RESOLUTION OF DIFFERENCES IN CONCENTRATION OF NATURALLY OCCURRING TRITIUM IN GROUNDWATER TRACER STUDIES

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Abstract. The objective of this article is to describe the technique for improving the detection level of tritium in water by employing tritium enrichment. The utility of the method will be demonstrated with real data from a variety of ground and surface water sources. Data are presented that emphasize the insensitivity of the analysis to the source of water and its chemical constituents, the reproducibility of the analysis, and the sensitivity of the analysis to small differences in tritium concentration. In summary, the utility and current limits of application of naturally occurring tritium as a ground water tracer will be discussed.

INTRODUCTION

Tritium, the heaviest isotope of hydrogen, is in constant production in the atmosphere from the interaction of the energetic products of cosmic radiation and nuclei found there. Tritium, thus produced, is quickly incorporated into the water molecule, condensed as precipitation, and enters the terrestrial and aquatic water inventory.

Natural levels of tritium in ground water, surface water, and sea water may be higher than 40 T.U. in some cases, but average less than 20 T.U. in the majority of these water sources. In perched or sequestered water tritium concentrations approach zero T.U. and is referred to as 'dead' water. The fact that tritium concentration is nearly constant, supports the idea that tritium decay and tritium production rates are very nearly equal (Kaufman, 1954). Tritium labeled water is, by some estimates, a nearly conservative tracer and an ideal one for hydrological studies. In fact useful natural tritium concentrations can be less than the detection level of modern instrumentation, which is ~ 0.4 T.U. ± 100%.

One way to measure environmental tritium levels that are less than the detection level of the counters requires tritium enrichment prior to analysis (Östlund,1962). The use of tritium as an environmental tracer has become a more attractive technique as ultra low background liquid scintillation counters have been developed and tritium enrichment perfected. Liquid scintillation analysis following tritium enrichment of the sample is the most cost effective means currently available. Other analytical means are available that provide high quality data but are more costly (Neary, 1997).

TRITIUM ENRICHMENT

Tritium enrichment methods have been investigated that employ the sample volume reduction as a means of determining the enrichment factor (Östlund,1962). Because of spray and evaporative losses during electrolysis such a calibration means is crude at best. Currently, the most repeatable and accurate calibration means relies on the measurement of the enriched of deuterium, which is naturally occurring, and enriching simultaneously with tritium. Thus each sample has an internal standard that can be used to measure the enrichment factor. Tritium enrichment is usually employed when the amount of water available, before enrichment, exceeds the amount that can be counted in a particular vial of a given volume. The minimum detectable concentration, MDC, will determine the lower quantitative limitation of the analysis for a given amount of tritium enrichment (Currie, 1968). When lower tritium levels are to be measured, then more enrichment -a larger enrichment factor- will be required.

Tritium enrichment results in two significant changes in the sample. The first is an increase in the tritium activity, hence enrichment; and second a reduction in volume. Tritium enrichment is usually employed when the 'traditional' background measurement predicts a lowest level of detection, LLD, that is greater than that required. The LLD is minimum when the background is minimum and the counting time is greatest. The MDC is minimum when the LLD is minimum, the counting efficiency is

maximum, and the maximum effective volume of sample is counted, the lowest possible MDC will result. The lowest possible MDC permits the measurement of the minimum tritium concentration that is statistically significant with respect to the prevailing background. The maximum effective sample volume is the product of the enrichment factor and the volume of enriched sample actually counted.

Minimum Detectable Concentration

The Minimum Detectable Concentration, MDC , expressed in Tritium Units, T.U. or pico Curies per Liter, pCi/L, is based on the lowest level of detection, LLD, expressed in counts per minute, cpm. LLD is a signal- to-noise consideration, which is computed in terms of the numerical risks selected for Type I and Type II errors and the counting time. The MDC relationship depends on a units scaling factor, the LLD, the volume of water counted, the enrichment factor, and counting efficiency.

The primary reason to enrich the tritium in water is when the selected MDA is lower than can be achieved with the volume of water to be counted, given the traditional or expected background, and counting efficiency. As a practical matter, enrichment is always an option if the available water sample exceeds volume of water that can be incorporated into the smallest counting vial available, because the smallest vial/volume will always exhibit the lowest LLD all other parameters being equal.

The LLD relies on a pre-selected probability that a false positive will result and a pre-selected probability that a true positive will result during the sample count measurement. Suppose:

1. " = the probability that it will be falsely concluded that activity is present in a sample or the probability of a Type I error (false positive); and
2. $ = the probability that it will be falsely concluded that activity is absent from the sample or the probability of a Type II error (false negative).

Thus the following relationships hold:
3. 1-" = the probability that it will be correctly concluded that activity is present in the sample, the probability of a true positive and
4. 1-$ = the probability that it will be correctly concluded that activity is absent from the sample, the probability of a true negative.

The strategy of (Currie,1968) has been widely adopted by radio chemistry laboratories. The development of a measure of the limit of detection that accounts for both Type I and Type II error is outlined in (Currie, 1968, Neary ,1997). The LLD net count rate, R_N, as it approaches the background rate, R_B, may be expressed by the following,

$$LLD = 4.653 \left(\sqrt{\frac{R_B}{t_B}} \right) \quad (1.)$$

For detectors that have very low backgrounds and low counting efficiency, Equation (1) include another term to account for the probability of falsely concluding that activity was present in the sample. The magnitude of the term is usually about 2.7.

From Equation (1) it is clear that the magnitude of the LLD or the minimum net counting rate detectable over the background rate can be reduced by either background rate reduction and/or increasing the counting time. The relationship between MDC and the LLD is given by Equation (2). To further illustrate the circumstances under which tritium enrichment serves to permit a particular MDC, the relationship between MDC and the LLD is given in terms of the enrichment factor

$$MDC = \frac{LLD}{7.151 \left(eff \left(decay \left(yield \left(quantity \left(enrich \right. \right.\right.\right.\right.} \quad (2)$$

where:
7.151 = the ratio of DPM to Tritium Units (T.U.),
eff = the counting efficiency or the ratio of CPM to DPM,
decay = the radioactive decay or ingrowth that occurs during the count time and is unitless,
yield = the fraction of the total amount of the nuclide present in the sample that is actually retrieved by the chemical preparation of the sample aliquot and counted,
enrichment
factor = the enrichment factor or ratio of the initial to final tritium concentrations, and
quantity = the amount of enriched sample counted.

The expressions for MDA and LLD, derived in detail (Neary 1997), must govern the selection of the counting experiment parameters. The decision to enrich tritium in a water sample is based on the MDC required and the quantity of water available to enrich. Thus, the

background counts, the counting time, the counting efficiency, the sample volume to be counted, and the enrichment factor will determine the MDC. The estimated enrichment factor may rely on traditional values of the counting efficiency, and background, and a selected counting time. Thus, in advance of the water sampling, it is possible to determine the volume to be collected and the analytical parameters shown above.

PROCEDURE

The basis for the tritium enrichment method is electrolysis of water (Ostlund, 1962). The typical electrolysis cell can electrolyze about 160 ml at a time; but with periodic additions of sample to the cell much more of the sample can be electrolyzed. For any sample volume the minimum final or recovered volume is ~5.00mL. The electrode assembly is comprised of a Nickel anode and an Iron cathode. Prior to electrolysis the electrolyte is made alkaline with sodium peroxide (~10 mg/ml). The enriched product is neutralized Dry CO_2 gas. The neutralized product is vacuum distilled with a double dry ice-isopropanol slush trap collection system.

Both the method and apparatus are described in detail elsewhere (DOE,1990, EPA, 1980, Neary,1997)

EXPERIMENTAL

Tritium enrichment results in a single significant change in the sample, the increase in the tritium concentration, hence tritium enrichment. With the background minimized, counting efficiency maximized, and sample tritium concentration maximized, the lowest minimum detectable concentration, MDC, will define the lowest tritium concentration that can be detected.

The MDC is based on the lowest level of detection, LLD, a signal to noise consideration, which is computed in terms of the numerical risks selected for Type I and Type II errors and the counting parameters (Currie, 1968, Neary,1997). The MDC relationship depends on the volume of water counted, and counting efficiency. As a practical matter, enrichment is always an option if the sample water exceeds the volume of water that can be accommodated by the smallest counting vial available. Because the smallest vial/volume will always exhibit the lowest LLD, all other parameters being equal, some advantage will accrue from enrichment.

Thus, the necessity and extent of tritium enrichment

should be defined by the analytical requirements of the experiment.

DATA

All of the results were expressed in Tritium Units T.U. where 1 T.U. corresponds to 1 tritium atom in 10^{18} protons. The uncertainty is given at a 1 F confidence level and is the propagated uncertainty. The MDC is calculated according to (Neary,1997). Where deuterium data are listed, they are presented in parts per million, ppm. Deuterium concentration by enrichment can be related to the tritium enrichment and thus serves as an internal standard.

The first data sets demonstrate the analytical advantage conferred by tritium enrichment. The first set of data are the results of analyzing tritium in the samples indicated *without enrichment.* The second data set are their results of analyzing the tritium concentration in the same samples *after tritium enrichment.* The counting conditions are the same in both cases except the counting time without enrichment was half that of the counting time with enrichment. For the data from the *without enrichment* measurements none of the tritium results are statistically significant because they are all less than the MDC; and their propagated errors are greater than the corresponding tritium result.

Table 1. Arctic Ocean Water

Without Enrichment

Sample ID	Tritium Concentration. T.U	Propagated Error ± T.U.	MDC T.U.
1	2.11	11.01	14.6
2	2.45	10.96	14.6
3	8.67	11.17	14.5
4	7.28	11.45	14.5
5	1.41	11.01	14.5
6	7.48	11.18	14.4

With Enrichment

Sample ID	Tritium Conc. T.U	Propagated Error ± T.U.	MDC T.U.	Enrichment Factor
1	1.63	0.43	0.70	17.25
2	1.62	0.35	0.53	22.80
3	5.91	0.43	0.46	26.45
4	3.84	0.36	0.47	25.11
5	4.20	0.58	0.42	28.81
6	3.85	0.44	0.45	27.01

In the next example, Spring Water fed by a confined aquifer in the American Southwest was enriched prior to tritium analysis. The results show ± 0.6 T.U. (CI=1) agreement between the sample and its duplicate results and very low MDCs. It is clear from the results for the other spring that recharge patterns may be different in the aquifer if it feeds both springs. The results could provide clear support of such a claim. The dead water, DW, verifies that no contamination occurred during the preparation and measurement of the sample tritium concentration.

Table 2. Spring Water American Southwest

Sample ID	Tritium Concentration T.U.	Propagated Error ± T.U.	MDC	T.U.
DSpring	12.98	0.60	0.73	
DSpring dup	13.09	0.61		0.74
RSpring	9.57	0.53	0.83	
DW	0.24	0.20		1.06

The next example demonstrates a well mixed water source that drawn from a large irrigation reservoir in the American Southwest. The fact that it is well mixed is suggested by the agreement among and between the tritium concentration in the samples. The agreement of the duplicates at the 5 TU level provides confidence in the results for the other samples.

Table 3. American Southwest Reservoir Water

Sample ID	Tritium Conc. T.U.	Propagate Error ± T.U.	MDC T.U.	D ppm
1	5.31	0.44	0.24	140.98
2	5.38	0.29	0.10	142.40
3	5.51	0.32	0.13	148.66
4	5.99	0.40	0.21	140.15
5	5.46	0.32	0.55	141.61
5 dup	5.34	0.31	0.55	141.79
6	5.73	0.37	0.75	146.12
DW	0.47	0.13	0.60	161.36

Table 4. American South - Tunnel Seep

Sample ID	Tritium Conc. T.U.	Propagated Error ±T.U.		MDC T.U.	D ppm
JD 1	9.14	0.50		0.71	148.00
JD 2	8.12	0.48		0.80	147.94
JD 3	16.24	0.89	1.34	147.53	
JD 4	15.40	0.81	1.14	147.61	
JD 5	8.23	0.44	0.62	147.42	
JD 6	9.44	0.50	0.70	147.94	
JD 7	8.17	0.50	0.91	147.64	
JD 7 D	8.66	0.53	0.75	147.64	
DW 1	0.57	0.19	0.56	151.25	
DW 2	0.20	0.20	0.20	151.41	

The last set of samples is from selected seeps in a tunnel in the American South. The results were used ultimately to establish that surface water was entering the aquifer and selectively feeding two of the seeps sampled in a tunnel, JD 3 and JD 4.

DISCUSSION

Comparing the measured tritium concentrations listed in Table 1. for 'With Enrichment' and 'Without Enrichment', a trend toward lower tritium concentration for the tritium enriched samples is evident that cannot be justified on the basis of the estimated propagated uncertainty and the MDC, also listed in the table. It is often the case for tritium concentrations near background that it is unusually neither practical nor possible to measure tritium concentrations that meet the statistical criteria specified by the propagated error and the MDC. From the tritium concentration measured for these samples after tritium enrichment however the statistical criteria are meet without exception. These samples were drawn from the Arctic Ocean with in the normal range of salinity 34 to 36 0/00. Each sample was first carefully distilled, making certain the spray from the boiling pot did not carry over into the receiver. Reversible electrolytic couples can result for metal chlorides that extend the electrolysis time. In the case of these samples enough raw sample was distilled to provide 150 mL of distillate for electrolysis. Enrichment factors varied from 17X to 28X, averaging about 25X after 7-8 days of electrolysis. The details of the electrolysis are described in detail elsewhere (Neary,1997).

Table 2. Lists tritium concentration measured in carbonate rich spring water after electrolysis of a distilled aliquant. This sample type presents the same problems encountered with brackish or brine waters. They must be stripped of their salt burden by distillation or other ion selective means. Duplicate results from the sample DSpring are shown to indicate that the reproducibility of the analytical method is acceptable ±0.06 T.U.. The difference in the tritium measured in the samples RSpring and DSpring is statistically significant and therefore uniquely identifies one source over the other. A tritium measurement in 'dead' water is supplied to represent a reference background level.

Table 3. lists tritium concentrations in water samples drawn from the same depth of a quiescent irrigation reservoir before the introduction of spring run-off. A striking feature of the data is its dispersion. Likewise for the deuterium listed as well. Deuterium is measured before and after each electrolysis as a means of determining the enrichment factor. The reproducibility was ±0.03 T.U. .

Table 4. lists tritium concentrations in water samples drawn from tunnel seeps. The magnitude of the tritium concentrations, the associated propagated error estimates, and MDC meet the needed statistically criteria to establish uniqueness between JD3 or JD4 and the rest of the samples. The deuterium data could not have served that purpose.

In conclusion, tritium enrichment prior to analysis permits the identification of statistically unique levels and differences in tritium concentrations at ~1 T.U. level of <1 T.U.. With greater enrichment factors even lower levels may be measured. Such a measurement without tritium enrichment would be hopeless below ~10 T.U. and daunting at 20 T.U.. To better access water resources facile tracers with improved sensitivity are useful. The use of tritiated water as a tracer at or below ambient concentrations can be significantly broadened improved by tritium enrichment.

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