**Preliminary Report on Isotope Abundance Measurements
in Groundwater Samples from the Talbert Injection Barrier
Area, Orange County Water District**

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February 1995

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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Introduction

This report discusses isotope abundance measurements made on a collection of groundwater samples from the Orange County Water District. The water samples were collected in May, 1994 as part of a preliminary study conducted by LLNL to assess the feasibility of tracing and dating reclaimed water used in the Talbert Injection Barrier. A set of samples were collected both near to and far from the barrier and also at different depths in available monitoring wells. A variety of elements were selected for isotopic analysis; hydrogen (tritium), helium, neon, carbon, chlorine and strontium and the results are given in Table 1. The tritium abundance combined with the ^3He and Ne abundance provides a method for age dating young (< 40 yr.) groundwater. The abundance of ^{14}C provides an age dating technique for older (1000-50,000 yr.) groundwater. The concentrations of Cl and Sr isotopes give information on sea water mixing and water-rock chemical interactions.

General Aqueous Chemistry

Groundwater in and around the Talbert Gap and barrier region range in total dissolved solids (TDS) from ~300 mg/L to as high as 15,500 mg/L. The lowest TDS water occurs in close proximity to the groundwater barrier while the highest TDS groundwater occurs adjacent to the ocean shore (M-31). Figure 1 is a Piper diagram of the different groundwaters sampled during this study. Figure 2 is a map showing well location. In fig. 1, in the cation triangle, groundwater occurs as a mixture between a predominantly Ca-rich end member and a predominantly Na-rich end member with most samples lying in between the two types. In the anion triangle the data ranges from a HCO_3 -rich end member to a Cl-rich end member but with a mixture of the two with a water that has a higher proportion of SO_4 . In the combined field of the data above the ionic triangles, four distinct end member groundwaters are discernible, 1) a CaHCO_3 -type groundwater with moderately low TDS (~100-800 mg/L), 2) a NaHCO_3 groundwater with a low TDS (~300 mg/L), 3) a NaCaHCO_3 groundwater that has some of the lowest TDS values (~200 mg/L) but also range up to ~600 mg/L, 4) a NaCl water with the highest TDS values.

As will be further indicated by the isotope data, the CaHCO_3 groundwater is related to natural shallow groundwater that has been unaffected by injection water. The NaHCO_3 water is from the deeper aquifers. Its high Na relative to Ca is probably due to ion exchange processes on clay sites, a process that takes 100's to 1000's of years and is consistent with the older ages of the deep groundwaters (see below). Nevertheless, the

Na/Ca ratio contrast between the deep groundwater and the shallow natural groundwater is obvious.

Water used for injection is treated waste water blended with the deeper groundwater (DW-1). The mixed water (Q-10) has a NaCaHCO₃ character and lies just outside the larger field of NaCaHCO₃ (Fig 1) groundwaters sampled from monitoring wells surrounding the barrier. A general mixing of the CaHCO₃ groundwater and the NaCaHCO₃ injected water (Q-10) is apparent where the field of barrier water forms a cluster intermediate to either end member. The high TDS NaCl groundwater is undoubtedly the sea water intrusion where the NaCl water mixes with a CaHCO₃ groundwater.

Tritium - Helium-3 dating of OCWD Groundwaters

Age dating of the injected water measures the time between sampling and the last time the water was in equilibrium with the atmosphere shortly before being injected into the ground. For the short ages expected (less than 20 years), the tritium (³H) - helium-3 (³He) system provides an excellent dating technique. Tritium is a naturally occurring radioactive isotope of hydrogen (half-life = 12.4 yr.) and is produced by cosmic-ray interactions in the atmosphere. Tritium decays by emitting a low energy electron (average energy about 20 keV). In doing so, it becomes a stable ³He atom. In addition to cosmic ray production, ³H is released into the environment by human activities such as nuclear energy production and biomedical research. The ³H-³He dating technique relies on being able to identify ³He in water samples due to the decay of ³H. When a ³H atom, as part of a water molecule, decays in a saturated aquifer, the resulting ³He atom remains in solution and continues to move with the water. Thus the sum of ³H and ³He atoms per unit volume remains constant and equals the number of ³H atoms initially present. Knowing the original number of ³H atoms and the current number of ³H atoms, we compute the age by:

$$(\text{number } ^3\text{H now})/(\text{number } ^3\text{H originally}) = ^3\text{H}/(^3\text{H}+^3\text{He}) = e^{-0.0558T}$$

where ³H is the number of ³H atoms, ³He is the number of ³He atoms due to ³H decay, (the decay constant = $\ln(2)/t_{1/2} = 0.0558$) and T is the age in years. In general, this technique works because ³He is naturally very rare. The abundance of ³He in groundwater (without ³H present) of about 1 part in 10¹³. This technique has been applied successfully in several circumstances. Recent work of Ekwurzel et al.(1994) has compared ³H-³He dating to two other dating techniques (⁸⁵Kr and chlorofluorocarbons) and has shown excellent agreement exists for all three dating systems.

In groundwater, He and Ne come from interaction with the atmosphere before and during recharge and from the build up of nuclear reaction products such as ^3He from ^3H decay after recharge. In some simple systems, ^4He comes only from the atmosphere and can be used to directly monitor how much ^3He comes from the atmosphere. However when older (> about 5,000 yr.) groundwater is present, we find contributions from the decay of U and Th which produce ^4He (alpha particles) and we can no longer use ^4He as an air monitor. The decay of U and Th also indirectly produce a small amount of ^3He but it is negligible for the OCWD samples considered here.

For the OCWD samples, we have chosen to use the abundance neon to determine how much ^3He comes from sources other than ^3H (*These equations are an approximation that is appropriate for samples with little excess air*).

$$\begin{aligned} ^3\text{He}_{(\text{meas})} &= ^3\text{He}_{(\text{air})} + ^3\text{He}_{(\text{tritium})} \\ ^{20}\text{Ne}_{(\text{meas})} &= ^{20}\text{Ne}_{(\text{air})} \end{aligned}$$

$$\text{or: } ^3\text{He}_{(\text{tritium})} = ^{20}\text{Ne}_{(\text{meas})} * ((^3\text{He}/^{22}\text{Ne})_{(\text{meas})} - (^3\text{He}/^{22}\text{Ne})_{(\text{air})})$$

Figure 3 illustrates that the ratio of $^3\text{He}/^{22}\text{Ne}$ is constant in samples where we know there is not ^3He from ^3H decay. In contrast, samples containing injection water show elevated levels of ^3He from ^3H decay. Table 2 gives ^3H - ^3He ages for samples containing measurable ^3H . Samples not showing detectable ^3H correspond to ages greater than 40 years.

Measured ^3H concentrations in OCWD samples range from essentially zero ($<3 \times 10^4$ ^3H atoms/gram) to rather high levels (about 5×10^7 ^3H atoms/gram, drinking water standard = 4×10^8 ^3H atoms/gram). Tritium concentrations are often reported using a variety of units:

$$\begin{aligned} 1 \text{ Tritium unit (TU)} &= 6.7 \times 10^4 \text{ } ^3\text{H atoms/gram} \\ 1 \text{ pCi/liter} &= 0.3 \text{ TU} \\ &= 2.0 \times 10^4 \text{ } ^3\text{H atoms/gram.} \end{aligned}$$

The low ^3H concentrations are associated with wells not containing reclaimed water (far away from the injection barrier) and are interpreted to represent groundwater residence ages greater than 40 years. The ^3H concentrations in some of the samples are higher than found in typical surface waters and must have some local origin. The high levels of ^3H observed

in the injection water are also accompanied with elevated levels of ^{14}C and the atom ratio of $^3\text{H}/^{14}\text{C}$ ranges from about 1 to 3, which is strongly suggestive of biomedical research waste streams. The ^3H and ^{14}C are present at concentrations well below current drinking water standards for all samples examined in this work.

The majority of the measured ^3H - ^3He ages are short compared to the half-life of ^3H (12.4 years) and we see much more ^3H than ^3He in the samples. Roughly the ^3H - ^3He ages increase with distance from the injection barrier. The M-21 well is quite close to the barrier and shows very little ^3He from ^3H decay despite high ^3H levels. The M-21 well samples water at four depths and is located about 400 ft. down gradient from the injection barrier. The ages of the four levels range from 0.5 to 1.7 years. The uncertainties in the ages due to analytical measurement uncertainties are fairly small and suggest that there are resolvable differences, however there are additional uncertainties due to the effects of dispersion. These effects are hard to quantify at this point, but are of some concern since the ^3H content of the injected water apparently fluctuates significantly leading to significant ^3H concentration gradients. Based on the modeling work of Solomon and Sudicky (1991) it appears that errors due to dispersive transport of ^3He will be much less than a factor of two.

Monitoring well M-19 is at a similar distance up-gradient from the injection barrier. The upper section of M-19 (M-19-1) shows only a trace of ^3H indicating that injection water is largely not present. But in the lower sections, we see ages comparable to those for M-21. Based on wells M-19 and M-21 we conclude that the average groundwater speed is about 400 ft. per year. The monitoring wells M-7a (down gradient) and M-11 (up-gradient) are similar to M-21 and M-19 but are roughly a bit more than twice as far away from the barrier. Their ages range from 2.1 to 3.4 years, which again corresponds to a groundwater speed away from the barrier of about 400 ft per year. The HB-Dyke well is about the same distance as M-7a and M-11 but is at the edge of the injection barrier and it shows a ^3H - ^3He age of 2.5 years indicating a groundwater travel speed just slightly larger than the other wells.

The next closest well to the barrier that we sampled (Saki-FV) shows little or no ^3H present. The Saki-FV well is about 5000' up-gradient of the injection barrier. If we assume 18 years of water injection and 400 ft/yr. speed, injection water would have reached the Saki-FV well in about 12 years, which is apparently not the case. Of course at a distance this large, the injection barrier begins to look more like a point source than a line source and the flow speed would be slower at larger distances. The M-26 well is about 7000' down-gradient from the injection barrier and shows no ^3H . This sample received extra

attention in the ^3H measurement and shows less than 0.1 TU of ^3H . Based on this limit we can be confident that injection water constitutes less than 1% of the M-26 water.

Water Mixing Ratios

In order to understand the meaning of these ^3H - ^3He ages, we need to evaluate the mixing ratio of injection water with ambient background water (i.e. the water present in the aquifer before the injected water arrived). Several samples were collected at sufficient distance to completely preclude the possibility of injection water being present, in particular the CTG-1 well (4 different zones). All of the samples away from the barrier show little if any ^3H . In addition, we see ^{14}C well below modern levels for these ambient water samples. The lack of ^3H and low values for ^{14}C (and ^{36}Cl) indicate that the ambient water away from the barrier is at least 40 years old and probably 100's to 1000's of years old. Because the ambient water contains no ^3H , the ^3H - ^3He ages reported in Table 2 are just the age of the injected water. The ^3H - ^3He age is the mean age of the ^3H in the system. Therefore, the addition of ^3H -free water has no effect on the apparent age.

In addition to measuring the age, we estimated the relative contributions between injection water and ambient water. The clearest indication of the presence of injection water is the observation of ^3H . However, because the ^3H concentration in the injection water is variable, ^3H information is only useful in determining if any injection water is present. For example, the sample M19-1 shows a little less than 1% of the average injection water ^3H concentration. As a result, we can conclude that virtually no injection water has reached this point. All of the isotope abundance data and physical measurements (i.e. temperature) show some distinction between ambient and injected water, but most of the injection water isotopes have been variable over the course of time and this complicates their interpretation. One element, neon, appears to be fairly constant in the injection water. Most groundwater contains neon at concentrations about 30-40% greater than the prediction of equilibrium solubility with the atmosphere. This effect is generally attributed to the incorporation of air in the vadose zone at the transition from unsaturated to saturated conditions. The actual nature of this 'excess air' component is uncertain, but it is present in virtually all naturally occurring groundwater. We were surprised initially when many of the samples showed little or no excess air, however it seems clear that the injection water is in equilibrium with the atmosphere and never goes through the recharge process that incorporates 'excess air' in groundwater. While the neon concentration of the injection water appears to be constant, the amount of 'excess air' in the ambient water is likely to be somewhat variable, so in contrast to using ^3H , this indicator is only useful when the fraction of injection water is

near one. Using ^3H and neon we can sort the samples into three categories, either 1) samples containing little or no injection water, 2) samples consisting mostly of injection water, and 3) sample containing significant amounts of both injection water and ambient water. Table 3 shows these groupings and gives group averages for some of the measured parameters.

Carbon in OCWD Groundwaters

Natural Shallow Groundwater - The carbon isotope signatures of shallow groundwater that have no apparent mixed injected water can best be seen in wells WM-3, SAKI-FV, CTG1-1 and 2, and M19-1. The $\delta^{13}\text{C}$ ($\delta^{13}\text{C}$ is defined as the deviation of $^{13}\text{C}/^{12}\text{C}$ from a standard ratio in parts per thousand) values of these groundwaters range from -10.9 to -13.5‰, and they are of the CaHCO_3 -type groundwater with alkalinity around 200 mg/L. The range in concentration and $\delta^{13}\text{C}$ values are typical for natural groundwaters recharging young alluvial basins in California. Such groundwaters recharge through predominantly C_3 type plant roots and probably establish their ^{13}C signatures under semi-open to open conditions. The $\delta^{13}\text{C}$ values of the groundwaters are 12 to 15‰ higher than the expected average $\delta^{13}\text{C}$ value of plant respired CO_2 of -25‰. Under equilibrium fractionation between dissolved HCO_3 and CO_2 gas, the difference should be around 9 to 10‰ at $\sim 20^\circ\text{C}$ mean temperature. The small discrepancy between the expected and observed fractionation could be accounted for in 1) groundwater recharge under semi-open conditions in the vadose zone particularly during pH neutralization through any calcite dissolution, which would drive the $\delta^{13}\text{C}$ value of the HCO_3 slightly higher, or 2) a mixture of C_4 plants (perhaps grasses) occur in the recharge area and is contributing a higher $\delta^{13}\text{C}$ component to the root zone CO_2 . Mixing of atmospheric CO_2 has not been explored and further field work and modeling is needed to characterize this difference.

The ^{14}C abundances in these shallow groundwaters range from 58 to 83 pmc. Wells WM-3 and Saki-FV share common aquifers and have almost identical ^{14}C abundances. On the other hand, CTG1-1 and M19-1 also share similar aquifers, but have differing ^{14}C abundances. Well M19-1 and possibly well Saki-FV have measurable ^3H suggesting that the water discharging from these two wells are a mixture of young and old water. M19-1 may also have a small mixture of injection water that contributes the minor ^3H levels. Further work is needed to understand the extent of mixing in the aquifers and well discharges.

The calculated ages for the groundwater in these wells range from ~ 1500 (Saki-FV) to 4500 (CTG1-2) years old. These are maximum possible ages for these groundwaters.

It is possible that when these groundwaters recharged their ^{14}C abundances were slightly modified by calcite dissolution under semi-open conditions. For example, if the discrepancy noted in the $\delta^{13}\text{C}$ values was due entirely from semi-open conditions during recharge, then a potential 20-30% of the HCO_3 dissolved in the groundwater could be from dead carbon that did not re-equilibrate with the soil CO_2 , and hence, reduced the total ^{14}C abundance of the recharge water by 20-30 pmc. Under these circumstances, wells WM-3, SAKI-FV, and M19-1 may be younger than 100 years but older than 40 years. Groundwaters younger than 40 years typically have bomb-pulse ^{14}C abundances that resulted from injection of excess ^{14}C into the upper atmosphere during atmospheric testing in the 1950's and 1960's. CTG1-1 and 2, on the other hand, would still be less than 100 pmc with a 20-30 pmc correction of ^{14}C data. Therefore, the youngest possible ages are ~400 years for CTG1-1 and ~1100 years for CTG1-2.

Deep Groundwater - Two well waters sampled and analyzed define the deep groundwater in this area. These are DW-1 completed to (?) and CTG1-4 perforated from 1060 to 1220 feet below the surface. Both wells show ^{14}C abundances of ~28 pmc. Their $\delta^{13}\text{C}$ values though differ by 3.3‰, with the lower value in CTG1-4. The calculated apparent ^{14}C age for both wells is 10,500 years old. The $\delta^{13}\text{C}$ values of both these wells are lower than the $\delta^{13}\text{C}$ values observed in the shallow groundwaters. Two possible reasons explain this difference, 1) the deeper groundwater recharged under different root zone conditions than the shallow groundwaters, such that in the absence of calcite dissolution, the soil CO_2 dissolved in the infiltrating waters but did not fully equilibrate with the soil CO_2 gas, a condition that might exist under rapid recharge, 2) organic carbon of the deeper aquifer is oxidizing to CO_2 that adds a low $\delta^{13}\text{C}$ value HCO_3 to the groundwater. The deeper aquifer is high in fine organic particulate matter that should have typical low $\delta^{13}\text{C}$ values. It is possible that the ^{13}C in the organic matter is simply exchanging with the dissolved HCO_3 , but such exchanges would be expected to be very slow. The oxidation of organic matter seems more plausible at this time. Furthermore, the deep groundwater is of a NaHCO_3 -type that probably reached a high Na/Ca ratio by ion exchange on clay sites. Such ion exchange would cause calcite to be undersaturated in the groundwater and promote dissolution of carbon-bearing phases.

Let us assume that the original groundwater had a $\delta^{13}\text{C}$ value of ~-12.0‰ before any oxidized organic CO_2 is added to the groundwater, the $\delta^{13}\text{C}$ value of the organic matter is -27.0‰, and the organic matter is ^{14}C depleted. By mass balance calculation, this would suggest that 22% of the HCO_3 in well DW-1 is derived from dead organic

matter, and 44% is from dead organic matter in well CTG1-4. Applying these percentages to the ^{14}C abundances, then the resulting ^{14}C for DW-1 would be 35 pmc and for CTG1-4, 50 pmc. These give comparative calculated ages of ~8700 years for DW-1 and ~5700 years to CTG1-4. These ages probably represent a minimum age for these groundwaters. Further work is needed to test the source of the dissolved carbon in the deep groundwater and the extent of any carbon exchange.

Talbert Gap Groundwater - Three non-injected waters were measured in the Talbert Gap south of the barrier where sea water intrusion historically has been a problem. These wells include SA10-1, M-31, and sea water collected at the Newport Pier. The chlorine concentration of the water increases from 2100 mg/L in SA10-1 to 19,500 mg/L in the sea water, with M-31 being about half the salinity of the ocean. The alkalinity of the groundwater increases from 300 mg/L at SA10-1 to 600 mg/L at M-31. The $\delta^{13}\text{C}$ value of the sea water sample is +1.5‰, a value expected for sea water HCO_3 in equilibrium with atmospheric CO_2 . The ^{14}C abundance of the sea water is 106 pmc, indicating incorporation of bomb-pulse atmospheric ^{14}C . The current level of atmospheric ^{14}C in CO_2 is ~114 pmc. The sea water has less ^{14}C than the atmosphere most likely due to upwelling of deep bottom waters off the Pacific Coast that are hundreds of years old and have lower ^{14}C abundances.

Well SA10-1 has a $\delta^{13}\text{C}$ value similar to the shallow groundwaters discussed above. The ^{14}C abundance of this well water, though, is only 25 pmc. Likewise, M-31 has a $\delta^{13}\text{C}$ value of -2.1‰ and a ^{14}C abundance of only 5 pmc. The chlorine concentration indicates sea water intrusion and mixing with the potable groundwater in the Talbert Gap, but the carbon isotopes are behaving independently of simple conservative mixing and appear to be controlled by water-rock reactions. This is evidenced in the fact that the alkalinity increases toward the ocean simultaneous with the isotopic shifts. The fact that the ^{14}C abundance is decreasing towards the ocean and the $\delta^{13}\text{C}$ value is increasing suggests that a "dead", inorganic carbon source is dissolving into solution as the salinity of the water increases. This carbonate source is most likely sea shells deposited within the near shore fluvial-marine sediments of the gap. Sea shells will have $\delta^{13}\text{C}$ values around 0‰ and probably "dead" ^{14}C . As a result, the dissolution of the seashells into the groundwater causes a rise in the $\delta^{13}\text{C}$ of the dissolved HCO_3 in the groundwater and a decrease in the ^{14}C abundance. A mass balance calculation between mixing of sea water alkalinity with the original freshwater alkalinity suggests that the freshwater that mixed in M-31 should have an alkalinity of ~30 mg/L. Likewise the same mass balance calculation

for SA10-1 suggests that the original freshwater alkalinity should be ~70 mg/L. These values are low compared to the natural shallow waters further north and more work is needed to resolve this discrepancy. Moreover, simple calcite solubility calculations indicate that dissolution of calcite should not be occurring at the observed rate and further study is needed.

Injection Water - The ^{14}C values of groundwater that are considered in this report to be derived from injected waste water vary from 80 to 550 pmc. Most of the waste water values exceed that which is expected for bomb-pulse carbon signatures, and indicate another anthropogenic source. The high ^{14}C values are closely associated with high ^3H levels and suggest sources from biomedical tracer research, which could easily be incorporated in the Orange County waste stream. The levels of ^{14}C and ^3H in this report fall safely below the current drinking water standards for these radio-elements.

The ^{14}C values for Waste water 22A and 22B, both collected 5/94, are below 100 pmc. This suggests that the high ^{14}C values observed in barrier wells are a result of a transient ^{14}C pulse(s) that has entered the waste-water stream. Comparison of the ^{14}C values and the ^3H - ^3He ages calculated in this report, indicate that the highest ^{14}C values in the waste water occurred approximately 2 years ago. The ^{14}C values decreased to more environmental levels in the waste water subsequent to this time. Carbonate scale from a recarbonation pond manifold was sampled at the water factory during this study. The scale builds up over a period of about a year (T. Sovitch, pers. comm.). The scale also has an elevated ^{14}C value. The presence of high ^{14}C in the carbonate suggests that the ^{14}C pulse in the waste water stream has been recirculated by incorporation into flocculated lime and reintroduced into the waste water via the CO_2 off-gas from the regeneration plant. This recirculation in effect creates a longer residence time for ^{14}C in the water factory treatment process.

The $\delta^{13}\text{C}$ values for the waste water are distinguishable from the natural groundwater. Waste water 22A has the lowest value of -30.4‰. The ^{13}C is slightly enriched to -24.3‰ during the RO process. The low $\delta^{13}\text{C}$ values are probably mostly controlled by the $\delta^{13}\text{C}$ value of the CO_2 in the recarbonation pond, which is most likely less than -35.0‰. The $\delta^{13}\text{C}$ of the scale carbonate (-29.5‰) also provides evidence for the low value for the CO_2 .

Chlorine and Strontium in OCWD Groundwaters

Stable chlorine is an excellent tracer for sea water intrusion into the groundwater system. Elevated Cl levels are seen in samples from M-31, M-28, SA-10 and M-26. In

addition to the stable Cl isotopes, we measured Chlorine-36 (^{36}Cl), a radioactive isotope, with half-life of about 300,000 years. Chlorine-36 is produced mainly by cosmic-ray interactions with argon in the atmosphere. Since ^{36}Cl has a different origin than stable Cl, we might expect to see variable mixing of Cl sources in the OCWD samples. Figure 4 shows a graph of $^{36}\text{Cl}/\text{Cl}$ vs. $1/\text{Cl}$ for the OCWD groundwater samples. Sea water is high in Cl but very low in ^{36}Cl , precipitation is low in Cl but relatively high in ^{36}Cl . In fig. 4, mixing between sea water and a poorly defined meteoric source is observed. Evaporation can produce horizontal movement of points in this type of graph and probably explains the broad horizontal distribution of data seen in fig. 4.. In general, the ^{36}Cl is completely consistent with sea water being the source of Cl in the Cl-rich samples, but is not especially definitive. Probably more interesting is the lack of elevated ^{36}Cl concentrations in samples with high ^3H and ^{14}C . The lack of ^{36}Cl rules out nuclear energy production as a source of the high ^3H and ^{14}C . Since Cl is a common element and ^{35}Cl has a large probability for capturing neutrons thus making ^{36}Cl , any nuclear power production or research produces lots of ^{36}Cl along with other isotopes such as ^3H and ^{14}C .

The isotope ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ is often of interest in groundwater investigations as a tool for investigating water-rock chemical interaction. Here we focus just on the elemental concentration of Sr. Strontium is present at low concentration in the injected water. The Sr concentration in shallow groundwaters away from the injection barrier are much higher (500ppb vs. 35 ppb) so it is interesting to look at the evolution of the Sr concentration in the injection water. Figure 5 shows a graph of Sr concentration vs. the ^3H - ^3He age. There is a rough increasing trend in Sr concentration with age. The rate of increase in the Sr concentration is quite rapid relative to dissolution of aquifer materials and is probably more likely due to ion-exchange effects of weathered materials. Whatever the precise reason, here we see another parameter correlating with age in a expected fashion.

Summary

The injection water is easily traced by measuring ^3H . By adding measurements of helium and neon, we can accurately determine how long the injected water has been underground using the ^3H - ^3He dating technique. The measured ages of the injected water combined with estimated travel distances give an average flow velocity of about 400 ft per year near the injection barrier. The mixing ratio between injected water and ambient water can be roughly estimated from ^3H and neon abundance data. In the majority of cases, the sampled water is either mostly injection water or mostly ambient water. Measurement of carbon isotopes suggests that ambient groundwater is fairly old, perhaps some as old as 10,000 years.

Future work on the injection barrier system

In this work, application of the ^3H - ^3He method to dating injected water is straightforward. We recommend that these measurements be repeated for confirmation and to begin to look for temporal variations. Questions about the role of ^3He diffusion could be better answered with additional ^3H - ^3He measurements. In general if we get the same age at different samplings, then diffusion of He is not a concern.

Based on measured ^3H concentration versus age, we conclude that the ^3H concentration of the injected water is quite variable in time. The temporal variations of the ^3H could lead to an alternate dating technique based on the matching temporal variations. To do this, frequent monitoring of ^3H would be required, however, relatively inexpensive liquid scintillation beta counting of un-enriched water samples would be satisfactory. Samples should be collected daily, but then combined into larger groups.

Two other methods of age dating exist. The abundance of ^{85}Kr (half-life = 10.7 yr.) can be used for dating because the atmospheric abundance is accurately known as a function of time. Equipment for ^{85}Kr measurements is currently being built at LLNL. A ^{85}Kr study of injection barrier samples could be desirable for system development since the ^3H - ^3He ages of the injection water are well defined. The other dating technique uses artificial noble gas tracers. Very small amounts of non-toxic noble gas isotopes can be added to the injection water and then detected later at monitoring wells. A suitable tracer is already at the OCWD. In general, the tracer cost is very small compared to analysis costs. The disadvantage of the tracer is that one has to wait for it to appear. However, we would recommend going ahead with a tracer experiment just on the chance we would still be interested in age determinations 2-3 years in the future. The comparison of ^3H - ^3He ages and tracer appearance ages would be interesting and could provide additional confidence in the ^3H - ^3He dating system.

By using ^3H and neon concentration measurements, we have been able to estimate mixing ratios between injected water and ambient water. We believe measurements of other dissolved noble gases besides Ne would improve the resolution in the mixing ratio measurements. The injection water is about 5°C warmer than the ambient water recharge temperature (25°C versus 20°C). The abundances of the dissolved gases are temperature dependent with xenon showing the greatest shift with temperature (4% per 1°C , for a total effect of 20%). The advantage to using xenon measurements is that xenon concentration is well defined for both end-members instead of just one as is the case for ^3H and neon. A byproduct of measuring argon, krypton and xenon in addition to neon, is that the

calculation of ^3H -derived ^3He becomes more accurate and reliable because the air contribution can be better identified.

This work was performed under the auspices of the U.S.D.O.E. by LLNL under contract number W-7405-Eng-48.

REFERENCES

Ekwurzal B., Schlosser P., Smethie W.M., Plummer L.N. and others, Dating of shallow groundwater - comparison of the transient tracers H-3/He-3, chlorofluorocarbons and Kr-85. Water Resources Research, 1994 JUN, v30 n6:1693-1708.

Solomon D.K., Sudicky E.A., Tritium and helium-3 isotope ratios for direct estimation of spatial variations in groundwater recharge. Water Resources Research, 1991 SEP, v27 n9:2309-2319.

Table 1. Isotope abundance data for OCWD samples

Sample Name	Well/Sample Information	Aquifer	3H (atom/g)	4He (atom/g)	3He (atom/g)	22Ne (atom/g)	14C frac modern	delta 13C	36Cl/Cl (x1e15)	Cl mg/L	Sr ug/L
Waste Water 22A (WW-1)			1.76E+06	1.45E+12	1.69E+06	4.64E+11	0.83	-30.4			
Waste Water 22B (WW-3)				1.19E+12	1.59E+06	4.56E+11	0.82	-23.1	83.5	20	20
Q-10	injection point		1.11E+06	1.59E+12	1.67E+06	4.62E+11	0.37	-16.2	64.8	22	37
DW-1	deep well		<3.00E+04	2.79E+12	2.01E+06	5.83E+11	0.27	-15.3		8	56
SAKI-FV	production well	BI,BII,L	<3.00E+04	2.02E+12	2.80E+06	7.55E+11	0.83	-13.5	61.9	60	
HB-DYKE	production well	A	1.60E+07	2.00E+12	4.24E+06	5.26E+11	2.83	-20.7	75.5	95	289
OCWD-M5-1	monitoring well	T	5.19E+06	1.81E+12	2.22E+06	4.85E+11	1.95	-18.6	85.3	70	252
OCWD-M5-4	monitoring well	L	1.86E+06	1.77E+12	3.47E+06	5.70E+11	0.92	-13.7	82.5	42	508
OCWD-M19-1	monitoring well	T	5.02E+04	1.93E+12	2.73E+06	7.42E+11	0.81	-13.1	69.8	65	649
OCWD-M19-2	monitoring well	A	1.50E+06	1.93E+12	2.44E+06	6.85E+11	1.32	-14.1	96.2	75	425
OCWD-M19-3	monitoring well	B	1.22E+07	1.80E+12	2.90E+06	5.07E+11	2.19	-19.3	85.5	58	244
OCWD-M21-1	monitoring well	T	1.89E+06	1.66E+12	1.92E+06	5.15E+11	0.98	-16.7	103.0	33	62
OCWD-M21-2	monitoring well	A	6.56E+06	1.68E+12	2.05E+06	4.91E+11			104.0	75	203
OCWD-M21-3	monitoring well	B	2.51E+06	1.63E+12	1.95E+06	4.78E+11	1.43	-16.8	94.5	40	64
OCWD-M21-4	monitoring well	L	1.28E+07	1.61E+12	2.17E+06	4.99E+11	1.44	-16.2	91.9	36	92
OCWD-M11-1	monitoring well	T	7.55E+06	1.74E+12	3.32E+06	4.93E+11			87.3	90	419
OCWD-M11-4	monitoring well	L	5.40E+07	1.79E+12	8.62E+06	4.94E+11	5.55	-19.5	70.0	80	408
OCWD-M7A-1	monitoring well	T	1.19E+07	2.05E+12	3.98E+06	5.94E+11	3.03	-18.6	81.5	80	328
OCWD-M7A-3	monitoring well	B	1.67E+07	2.03E+12	4.83E+06	5.94E+11	3.10	-19.5	87.1	80	396
OCWD-M26	monitoring well	T/L	<3.00E+04						6.2	1000	
OCWD-M31	monitoring well	T	1.26E+05				0.05	-2.1	3.8	9000	
OCWD-CTG1-1	monitoring well	A	<3.00E+04	1.78E+12	2.42E+06	6.82E+11	0.64	-12.1	42.8	42	669
OCWD-CTG1-2	monitoring well	L,O	<3.00E+04	1.76E+12	2.13E+06	6.25E+11	0.59	-10.9	62.1	15	395
OCWD-CTG1-3	monitoring well	R,M	<3.00E+04	2.04E+12	1.89E+06	5.31E+11				18	65
OCWD-CTG1-4	monitoring well	LM	<3.00E+04	3.13E+12	1.99E+06	5.47E+11	0.28	-18.6		20	40
WM-3	production well	B,L?	<3.00E+04				0.81	-12.0	101.0	40	561
MSP-10	monitoring well	T	6.28E+04								
SA10-1	monitoring well	T	8.38E+04				0.26	-10.5	<8	2100	2507
OCWD-M28	monitoring well	T	8.38E+04						2.2	4500	
Seawater	Newport Pier		1.26E+05				1.07	1.5	<.5	18000	6807
Scale -carbonate	recarbonation						4.02	-29.5			

Table 1. (con't) Field data for OCWD samples

Sample Name	Elevation water table	Elevation ground level	Alk mg/liter	T (oC)	pH	EC uohm/cm
Waste Water 22A (WW-1)			60	23.3	6.93	1078
Waste Water 22B (WW-3)			15	25.1	6.71	150
Q-10			50		7.46	243
DW-1			160	26.0	8.70	374
SAKI-FV		32.0	200	19.8	7.73	804
HB-DYKE		53.7	170	26.0	7.74	736
OCWD-M5-1	11.1	22.1	150	24.9	7.76	638
OCWD-M5-4	0.0	22.1	160	22.7	7.64	580
OCWD-M19-1	9.3	21.9	200	20.2	7.45	820
OCWD-M19-2	5.9	21.9	175	21.3	7.54	733
OCWD-M19-3	4.4	21.9	140	23.0	7.65	549
OCWD-M21-1	5.8	22.1	100	25.4	7.34	318
OCWD-M21-2	5.7	22.1	100	25.0	7.90	522
OCWD-M21-3	1.7	22.1	70	26.4	7.29	334
OCWD-M21-4	-4.8	22.1	110	25.0	7.59	420
OCWD-M11-1	6.8	18.7	170	22.3	7.67	704
OCWD-M11-4	4.7	18.7	140	25.1	7.93	708
OCWD-M7A-1	4.9	16.5	180	22.8	7.81	714
OCWD-M7A-3	4.3	16.5	150	22.9	7.81	662
OCWD-M26	2.9	8.4	190	22.5	7.40	3170
OCWD-M31	2.8	10.5	600	20.5	7.46	17850
OCWD-CTG1-1	31.8	34.0	200	21.2	7.75	755
OCWD-CTG1-2	-43.8	34.0	180	22.9	7.80	456
OCWD-CTG1-3	-29.4	34.0	145	22.1	8.91	370
OCWD-CTG1-4	-13.2	34.0	180	22.9	9.10	403
WM-3		25.0	230	18.4	7.60	739
MSP-10	21.8	37.0	350	19.5	7.12	1117
SA10-1	1.8	7.0	300	21.0	7.57	6120
OCWD-M28	2.3	5.8	450	20.6	7.39	14490
Seawater	0.0	0.0	125	17.3	8.30	50800

Table 2. 3H-3He ages

Sample Name	Aquifer	3He/22Ne	Fraction 3He due to 3H	3He* (atom/g)	+ (atom/g)	3H/ (3H+3He)	Age (years)	+ (years)
<i>Zero age samples</i>								
WW-1		3.64E-06	2%	3.23E+04	4.61E+04			
WW-3		3.48E-06	-3%	-4.00E+04	4.53E+04			
Q-10		3.61E-06	1%	2.01E+04	4.59E+04			
<i>Zero 3H samples</i>								
DW-1		3.45E-06	-4%	-7.26E+04	5.79E+04			
OCWD-M19-1	T	3.68E-06	3%	8.37E+04	7.37E+04			
OCWD-CTG1-1	A	3.54E-06	-1%	-1.78E+04	6.77E+04			
OCWD-CTG1-2	L,O	3.41E-06	-5%	-9.80E+04	6.21E+04			
OCWD-CTG1-3	R,M	3.55E-06	-1%	-1.02E+04	5.27E+04			
OCWD-CTG1-4	LM	3.63E-06	2%	3.14E+04	5.44E+04			
SAKI-FV	BI,BII,L	3.70E-06	4%	9.91E+04	7.50E+04			
HB-DYKE	A	8.06E-06	56%	2.36E+06	5.22E+04	0.87	2.5	0.2
OCWD-M5-1	T	4.57E-06	22%	4.86E+05	4.82E+04	0.91	1.6	0.2
OCWD-M5-4	L	6.08E-06	41%	1.43E+06	5.66E+04	0.57	10.2	0.8
OCWD-M19-2	A	3.57E-06	0%	-2.64E+03	6.80E+04	1.00	0.0	0.8
OCWD-M19-3	B	5.71E-06	38%	1.09E+06	5.04E+04	0.92	1.5	0.2
OCWD-M21-1	T	3.73E-06	4%	8.28E+04	5.11E+04	0.96	0.8	0.5
OCWD-M21-2	A	4.17E-06	14%	2.93E+05	4.88E+04	0.96	0.8	0.1
OCWD-M21-3	B	4.08E-06	12%	2.42E+05	4.75E+04	0.91	1.7	0.3
OCWD-M21-4	L	4.35E-06	18%	3.91E+05	4.96E+04	0.97	0.5	0.1
OCWD-M11-1	T	6.74E-06	47%	1.56E+06	4.90E+04	0.83	3.4	0.3
OCWD-M11-4	L	1.75E-05	80%	6.86E+06	4.90E+04	0.89	2.1	0.2
OCWD-M7A-1	T	6.70E-06	47%	1.86E+06	5.90E+04	0.87	2.6	0.3
OCWD-M7A-3	B	8.13E-06	56%	2.71E+06	5.90E+04	0.96	2.7	0.3

Table 3. Ambient versus injected water mixing ratios

Sample Name	3H (atom/g)	22Ne (atom/g)	delta 13C	T (°C)
Mostly ambient water				
DW-1	<3.00E+04	5.83E+11	-15.3	
SAKI-FV	<3.00E+04	7.55E+11	-13.5	19.8
OCWD-M19-1	5.02E+04	7.42E+11	-13.1	20.2
OCWD-CTG1-1	<3.00E+04	6.82E+11	-12.1	21.2
OCWD-CTG1-2	<3.00E+04	6.25E+11	-10.9	22.9
OCWD-CTG1-3	<3.00E+04	5.31E+11		22.1
OCWD-CTG1-4	<3.00E+04	5.47E+11	-18.6	22.9
WM-3	<3.00E+04		-12.0	18.4
average	<3.00E+04	6.38E+11	-13.6	21.1
std dev		14%	19%	8%
Both ambient and injection water				
OCWD-M5-4	1.86E+06	5.70E+11	-13.7	22.7
OCWD-M19-2	1.50E+06	6.85E+11	-14.1	21.3
OCWD-M7A-1	1.19E+07	5.94E+11	-18.6	22.8
OCWD-M7A-3	1.67E+07	5.94E+11	-19.5	22.9
average	7.99E+06	6.11E+11	-16.5	22.4
std dev	94%	8%	18%	3%
Mostly injection water				
WW-1	2.09E+06	4.64E+11	-30.4	23.3
WW-3	2.09E+06	4.56E+11	-23.1	25.1
Q-10	1.11E+06	4.62E+11	-16.2	
HB-DYKE	1.60E+07	5.26E+11	-20.7	26.0
OCWD-M5-1	5.19E+06	4.85E+11	-18.6	24.9
OCWD-M19-3	1.22E+07	5.07E+11	-19.3	23.0
OCWD-M21-1	1.89E+06	5.15E+11	-16.7	25.4
OCWD-M21-2	6.56E+06	4.91E+11		25.0
OCWD-M21-3	2.51E+06	4.78E+11	-16.8	26.4
OCWD-M21-4	1.28E+07	4.99E+11	-16.2	25.0
OCWD-M11-1	7.55E+06	4.93E+11		22.3
OCWD-M11-4	5.40E+07	4.94E+11	-19.5	25.1
average	1.03E+07	4.89E+11	-19.7	24.7
std dev	142%	4%	22%	5%
water at 25°C		4.61E+11		
average groundwater		6.87E+11		

List of Figures

1. Piper diagram of groundwaters sampled for isotopic analysis. The different groundwater types are indicated. Some TDS values (circles) are too large for this figure and are not shown.
2. Map of the Talbert Gap study area.
3. Graph of $^3\text{He}/^{22}\text{Ne}$ showing excess ^3He in some samples. The samples which are zero age or have zero ^3H give a value nearly identical to that for water in equilibrium with air.
4. Chlorine isotopes show the effects of evaporation which concentrates Cl but does not change the ratio of $^{36}\text{Cl}/\text{Cl}$ and the addition of seawater which is rich in stable Cl but not radioactive ^{36}Cl ($t_{1/2} = 3 \times 10^5$ yr). Most notable is the lack large amounts of ^{36}Cl in samples high in ^3H .
5. Strontium concentration increases as a function of time (as measured by ^3H - ^3He ages) in the aquifer unit. The increase is not due to mixing (as shown by the Ne data) and must be the result of chemical interaction between aquifer materials and the blended injection water.

Figure 1. Piper diagram of groundwaters sampled for isotopic analysis.

Figure 2. Talbert Gap (Orange County, CA)

STUDY AREA AND WELL LOCATION MAP

Figure 4. Chlorine Isotope Trends

Fig. 5 Evolution of Sr concentration