the organic geochemistry of deep groundwaters. For example, the presence of oxalic acid appears to make radionuclides less mobile in the near-field repository environment of 150-200°C (Means, 1982a, pp. 10-11). However, oxalic acid is a dicarboxylic acid and is bound to behave differently from an aliphatic acid. For example, oxalic acid is a well-studied ligand that forms complexes with metal ions. Therefore, are high concentrations of aliphatic acids favorable for waste isolation? The author should state explicitly what can be inferred from the currently available data and should state what additional research efforts are required to more completely predict radionuclide transport behavior in the near-field environment of a repository located in the Palo Duro Basin.

5 PAGE-BY-PAGE COMMENTARY

<u>Page</u>	<u>Line(s)</u>	<u>Comment</u>
i	2	The word "different" is extraneous.
i	14-15	The phrase "is also discussed" is inappropriate in an abstract. A summary statement of the relevance of these compounds would be preferable.
1	6-9	References are needed.
1	22-25	The use of organic compounds as a petroleum exploration tool has not yet been refined. Provide a reference or delete.
1	28	The word "issues" is extraneous.
3	9	Use the names of the authors with the years of publication in parentheses rather than "their." This discussion could be improved by additional references.
4	3-4	To avoid awkwardness, begin the sentence with "as of August 1983, a total..."
4	19	The reader should be referred to publications that discuss the long-term leaching experiments, or the experimental results should be included.
5		In the title, the word "compositions" should be singular.
6		Add the meaning of the arrows to the legend.
7	5-8	Explain what a thiocyanate tracer is and where and when it was introduced.
9	2	Insert the word "chromatography" after "filtration."
9	26-28	Do not use two different abbreviations for same thing, that is, mg/l and mg/l.
10	22-24	Give the results.
13		Use the selected symbol for milliliters for the elution volume.
14	10-13	Include references or data indicating that the broad peaks in GFC profiles from 260 mLs to 500 mLs (elution volume) are likely to represent inorganic solutes.

<u>Page</u>	<u>Line(s)</u>	<u>Comment</u>
17	28-30	No attempt has apparently been made to identify the high-molecular-weight substances.
20		Use error bars to represent the standard deviations listed in Table 4-2. Curves other than the one shown are possible.
21	17-18	Possibly too much conjecture is evident here.
21	26-33	References are needed for the two "points of view."
21	27	The word "different" is extraneous.
21	32-33	The last sentence of the paragraph is ambiguous.
25	15	Wouldn't 10,000 g damage a microbalance?

REFERENCES

- Bassett, R.L., et al., *Predicting the Reaction State of Brines in Proposed Regions of Nuclear Waste Isolation*, in *Scientific Basis for Nuclear Waste Management*, Vol. 3, J.G. Moore, ed., Plenum Press, New York, N.Y., pp. 27-34 (1981).
- Carothers, W.W., and Kharaka, Y.K., *Aliphatic Acid Anions in Oil-Field Waters — Implications for Origin of Natural Gas*, *American Association of Petroleum Geologists Bulletin*, 62(12):2441-2553 (1978).
- Daniels, W.R., et al., *Summary Report on the Geochemistry of Yucca Mountain and Environs*, Los Alamos National Laboratory Report LA-9328-MS (Dec. 1982).
- Dutton, S.P., et al., *Petroleum Potential of the Palo Duro Basin, Texas Panhandle*, University of Texas at Austin, Bureau of Economic Geology, Report of Investigations No. 123 (1982).
- Means, J.L., *The Importance of Organic Compounds in Ground Water as Radionuclide-Mobilizing Agents*, Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, ONWI-348 (1982a).
- Means, J.L., *The Organic Geochemistry of Deep Ground Waters*, Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, ONWI-268 (1982b).
- Means, J.L., and D.W. Hastings, *Status Report on the Importance of Natural Organic Compounds in Groundwater as Radionuclide-Mobilizing Agents*, Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, ONWI-84 (Dec. 1979).
- Means, J.L., et al., *The Organic Geochemistry of Deep Ground Waters and Radionuclide Partitioning Experiments under Hydrothermal Conditions*, Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, ONWI-448 (1983).
- Molecke, M.A., *A Comparison of Brines Relevant to Nuclear Waste Experimentation*, Sandia National Laboratories Report SAND-83-0516 (May 1983).
- Steindler, M.J., et al., *Fuel Cycle Section Quarterly Progress Report, July-September 1983*, Argonne National Laboratory Report ANL-83-88 (1983).
- Stewart, D.B., and R.W. Potter, *Application of Physical Chemistry of Fluids in Rock Salt at Elevated Temperature and Pressure to Repositories for Radioactive Waste*, in *Scientific Basis for Nuclear Waste Management*, Vol. 1, G.J. McCarthy, ed., Plenum Press, New York, N.Y., pp. 297-311 (1979).
- U.S. Nuclear Regulatory Commission, *Standard Format and Content of Site Characterization Reports for High-Level Waste Geologic Repositories*, Regulatory Guide 4.17 (July 1982).

15/16

APPENDIX A

U.S. DEPARTMENT OF ENERGY LETTER REQUESTING PEER REVIEW

17/8

**Department of Energy
National Waste Terminal
Storage Program Office
505 King Avenue
Columbus, Ohio 43201**

October 27, 1983

Wyman Harrison
EES - 362
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Dear Dr. Harrison:

REVIEW OF ONWI REPORT "THE ORGANIC GEOCHEMISTRY OF DEEP GROUNDWATER FROM THE PALO DURO BASIN, TEXAS"

DOE requests your assistance in performing a review of the subject report by J. L. Means in regard to the following points:

- o Purpose - Does the study satisfy its stated purpose?
- o Procedures - Are the methods used appropriate; are there others we should be using?
- o Are the conclusions valid based on the data presented?
- o Is there an adequate correlation and integration between geochemical interpretation and knowledge of the geologic setting?

We would appreciate receiving any comments by November 21, 1983.

Sincerely,

Thomas A. Baillieul

Thomas A. Baillieul
Acting Director
Site Exploration Office
NWTs Program Office

NPO:LKM:ksw

cc: P. Doyle, DPC

GS# 51-84

19/20

APPENDIX B
CONCURRENCE SHEET

APPENDIX B

CONCURRENCE SHEET

I concur that the Argonne National Laboratory report on ONWI's final report entitled *The Organic Geochemistry of Deep Ground Waters from the Palo Duro Basin, Texas* fairly represents my comments, where incorporated, to the peer review panel.

Douglas G. Brookins

Abraham Lerman

David F. Fenster

Martin G. Seitz

Wyman Harrison

Vassilis Stamoudis

APPENDIX C

CREDENTIALS OF PEER REVIEW PANEL MEMBERS

Douglas G. Brookins

Santa Rosa Junior College: A.A. (1956)

University of California, Berkeley: A.B., Geology (1958)

Massachusetts Institute of Technology: Ph.D., Geochemistry (1963)

Professor Brookins joined the faculty of the Department of Geology at the University of New Mexico, Albuquerque, in 1971 and served as Chairman from 1976 through 1979. He holds part-time positions with the geological surveys of Maine and the United States. Dr. Brookins has been an active participant in several symposia on the scientific basis for nuclear waste management and an active researcher on the Oklo natural reactor and natural analogs. He has served as a consultant to Sandia Laboratories for geochemistry and geochronology at the Waste Isolation Pilot Plant site.

Prior to accepting the position at the University of New Mexico, Dr. Brookins served first as Assistant and then as Associate Professor of Geology at Kansas State University from 1963 to 1971. During that time he had a part-time appointment as a geochemist with the Kansas State Geological Survey. Professor Brookins had had prior experience at the Geochronology Laboratory at MIT; ANCO Corporation, Wilmington, Mass.; California Co., Wy.; Cabot Spectrographic Laboratory at MIT; and Bear Creek Mining Co.

Professor Brookins has published extensively in the fields of geochronology, trace-element studies, isotope geochemistry, uranium deposits, and radioactive waste disposal. His publications related to radioactive waste isolation are on such topics as isotope composition of halite and included brines, the Oklo natural reactor, shale as a repository host rock, thermodynamics of radionuclide migration, Rb-Sr systematics of the Salado Formation (Upper Permian), clay minerals suitable for overpack material, clay mineral-brine interaction during evaporite formation, long-term stability of evaporites, and near-field reactions in evaporites.

Professor Brookins is a member of 31 honorary and professional societies. He is a Fellow of the Geological Society of America and a member of the American Institute of Chemists, the Mineralogical Society of America, and the Explorers Club.

David F. Fenster

City College of the City University of New York: B.A., History (1967)
University of Illinois: M.A., History (1968)
Queens College of the City University of New York: M.S., Geology (1975)
Certified Professional Geologist, No. 4668, American Institute of
Professional Geologists
Certified Professional Geologist, No. 85, State of Indiana

Mr. Fenster joined the staff of the Geoscience and Engineering Group of the Energy and Environmental Systems Division of Argonne National Laboratory in 1982. He is currently Technical Project Manager and member of the multidisciplinary core peer review staff, which is reviewing technical documents for the Salt Repository Project Office of the Civilian Radioactive Waste Management Program. He also served as a technical reviewer for parts of Argonne's Lake Superior regional report related to siting repositories for high-level radioactive waste in crystalline rocks.

Prior to coming to Argonne, Mr. Fenster was Project Geologist with Dames & Moore, Park Ridge, Ill. He had been with Dames & Moore since joining the staff of the Cranford, N.J., office in 1974. During his tenure with Dames & Moore, Mr. Fenster acquired extensive experience in seismotectonics, structural geology, radioactive and hazardous waste disposal, regional geology, engineering geology, hydrogeology, and general geologic field mapping. For example, Mr. Fenster was Principal Investigator for Stratigraphy for the Generic Environmental Impact Statement concerning disposal of radioactive waste in bedded salt, granitic rocks, and argillaceous formations for Oak Ridge National Laboratory. He also worked on a revised draft (unpublished) of a national screening document concerning selecting sites for repositories in crystalline rocks for isolating high-level radioactive waste.

Mr. Fenster also worked on geologic investigations related to nuclear power plant siting and licensing. He is familiar with U.S. Nuclear Regulatory Commission review and licensing procedures, having worked on early site reviews, preliminary safety analysis reports, final safety analysis reports, and detailed fault investigations.

Mr. Fenster has published on the siting of repositories for high-level radioactive waste, midcontinent tectonics, and structural geology in the Northeast, and has worked on more than 30 consulting reports. He is a member of five professional societies, including the Association of Engineering Geologists.

Wyman Harrison

University of Chicago: S.B., Geology (1953), after three years of undergraduate work at Stanford University

University of Chicago: S.M., Geology (1954)

University of Chicago: Ph.D., Geology (1956)

Registered Geologist, No. 2476, State of California

Certified Professional Geologist, No. 134, American Institute of Professional Geologists, and No. 487, State of Virginia

Dr. Harrison is Associate Director for Geoscience and Engineering for Argonne National Laboratory's Energy and Environmental Systems Division. He directs a 25-person group that performs analytical and experimental studies related to management of energy and mineral resources and to development and deployment of related technologies. Major activities of the group include (1) acquisition of geophysical and geotechnical data bases, (2) analysis of the data of geoscience to support design and deployment of energy technologies, and (3) development of physical and mathematical models of geophysical/geotechnical systems.

Dr. Harrison's group recently completed comprehensive surveys of the geoscience data pertaining to crystalline rock complexes in the northeastern and Lake Superior regions of the United States to help assess their potential as possible sites for repositories for high-level radioactive waste. Dr. Harrison has conducted numerous other geological and geotechnical studies at Argonne, ranging from estimating the petroleum resources of selected basins in the Soviet Union to determining near-shore circulation in Lake Michigan.

From 1971 to 1975, Dr. Harrison was Professor of Geography (Associate Department Chairman) at the University of Toronto, where he specialized in geophysical studies related to slope stability in sedimentary terrains and the siting of supertanker ports. Prior to that, he was Associate Director for Physical, Chemical, and Geological Oceanography at the Virginia Institute of Marine Science and a Professor of Marine Science at the University of Virginia. Dr. Harrison was Director of Environmental/Science Services Administration's (now National Oceanic and Atmospheric Administration's) Land and Sea Interaction Laboratory from 1964 to 1968. Before that he was on the faculty of Dartmouth College's Department of Geology and a geologist with the Indiana Geological Survey.

An author of over 100 papers, reports, reviews, and books, Dr. Harrison was made Senior Scientist at Argonne in 1976.

Abraham Lerman

The Hebrew University: M.Sc., Geology (1960)

Harvard University: Ph.D., Geology (1964)

Dr. Lerman joined the Department of Geological Sciences at Northwestern University in 1971 as Associate Professor and has been Professor since 1975. Dr. Lerman has extensive experience in aqueous geochemistry, geochemistry of brines, isotope geochemistry, and radionuclide migration. He is a resource consultant on waste packaging and geochemistry for the Basalt Waste Isolation Project Overview Committee. During 1980 Dr. Lerman was a member of the Backfill Evaluation Panel for Battelle's Pacific Northwest Laboratory.

While associated with Northwestern University, Dr. Lerman has served, at various times, as a visiting professor at several European universities. Prior to joining the faculty at Northwestern, he was a Research Scientist in Chemical Limnology at the Canada Centre for Inland Waters (1969-1971), a Visiting Investigator and Senior Scientist in Isotope Research at Weizman Institute of Science (1966-1969), an Assistant Professor of Geology at the University of Illinois at Chicago Circle Campus (1965-1968), a Visiting Investigator (geochemistry) at Lamont-Doherty Geological Observatory of Columbia University (Summer, 1965), and a Lecturer and Assistant Professor of Geology at the Johns Hopkins University (1964-1965).

Dr. Lerman has published extensively in the areas of geochemical processes in water and sediments, halite and brines, chemical limnology, geochemical cycles, and radionuclides in sediments. He is a member of five professional societies and a Fellow of the Geological Society of America.

Martin G. Seitz

University of Missouri: B.S., Engineering Physics (1966)

Washington University: Ph.D., Geophysics (1971)

Dr. Seitz is a geochemist in the Geochemistry Group of the Chemical Technology Division of Argonne National Laboratory, where he manages applied and basic experimental programs. Ongoing applied programs related to nuclear waste disposal are to investigate interactions of materials proposed to be used in disposing of nuclear waste and to learn how backfill materials would be affected by the conditions of nuclear waste disposal. The basic research program of the group is to study trace-element migration in the earth's crust. Current work focuses on the role of organics in mobilizing heavy metals and on the movement of phenol compounds through water-bearing rock.

In the past year, Dr. Seitz served with seven others on the Panel to Assess the Technical Basis of 10 CFR 60, the proposed U.S. Nuclear Regulatory Commission rule for licensing a high-level waste repository. Dr. Seitz also completed experimental work on radionuclide retention in salt (Waste Isolation Pilot Plant) and helped develop logging methods in bore holes to detect petroleum. He has organized workshops on nuclear and hazardous waste disposal and has done geologic field work with university and U.S. Geological Survey staff.

Before coming to Argonne, Dr. Seitz worked as a fellow at the Geophysical Laboratory of the Carnegie Institution of Washington, where he studied the chemical partitioning and solid diffusion of trace elements in igneous rock. Having received a National Defense Act fellowship for graduate work, Dr. Seitz determined rock ages from products of spontaneous fission and studied the distributions of uranium and thorium in igneous rocks.

Dr. Seitz has published over 60 papers in scientific journals, primarily on geochemical topics.

Vassilis C. Stamoudis

University of Athens, Greece: B.S., Chemistry (1967)

Michigan State University: Ph.D., Organic Chemistry (1972)

Dr. Stamoudis is a principal investigator in the Geochemistry Section of the Geoscience and Engineering Group in the Energy and Environmental Systems Division at Argonne National Laboratory. He is currently working on several long-range interdisciplinary research programs to study the environmental and health effects of energy-related industrial plants. His major tasks include chemical characterization of process streams from coal-conversion pilot plants and process development units; development of schemes for rapid analysis of complex mixtures produced by synthetic fuel processes; and determination of chemical-structure/biological-activity relationships in coal-derived condensates. Dr. Vassilis is highly experienced in applying analytical techniques such as gas chromatography, gas-chromatography/mass-spectrometry, and high-performance liquid chromatography, with emphasis on computer-assisted interpretation.

Prior to joining the Argonne staff in 1978, Dr. Stamoudis was an Associate Marine Scientist and Assistant Professor at the Virginia Institute of Marine Science and College of William and Mary. He was coprincipal investigator of two comprehensive, interdisciplinary research programs to study the effects of oil spills in the marine environment. Dr. Stamoudis developed analytical methods for extraction and separation of organic compounds and conducted extensive analyses of numerous complex environmental extracts using liquid chromatography, thin layer chromatography, capillary-column gas chromatography, and gas-chromatography/mass-spectrometry/data-system. Additional experience was gained during a postdoctoral fellowship at the Department of Chemistry at Northwestern University from 1973 to 1975.

Dr. Stamoudis has published extensively in the fields of environmental and analytical organic chemistry. He is an author of over 41 papers and a member of eight professional societies.