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NUCLEAR WASTE PROGRAM

Report #5

Review of the "Hydrochemical Data Base
for the Hanford Site, Washington,"
T.O. Early, R.D. Mudd, G.D. Spice and
D.L. Starr, Rockwell Hanford Operations
February, 1985, SD-SBI-DP-061

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SUBJECT: Review of the "Hydrochemical Data Base for the Hanford Site, Washington", T.O. Early, R.D. Mudd, G.D. Spice and D.L. Starr, Rockwell Hanford Operations, February, 1985, SD-BWI-DP-061.

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INTRODUCTION

Rockwell Hanford Operations (RHO) have compiled a hydrochemical data base for the Hanford Site, with sample collection and analyses starting in 1977 and continuing until present. Studies utilizing the data base will be used to predict the ability of the repository to isolate nuclear waste over periods of time specified in the NRC (10 CFR Part 60) and EPA (41 CFR Part 191) standards.

The Hanford hydrochemical data base contains the data accumulated for the Basalt Waste Isolation Project (BWIP), and is divided into three main sections: 1) the sample event information (i.e., identifying label of sample, location of sample, date of sample collection, procedure for sample collection, and source of data), 2) field measurement results (i.e., conductivity, alkalinity, turbidity, pH, redox potential and surface and in situ temperatures), and 3) laboratory measurement results (i.e., major, minor and trace inorganic component concentrations, total carbon concentration, total organic carbon concentration (TOC), dissolved gases, stable isotope and radioactive component concentrations).

The majority of the data was collected and analyzed by Rockwell laboratories on samples collected by Rockwell personnel from 1977 to 1980. BWIP began sample collection in 1980, and by the year 1982,

BWIP was operating its own laboratory. However, some constituents (e.g., tritium) which require specialized equipment were analyzed by subcontractors (Graham, 1984). In all, the data base is comprised of data contributed by sixteen different sources. These sources include the Basalt Waste Isolation Project, Rockwell Hanford Operations, U.S. Geological Survey, Lawrence Berkeley Laboratories and Pacific Northwest Laboratories. It is essential for BWIP to demonstrate that no additional uncertainty in the data base is introduced by the numerous different laboratories that contributed to the project.

EVALUATION OF DATA BASE

Six methods to test sample representativeness have been applied to the data. Sample representativeness is a measure of how closely the sample represents true formation groundwater conditions (Graham, 1984). BWIP will evaluate the integrity of the data base based on examination of 1) the charge balance for each sample, 2) total cation concentration versus specific conductance, 3) total anion concentration versus specific conductance, 4) comparison of duplicate analyses, and 5) participation in interlaboratory analyses programs (Early et al., 1985).

Calculation of the charge balance determines how closely an analyzed water sample achieves electrical neutrality. Since a water sample must be neutral in charge, deviation from neutrality indicates possible error in analyses. Therefore, BWIP proposes to utilize charge balance as a measure of sample representativeness.

To determine the charge balance error between the observed total cations and total anions (each measured in milliequivalents/L), the

following equation was employed:

$$\text{Calculated Balance} = \frac{\text{cations}}{\text{cations}} - \frac{\text{anions}}{+ \text{anions}} \times 100$$

The charge balance error is expressed as a negative or positive percentage. BWIP has tentatively adopted a maximum allowable deviation of +5 percent as a criterion to screen analyses for use in hydrochemical interpretation. The +5 percent criterion is an accepted standard for determining sample representativeness. Although no confidence limits can be applied to the +5 percent criterion, samples that fall within the set limits are considered analytically acceptable (Freeze and Cherry, 1979, page 97).

The NRC suggests that a +5 percent error acceptance criterion is too strict (SCR, March 1983, p. F-5). The NRC indicate that a +10 percent error acceptance limit would be considered satisfactory. The +10 percent limit would allow the retention of useful data that the +5 percent limit would exclude from the study. The NRC suggests that the total number of chemical analyses from the Grande Ronde is inadequate and elimination of data unnecessarily due to overly stringent criterion is unwarranted.

The charge balance evaluation is based on major inorganic species. The cations that BWIP studied include: K^+ , Mg^{2+} , Ca^{2+} and Na^+ ; whereas, the anions include: Cl^- , F^- , SO_4^{2-} , NO_3^- and PO_4^{3-} . Since the carbonate system must also be included in the total anion concentration, BWIP utilized $CaCO_3$ alkalinity field measurements to quantify the carbonate anion concentrations of HCO_3^- and CO_3^{2-} . Alkalinity is only an approximation for the carbonate concentrations.

It is defined as the capacity of water to accept protons and includes both carbonate (HCO_3^- and CO_3^{2-}) and noncarbonate (H_2BO_3^- , H_3SiO_4^- , OH^- , etc.) species. The H_3SiO_4^- concentrations measured range from 2 to 60 mg/L and will have a definite effect on the charge balance calculation. Since there is no general agreement as to the precise correction for noncarbonate alkalinity, the anion concentration calculated by BWIP is greater than the actual value. Since the carbonate concentration dominates the total anion concentration, an approximation for this value introduces uncertainty. It is difficult to quantify the precise amount of uncertainty introduced because the amount will vary from sample to sample depending on pH and the concentration of noncarbonate species.

Another problem that introduces potential error in the determination of the charge balance calculation is the inclusion of major inorganic concentrations (SO_4^{2-} , PO_4^{3-} and NO_3^-) that are not accurately known. These unknown, but detected concentration values are represented in the data base as numerical values preceded by the symbol "<" (Early et al., 1985). The detection limits of the ions with unknown concentrations are then incorporated into the calculation of the total anion and total cation concentrations which results in values greater than the actual value. In addition, it has been noted that discrepancies occur in the total anion concentrations of the samples as a result of incorporation of the anions NO_3^- , Br^- , and PO_4^{3-} in the summation. It has been observed that these anions are included in the calculation when values are presented in the data base; the concentrations are included whether the concentration had been analytically determined or just detected in the sample. However, in many cases, concentration values do not appear and gaps are present

in the data base. It is unclear why the analytical laboratories left gaps in the data, unless sample analyses were not properly conducted and could not be repeated; therefore, BWIP should clarify the presence of such gaps.

The uncertainties which are present in BWIP's calculation of total cation and total anion charge calculation (e.g., using an approximation for the carbonate species in solution over a wide range of pH, inclusion of inorganic species with unknown concentrations, and gaps in the data) suggest that the upper limit of ± 5 percent of neutrality, rather than the ± 10 percent limit suggested by the NRC, be kept. The present data base has been evaluated according to the ± 5 percent criterion set by BWIP (Early et al., 1985).

Based on the statistics of charge balance results, BWIP has calculated that over 90 percent of the samples are within ± 5 percent of neutrality (Early et al., 1985). However, this statistic is based on the charge balance results for all water samples tested; this includes unconfined aquifer, confined aquifer, precipitation, spring and surface water samples. Analyses performed on the unconfined aquifer, precipitation, spring and surface water samples are more representative of true formation conditions than those determined on the confined aquifer (problems arise from drilling fluid contamination, changes in temperature from in situ conditions to surface conditions, degassing, changes in pH and Eh, etc.). Since hydrochemical interpretation and long-range prediction depend on the representativeness of data obtained from the confined aquifers, it is recommended to evaluate the data base specifically in terms of the confined aquifer. When these calculations are made, it is found, as

indicated by BWIP (Early et al., 1985), that only 11 percent of the samples have been eliminated from the data base due to a charge balance exceeding ± 5 percent of neutrality. However, it can be easily verified that charge balance computations were not calculated for all samples; only 360 of the 470 confined aquifer samples were tested using the charge balance equation, and of the tested samples, 51 failed to meet the ± 5 percent criterion set by BWIP. Therefore, only 85 percent of the analyses presented are within the ± 5 percent acceptance limit.

In conclusion, the greatest source of uncertainty in calculation of the charge balance is the approximation made for the alkalinity measurement which incorporates high concentrations of noncarbonate species such as H_3SiO_4^- . The concentrations incorporated into the charge balance calculation due to inclusion of unknown, but detected anion and cation concentrations are insignificant relative to the carbonate contribution and will have little effect on the calculation. However, the accumulation of such errors could be significant.

The samples that failed to meet the ± 5 percent criterion probably did so as a result of poor analytical technique. Some anion analyses are very complicated and error may be introduced (Jones, 1982). Therefore, these samples should be excluded from further use in characterizing the repository because they may lead to misleading information concerning the solubility and sorption of key radionuclides.

In addition to the charge balance, BWIP utilized a comparison of total cation concentration versus specific conductance and total anion concentration versus specific conductance (Early et al., 1985). The specific conductance of an aqueous solution is attributed to the

conductances of the individual cations and anions in solution. Therefore, the conductance measurement provides an indication of the concentration based on the relationship:

$$C = AB$$

where C is defined as the conductance, B is defined as the total concentration of dissolved solids in units of meq/L, and A is a conversion factor (Hem, 1971). Based on methods published for the examination of water and wastewater (APHA, 1971), BWIP suggests that deviation from the relationship may indicate which component(s) are in error (Early et al, 1985). It may also indicate faulty analysis of specific conductance.

Several problems are inherent in this type of test and the results can not be regarded as more than an approximation because specific conductance can not be quantitatively compared to the sum of total anions and the sum of total cations individually. The sum of the anions usually deviates slightly from that of the cations and the above value of B must be taken as an average of both sums (Matthess, 1982). Therefore, the specific conductance can not be compared exactly to the individual concentrations as indicated by BWIP (Early et al., 1985).

In addition, the relationship between specific conductance and ionic concentration becomes more complicated as the solution becomes less dilute. For example, for total dissolved solid (TDS) concentrations (B = 3.0 to 10.0 meq/L). Matthess (1982) described the following relationship:

$$C = B(95.5 - 5.54(\log B))$$

where C is defined as the specific conductance and B is the ionic

concentration. As the relationship becomes more complex, the error increases to more than 15 percent. The TDS concentrations calculated for the Hanford Site fall into the 3.0 to 10.0 meq/L range which precludes the use of a linear relationship.

Finally, the measurement of specific conductance is subject to error due to temperature dependence. Conductivity exhibits an approximately 2 percent increase for every one degree Celsius rise in temperature (Hem, 1971). The BWIP laboratory assumes a temperature of 25°C which may differ significantly from field temperature and radically from in situ temperature, thus introducing uncertainty.

Based on the specific conductance versus total cation and total anion concentration comparisons, BWIP identified ten samples which were in error. The anomalous samples plotted outside the 95 percent confidence limit boundaries set by BWIP (Early et al., 1985) on a linear plot of specific conductance versus total cation (meq/L) and total anion (meq/L) concentrations at 25°C. It is recommended that these ten samples be omitted from future studies due to possible problems in analyses of concentrations and/or sample contamination.

Duplicate analyses were also utilized to test sample representativeness. Duplicate analyses were performed on nearly all samples analyzed after 1980 (Early et al., 1985). BWIP computed the deviation percent of duplicate samples using the following equation:

$$\text{Deviation Percent} = \frac{M_1 - M_2}{M} \times 100$$

where M_1 is defined as the ionic concentration in the first duplicate, M_2 is defined as the concentration in the second and M is the

concentration of either M_1 or M_2 . Duplicate samples with a deviation greater than ± 5 percent are designated as anomalous.

BWIP did not report the percentage of samples that exceeded the ± 5 percent criterion; however, it can be easily verified that 10 percent of the samples in the confined aquifer exceeded this criterion and should not be used in future studies. It is also suggested that both duplicate samples be eliminated in the event that one sample is designated as anomalous based on faulty charge balance calculation or specific conductance versus concentration.

It should also be noted that duplicate analyses were not performed for every constituent. Duplicate analyses were only performed on the major inorganic species: Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , F^- and SO_4^{2-} . The alkalinity measurement was not analyzed in duplicate analyses because BWIP considers it to be a "major, likely source of error". BWIP (Early et al., 1985) suggests that error in alkalinity may be detected in the total anion versus specific conductance check; however, total anion versus specific conductance is not an adequate method for identifying errors in alkalinity because it is not possible to compare individual components to specific conductance (Matthess, 1982). In addition, this type of comparison is highly site-specific and dependent upon concentration and temperature. Therefore, duplicate alkalinity analyses are needed, especially since alkalinity represents the entire carbonate system and is closely linked to pH.

Duplicate analyses were only determined for species with concentrations exceeding 5 mg/L of each species in solution. This restriction limits the data that will be checked and totally excludes trace element, radioisotope, and stable isotope concentrations from

being checked. Due to the analytical uncertainties, which increase as concentrations decrease, a comparison of duplicate analyses for trace element concentrations is necessary to insure a higher degree of confidence in data quality. BWIP proposes to include duplicate trace element comparisons in future studies; in that case, it would be crucial to evaluate representativeness of the data collected between 1977 and the start of duplicate trace element comparisons to the data evaluated by this new comparison.

EVALUATION OF SAMPLE REPRESENTATIVENESS

A major problem facing BWIP is the evaluation of sample representativeness in relation to sample collection. Drilling of the boreholes required the use of drilling fluids which consisted of a mixture of Columbia River water (with high tritium concentrations), bentonite, organic polymers, soda ash and chromium lignosulfonate (Graham et al., 1985). Before representative samples can be obtained, the drilling fluid must be removed and well development assessed. BWIP evaluates well development based on the ratio of the volume of drilling fluid removed divided by the volume of drilling fluid lost to the zone during drilling. Since the volume of fluid lost is only roughly known, the ratio is qualitative (Graham, 1984). BWIP defines an arbitrary well development ratio of 5 as representative. However, it is possible that some particulate material related to drilling fluid is still in the zone and removal of this material is slower than removal of the dissolved constituents at a development ratio of 5 and the well may still be contaminated. Hence, BWIP also evaluates the degree of well development by measuring the tritium, total organic

carbon (TOC) and fluorescein dye contamination. These three components act as tracers and aid in determination of true formation conditions within a well. However, fluorescein dye is a qualitative measurement and TOC is difficult to assess because drilling fluid composition can be variable. No definite criterion has been suggested to judge contamination (Early et al., 1983). Therefore, BWIP relies heavily on determination of tritium contamination to assess well development. Since tritium has a half-life of 12.3 years, groundwater isolated from the atmosphere for longer than 100 years should be free of tritium activity. The drilling fluid mixture contains Columbia River water, which has a natural tritium spike of 50 TU (TU, defined as a tritium unit, is equivalent to the concentration of 1 atom of tritium in 10^{18} atoms of hydrogen and is equal to 3.23 pCi/L); the river water is ideal for use in evaluating well development. However, several problems are associated with this method. Analysis of low tritium activities are time-consuming and expensive; therefore, BWIP only samples for tritium contamination when the final hydrochemical samples are collected. Actual results pertaining to tritium activity and well development take several weeks to evaluate. Hence, to assess well development in the field, BWIP depends on the qualitative methods of fluorescein dye and TOC, and utilizes tritium activity as a final check only.

To assess sample representativeness, BWIP has employed a series of checks to evaluate problems related to drilling and sampling techniques. These checks include: 1) comparison of multiple analyses from the same borehole, 2) evaluation of tritium contamination in groundwater, 3) evaluation of organic carbon contamination in groundwater, and 4) evaluation of dissolved gas

contamination.

BWIP reports that comparison of multiple analyses from the same producing zone in a borehole have been performed by different laboratories. However, BWIP indicates that these analyses were only performed "occasionally" and that several significant deviations result from intercomparisons of major chemical constituents (i.e., Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Si^{4+} , Cl^- , F^- , SO_4^{2-} and alkalinity). BWIP has chosen an arbitrary figure of 25 percent deviation from the mean to identify anomalous samples.

Problems in evaluating this technique result from BWIP's loose definition of the frequency in which samples were analyzed; the term "occasionally" has little meaning. In addition, the intercomparisons are limited to major constituents or ions with concentrations greater than 10 mg/L. Since a greater degree of uncertainty is associated with trace elements, stable isotope and radioisotope concentrations, greater attention should be directed toward assessing their representativeness before use in modeling.

To evaluate tritium contamination in samples, BWIP, in 1984, had designated an arbitrary figure of tritium ≤ 1 TU to indicate sample representativeness. But, using this definition, BWIP discovered that 79 samples exhibited contamination in the confined aquifer; hence, in 1985, BWIP re-evaluated their definition of tritium contamination and concluded that tritium values ≤ 5 TU were acceptable. Only 30 samples show contamination using the new criteria.

Although the change in definition allows BWIP to retain more data, the present definition of sample contamination (tritium activity ≤ 5 TU) may not adequately demonstrate sample representativeness and

may compromise ground water geochemical analyses. Graham et al. (1985) found that contamination from drilling fluid was apparent in borehole DC-14 at a tritium level ≤ 1 TU. After measuring TOC values well above base line concentrations, Graham et al. (1985) concluded that TOC and fluorescein dye are highly reactive and sorb to clays, thus being removed at a slower rate than tritium. Therefore, groundwater samples taken at this activity level may be contaminated with drilling mud and do not represent true formation conditions.

Analyses of sample contamination by drilling fluid in Borehole DC-14 (Graham et al., 1985) demonstrate that the concentrations of major inorganic species are affected. The concentrations of Na^+ , K^+ , Ca^{2+} , SO_4^{2-} and all carbonate species increased; whereas, the concentrations of Cl^- , F^- and Si^{4+} decreased as a function of drilling mud/fluid contamination. The concentrations of minor inorganic species (trace elements) were not analyzed.

Therefore, the definition of sample contamination due to drilling fluid contamination should be lowered to tritium activity ≤ 1 TU to insure sample representativeness.

The NRC is satisfied with the 1984 BWIP definition of contamination (tritium ≤ 1 TU) and indicate that they do not believe that this level of contamination will have a substantial influence on the "gross" chemical composition of samples. However, they are concerned that the drilling fluid could significantly alter the concentration of major inorganic cations such as Ca^{2+} , Na^+ and K^+ and jeopardize the integrity of the trace elements. Therefore, the NRC suggests that all future boreholes be drilled without the use of drilling fluid, but they do not offer any guidelines as to how the two data sets (samples collected from boreholes drilled with the fluid and

samples collected from boreholes drilled without the fluid) are to be combined.

BWIP may also determine sample representativeness on the basis of organic carbon contamination. As discussed above, organic components are included in the drilling fluid and high organic carbon concentrations in the samples ($\text{TOC} \geq 10 \text{ mg/L}$) may be indicative of contamination. However, the TOC measurement is highly qualitative due to variation in drilling fluid composition and it is difficult to assess. Therefore, the thirteen samples in the data base that exceed the "greater than 10 mg/L organic carbon content criterion" should be excluded from future studies due to the strong possibility of sample contamination.

BWIP is also utilizing oxygen content of samples as a check of sample contamination. BWIP suggests that samples containing significant amounts of oxygen (i.e., greater than 1 percent oxygen) are contaminated (Early et al, 1985). This is based on the idea that reducing conditions prevail in the groundwaters and oxygen concentrations should be low.

BWIP suggests that samples can be corrected for oxygen contamination using the normal composition of air. However, many very important parameters are affected by atmospheric exposure (e.g., pH and Eh), and it is not possible to accurately correct these values. Therefore, the sixteen samples in the data base which exhibit atmospheric contamination should not be considered as representative and should be eliminated from future work.

CONCLUSION

In conclusion, several key issues need to be addressed by BWIP before adequate interpretation of the data base can be made.

- 1) It is crucial that BWIP present detailed descriptions of their groundwater sampling and analytical procedures to enable better evaluation of the representativeness of the geochemical data base.
- 2) BWIP should explicitly describe the procedures followed before and after 1982 (the year BWIP became responsible for all field work and operations).
- 3) A thorough explanation detailing BWIP's procedure for combining data from different laboratories and different time periods is necessary to ensure quality assurance. Inclusion of percent error of data and accuracy and precision of instrumentation is recommended.
- 4) The 152 samples in the data base that did not meet the criteria set by BWIP (Early et al., 1985) should be considered anomalous and unrepresentative of true formation conditions. These samples should not be included in future studies that will lead to predictions concerning the Hanford Site as a possible nuclear repository.
- 5) More attention should be given to testing the integrity of the trace elements, radioisotope and stable isotope analyses. It has been noted several times by BWIP that these constituents are most subject to contamination, and yet, BWIP has done little to assess their representativeness.

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