LR-287-12
09/09/85

LETTER REPORT

TITLE: Review of Chlorine Isotopes as Environmental Tracers in Columbia River Basalt Groundwaters, RHO-BW-SA-372 P, March 1984, by D. Graham, S. Gifford, and H. Bentley.

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PROJECT TITLE: Technical Assistance in Geochemistry

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ACTIVITY NUMBER: ORNL #41 37 54 92 4 (FIN No. B0287)
NRC #50 19 03 01

SUMMARY

This report is one of the most comprehensive analyses of chlorine isotope systematics for a groundwater system. The authors, through an analysis of ^{36}Cl, ^{37}Cl, and deuterium data, clearly show that there are two sources of chloride in the groundwater system at the Hanford Site. The authors go on to suggest that some degree of vertical mixing of groundwater is occurring within the Wanapum basalt. The source of the deep, high-chloride groundwater (thought to be old, perhaps >300,000 years), is either: (1) leaching from the basalt, (2) transport into the basalt from below, or (3) a combination of (1) and (2). At least one sample of the deep groundwater was identified by the authors as being "old" (>300,000 years), although changes in the assumptions used for the analysis of mixing relationships could alter this conclusion to either exclude any groundwaters from being old or to include more groundwaters as being old. The report, correctly, does not attempt to relate the chlorine data to absolute groundwater velocities or travel times. The source of the deep, saline groundwater is too uncertain at this time to warrant such an analysis. Rather, the authors restrict themselves to the issues of recharge/discharge locations and the location and extent of vertical mixing within the hydrologic system at the Hanford Site. The analysis, though it could be strengthened in some specific areas (see detailed evaluation), provides a good basis for further characterization of the hydrologic system at the Hanford Site through studies of groundwater geochemistry.

REVIEW OF REPORT

This report, which was presented as a paper at the 17th International Congress of the International Association of Hydrologists, summarizes the results and preliminary interpretations of data on ^{36}Cl and ^{37}Cl isotopes in groundwaters from the Hanford Site. The authors report on the isotope systematics of chlorine and how they can be used to help evaluate the hydrologic setting of the Hanford site through the identification of: (1) groundwater recharge/discharge locations, (2) the location and extent of vertical leakage between aquifers, (3) sources of groundwater solutes, and (4) groundwater age and velocity (providing that the sources, sinks, and mixing characteristics can be confidently established).

The authors state that chlorine isotopes are considered good environmental tracers because they have little tendency to be sorbed onto geologic materials and their geochemical behavior is well known and relatively simple. Variations of the stable isotopic ratio $^{37}Cl/^{35}Cl$ in groundwaters are generally small, but measurable (e.g., <1 per mill deviation from SMOC [Standard Mean Ocean Chloride]). The authors recognize that although the mechanisms of fractionation are somewhat speculative at this time, $^{37}Cl/^{35}Cl$ systematics can be useful in identifying groundwater recharge/discharge and mixing relationships.

The radioisotope ^{36}Cl has a half-life of 300,000 years and is generated in groundwaters via three processes: (1) cosmic ray interactions in the atmosphere with subsequent incorporation into meteoric recharge waters, (2) cosmic ray spallation of K and Ca in near-surface rocks and soils, and (3) in the deep subsurface by neutron activation of ^{35}Cl from neutrons produced from the fission of ^{238}U and the interaction of alpha particles (from U and Th) with light elements. A pulse of ^{36}Cl, which peaked in 1958, was also produced as a result of tests of nuclear weapons conducted in the atmosphere.

The authors calculate two sets of mixing curves for the relationship $^{36}Cl/Cl$ vs 1/Cl (see report for equations used). Four meteoric waters and two deep groundwaters were used to generate the two sets of mixing curves. The characteristics of the waters used in the calculations are summarized in Table 1 below. The deep groundwater of Set 1 (Fig. 5, sheet 1 of 2) has an initial Cl concentration similar to the most concentrated groundwater found at Hanford to date. The $^{36}Cl/Cl$ ratio of this groundwater was assumed by the authors to be typical for a basalt. The deep groundwater of Set 2 (Fig. 5, sheet 2 of 2) was assigned characteristics representative of a source leached from basalt with a secular equilibrium value for $^{36}Cl/Cl$ of 4 x 10^{15}. The meteoric waters for Curves 1-3 had a range of Cl concentrations from 1.8 to 18 mg/L and a $^{36}Cl/Cl$ ratio similar to the highest value measured for the groundwaters at Hanford. The meteoric groundwater for Curve 4 was assigned 4.5 mg/L of input chloride having undergone 600,000 years of decay.

TABLE 1. Groundwater characteristics used for mixing calculations

	Meteoric waters		Deep groundwaters	
	Cl (mg/L)	$^{36}Cl/Cl$ (x 10^{15})	Cl (mg/L)	$^{36}Cl/Cl$ (x 10^{15})
Set 1 (Fig. 5, sheet 1 of 2)				
Curve 1	1.8	1000	600	4
Curve 2	4.5	1000	600	4
Curve 3	18.	1000	600	4
Curve 4	4.5	250 (approximate: decay of two ^{36}Cl half-lives)	600	4
Set 2 (Fig. 5, sheet 2 of 2)				
Curve 1	1.8	1000	Leached from Basalt (actual characteristics not reported)	
Curve 2	4.5	1000		
Curve 3	18.	1000		
Curve 4	4.5	250 (approximate: decay of two ^{36}Cl half-lives)		

The authors compared the data for 21 groundwater samples from the Grande Ronde, Wanapum, and Saddle Mountains basalts to the calculated mixing curves. The authors conclude that the Grande Ronde waters clustered near the deep, saline end member groundwater, while the Saddle Mountains and Wanapum samples grouped near the meteoric end member (although the authors point out that two Wanapum samples appear to have some component of the deep groundwater). One Grande Ronde groundwater plotted outside the range of mixing curves for the recent recharge waters (Curves 1-3) and was interpreted by the authors to suggest decay of greater than one half-life of ^{36}Cl. The authors state that the well-defined mixing trends suggest that another source of chloride besides meteoric recharge waters may be present in the hydrologic system at the Hanford Site. The Grande Ronde waters were interpreted to have a significant portion of nonmeteoric chloride, while the Saddle Mountains and Wanapum (most) waters appear to be meteoric. The authors suggest that data for a few Wanapum samples may be indicative of mixing of the two chloride sources within the Wanapum. The authors state that the results are not conclusive as to whether the source of nonmeteoric chloride is: (1) leached from the basalts, (2) transported into the basalt hydrologic system from below the basalts, or (3) some combination of (1) and (2). The authors suggest that the source of high-chloride water from below the basalts could be a sedimentary formation.

The ^{37}Cl/^{35}Cl data (Fig. 6) indicate a significant difference between the groundwaters from the McGee and Enyeart wells and all the other wells sampled. The authors suggest that, because the McGee and Enyeart wells have ^{36}Cl/Cl ratios representative of modern meteoric input, the McGee and Enyeart wells are receiving modern meteoric recharge, while the other wells are receiving some portion of their recharge from a nonmeteoric source. The ^{36}Cl/Cl and ^{37}Cl/^{35}Cl data suggest the source of the distinct deep water to be external to the basalts, rather than leaching from the basalt, although the authors state that because some component of each type of groundwater is present in all water samples, leaching of the basalt could be the source for the distinct chloride. The deuterium data support the influent water hypothesis because leaching would not add significant deuterium to the groundwaters (the deuterium values for the deep groundwater are higher than current meteoric water values). However, it is possible that the Grande Ronde was simply recharged under different climatic conditions than the Saddle Mountains and Wanapum aquifers, thus having different deuterium values.

The authors suggest a conceptual model of groundwater flow as follows: (1) downward recharge in the vicinity of the McGee and Enyeart wells (based on deuterium, ^{36}Cl/Cl, and ^{37}Cl/^{35}Cl data, (2) shallow circulation through the Saddle Mountains and Wanapum basalts (based on ^{36}Cl/Cl data, and (3) upward flow from the Grande Ronde to the Wanapum southeast of the RRL (based on ^{36}Cl/Cl data). The authors hypothesize that the Grande Ronde is being partially recharged from beneath with old (perhaps >300,000 years) waters of probable meteoric origin, and that this old water was recharged under different climatic conditions than the Saddle Mountains and Wanapum aquifers. The authors state that the source of the chloride is yet to be established.

EVALUATION OF REPORT

The subject report represents one of the most comprehensive studies of chlorine isotope systematics for a groundwater system. Unfortunately, the report is of a summary nature, and many of the important details are not included, nor referenced to previously published reports. The conclusions and context of the report are generally substantiated by the data presented. However, there are some specific concerns related to the data and interpretations that are discussed below.

1. The report is of a summary nature and contains no details pertaining to the sampling procedures used to collect and preserve water samples. No reference is made to previous reports that might contain this information. No justification is given for the particular choice of wells to be sampled. There are many other wells on and around the Hanford Site that could have been sampled which would help to substantiate, or negate some of the conclusions of the report. A discussion of how the chlorine data relate to other hydrologic data would greatly increase the utility of the report. For example, relating the chlorine data to major element chemistry, ^{14}C data, hydrologic head measurements, hydraulic conductivities, etc. could perhaps shed some light on some of the more equivocal interpretations of this report. No discussion of key areas for future work are discussed that could help to identify the weaknesses of the current study and to flag those areas that will be addressed in future studies.

2. The scattered geographic and depth distribution of samples from wells does not provide adequate support for the conclusions of the report. The available data are suggestive of interesting trends, but one can question whether the data quantitatively support any conclusive relationships. For example, on page 8 it is stated that "^{36}Cl data indicate that the McGee and Enyeart wells have a modern meteoric input similar to other Saddle Mountains and Wanapum samples." However, there is only one datum for ^{36}Cl reported — a sample from only one depth within the McGee well. Thus, the quoted statement is not substantiated by the data presented. In an analysis of any groundwater system, the three-dimensional characteristics are of critical importance to its interpretation. Relating the chlorine isotope systematics to other hydrologic parameters might help to identify relevant three-dimensional patterns that would quantitatively describe the hydrologic system (see comment #1), but the authors make no attempt to do this.

3. The authors state that eleven groundwater samples from the Grande Ronde basalt were analyzed for $^{37}Cl/^{35}Cl$ (page 5, paragraph 4). However, only seven samples from the Grande Ronde are listed in Table 2 of the report.

4. The reference to the unpublished thesis of Kuhn (1983 or 1984, both dates are referred to within the report) is not included in the list of references.

5. The report lists an analytical error of ±0.1 per mill for the $^{37}Cl/^{35}Cl$ values. However, the reference of Kaufmann et al. (1984) listed in the report states a total analytical standard deviation of ± 0.24 per mill as the best achievable in their laboratory. The interpretation and basis for the value of the stated analytical error needs to be substantiated. It should be noted that if the uncertainty on the $^{37}Cl/^{35}Cl$ values is doubled, the differences between the McGee and Enyeart wells vs the others wells remains (see Fig. 6), but the separation in $^{37}Cl/^{35}Cl$ becomes much less and the apparent difference between wells could be attributed to chloride concentration alone. It is also interesting to note that the deepest sample from the McGee well has distinctly different characteristics from the shallower samples. The $^{37}Cl/^{35}Cl$ and total chloride are more similar to some of the samples from other wells than to the upper portions of the McGee

well. One could speculate that the Grande Ronde basalt deep within the McGee well is part of a unique hydrologic system that is different from that in the shallower portions of the McGee well.

6. The following comments refer to the mixing curves on Fig. 5 (sheets 1 and 2).

6A. The sensitivity of the results and interpretations to the initial assumptions need to be established before substantial conclusions can be drawn from the analysis. For example, if end member compositions (especially the deep-water end member where only one value was used) are changed slightly, what is the result on the mixing relations? Would the one sample that shows decay of ^{36}Cl still fall outside the envelope of mixing of recent waters if the initial assumptions were altered slightly?

6B. The assumptions related to the deep-water end member for the mixing curves of Set 1 (see Table 1 of review and Fig. 5, sheet 1 of 2 of report) appear to be somewhat questionable. A groundwater with a chloride concentration of 600 mg/L is assumed to have a $^{36}Cl/Cl$ ratio typical for basalt. This $^{36}Cl/Cl$ relationship assumes that some degree of equilibration has occurred between the groundwater and the basalt. However, equilibration of water and basalt is not likely to evolve a chloride concentration of 600 mg/L (DAVIS 1982). Therefore, the end member water may have an inconsistent basis — a chloride value requiring an external source and a $^{36}Cl/Cl$ ratio assumed to result from equilibration. The implications of this apparent inconsistency to the results of the mixing analysis are not entirely clear, but certainly point out the need to perform a somewhat more extensive sensitivity analysis. A suggested alternative would be to assume various $^{36}Cl/Cl$ ratios to determine the sensitivity of the analysis to this parameter.

6C. The characteristics of the deep-water end member for the mixing curves of Set 2 (see Table 1 of review and Fig. 5, sheet 2 of 2 in report) are not defined. The $^{36}Cl/Cl$ ratio is given as 4×10^{15}, but the total chloride concentration is not defined. This value needs to be identified so that it can be checked for consistency with available field data and basalt/water interaction experimental data.

6D. The abstract states that "The highest ^{36}Cl ratios were interpreted as modern input of ^{36}Cl and are two to three times that predicted for this latitude." This apparent disagreement with predicted ^{36}Cl ratios is not discussed further within the report. The implication of this discrepancy needs to be addressed. Especially with regard to the choice of potentially anomalous meteoric end members for the mixing analysis. It is likely that the shape and extent of the mixing envelopes would change, thus affecting the interpretation of recharge/discharge and estimates of groundwater "age."

6E. Inspection of the Group 2 deep groundwaters (see Fig. 5) reveals that all the samples (#2,3,4,5) are from well DC-6. This reviewer is concerned that some special characteristics are associated with either the sampling procedures, the well characteristics, or with the actual hydrochemical characteristics of this well. Interpretations based on the differences of Groups 1 and 2 should be considered uncertain until the uniqueness of well DC-6 is more fully explained.

6F. Upon inspection of Fig. 5, this reviewer disagrees with the authors statement that "Meteoric chloride appears to be the dominant source of chloride for Saddle Mountains and most Wanapum Basalt groundwater." To this reviewer, the Wanapum samples clearly define a complete mixing trend from the deep-groundwater end member to the meteoric end members. This reviewer emphasizes that this relationship, based solely upon the data contained in this report, with its associated uncertainties, strongly suggests that the Wanapum is a major zone of mixing of deep groundwaters with modern meteoric waters.

6G. With the caveat discussed in comment 6E, it is interesting to inspect the slopes that the $^{36}Cl/Cl$ data define when Groups 1 and 2 are considered separately. Ignoring Group 1 data (for whatever reason may be associated with its uniqueness), the data for the other wells match, by visual inspection, the slopes of the mixing curves on sheet 1 better than sheet 2 of Fig. 5. This reviewer would interpet this relationship to suggest that the available data fit the model of the deep groundwater (assuming the meteoric waters are representative of the Hanford Site hydrologic system) being transported into the Grande Ronde basalt from an external source better than the model assuming the chloride characteristics result from the leaching of the basalt. This interpretation is in agreement with explanation #1 (page 8 of report) of the authors as well as being consistent with basalt/water interaction studies that suggest that high chloride concentrations cannot evolve through interactions with the basalts at the Hanford Site (APTED 1982).

7. The following comments refer to the conclusions of the report:

7A. The conceptual model hypothesized by the authors is that upward flow from the Grande Ronde to the Wanapum is occurring southeast of the RRL. This reviewer feels that the available data are too scattered (geographically and with depth) to unequivocally support this hypothesis. The chlorine isotope systematics allow an interpretation of upward flow in areas to the northwest of the RRL. It is likely that relating the chlorine data to other types of hydrologic information (see comments #1 and #2) would help to better define the hydrologic characteristics and zones of mixing within the Pasco Basin.

7B. The authors state that the presence of some component of each end member groundwater in all samples supports the hypothesis of leaching as the source of chloride. However, it is possible that some component of each end member could be distributed throughout the section via extensive vertical leakage and mixing. This hypothesis is supported by the mixing trend defined by the Wanapum samples (see comment 6F). Even assuming an external source, the groundwater would have to have been recharged under different climatic conditions to explain the deuterium data. The hypothesis of the authors that a sedimentary formation is the source of the deep, saline groundwater would be consistent with this interpretation of extensive vertical mixing.

7C. Based on the data and assumptions of this report, the authors conclude that at least one sample of Grande Ronde groundwater is "old" (>300,000 years). This conclusion is probably warranted by the available data, although the comments discussed above suggest that this interpretation could be altered somewhat by changes in certain assumptions to either exclude any waters being old or to include more samples as being old. The authors are to be commended for not attempting to extend their analysis into the issue of groundwater velocity or travel time. It would be particularly inappropriate in this case because of the uncertainty associated with the origin and history of the high-chloride groundwater. Although one sample may be "old", it could have just entered the Grande Ronde system and be part of a flow system with a siginifcant groundwater velocity. The "oldness" of the groundwater may have no bearing on the relative speed of groundwater within the hydrologic system of the basalts, especially if the deep, high-chloride groundwater has been transported from a sedimentary section below the basalts. The authors go on to comment, even, on their ability to estimate the age of the groundwater: "Thus our ability to 'date' the Columbia River basalt groundwaters by ^{36}Cl depends on hydrologic and geochemical data still being collected." The subject report represents an excellent study that has helped to describe the hydrologic system at the Hanford Site and should provide a good basis for further characterization.

REFERENCE

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