

## RADIOLYTIC H<sub>2</sub> SOURCE AT A RADIOACTIVE WASTE-CONTAMINATED SITE IN TENNESSEE. J.

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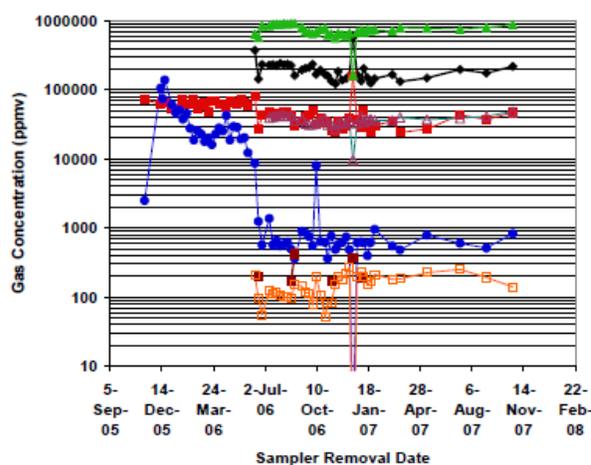
**Introduction:** For lithotrophic bacterial communities in the deep subsurface, sustainable energy sources, particularly hydrogen, are required [1]. This hydrogen-based chemoautotrophy is considered one of the first metabolisms that appeared on the early Earth. Hydrogen gas is also a key ingredient (electron donor) for the abiotic synthesis of organic compounds from oxidized carbon compounds such as CO<sub>2</sub>. To date several abiotic sources and mechanisms of H<sub>2</sub> in the Earth's subsurface have been discussed and identified, including serpentinization of mafic/ultramafic rocks, fracture-surface reactions of silicate rocks with water, and radiolysis of water. Although these abiotic reactions can be shown to produce H<sub>2</sub> in laboratory [2], the relevance and importance of fracture-surface reactions and radiolysis in natural settings are very poorly understood and documented.

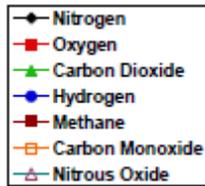
Field testing at a series of radioactive waste-contaminated and uncontaminated sites at the Oak Ridge Field Research Center (ORFRC) in Oak Ridge, Tennessee revealed unusually large equilibrium gas-phase H<sub>2</sub> concentrations in groundwater, ranging from 0.1 to 13.9%, by volume, in many monitoring wells surrounding four former radiological wastewater disposal ponds at the Y-12 plant in Oak Ridge, Tennessee [3, 4]. The source of this high H<sub>2</sub> gas is of great interest, and candidates include radiolysis, biogenic, chemogenic, electrolytic, geologic, and thermolytic. Distinct δ<sup>2</sup>H values of H<sub>2</sub> from different sources could provide insights into the source of elevated H<sub>2</sub> (up to 14%) encountered in groundwaters from the ORFRC site.

**Study Site:** The operation of the S-3 waste disposal ponds on the Oak Ridge Reservation in East Tennessee resulted in extensive areas of subsurface inorganic, organic, and radioactive contamination from historical and secondary sources. The Ponds received 3.2 x 10<sup>8</sup> liters of acidic, nitrate and uranium-bearing waste for 32 years until the Ponds contents were "neutralized", "denitrified", and capped in 1988. Residual sludge in the S-3 Pond contains average U and Th concentrations of 1023 and 479 mg/L. Although the Ponds are capped, the vast majority of contaminant mass has migrated away from the Ponds into the underlying geologic media. Groundwater is highly contaminated near the source with U (>60 ppm) and Tc (>40,000 pCi/L) and nitrate (1,000-10,000 ppm) and the solid-

phase U is as high as 1000 ppm. Other contaminants in the groundwater plume include thorium and volatile organic compounds. The ground water pH ranges from 3.2 close to the Ponds to over 7.0 in wells farther down-gradient. Fixed gases detected in groundwater include significant quantities of CO<sub>2</sub>, CO, N<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> [3, 4].

**Results and Discussion:** Unusually high hydrogen gas concentrations (up to 4% and 14%) have been observed in two monitoring wells (FW010 and FW112, see Figure 1) located within 10 m of the asphalt capped area of the S-3 ponds impoundment. In other proximate groundwater monitoring wells, H<sub>2</sub> concentrations greater than 1000 ppmv have been regularly measured; three additional wells within 50 m of this area and within the uranium, nitrate, and acidity contaminant plume have also been found to contain H<sub>2</sub> concentrations greater than 1000 ppmv when sampled on several dates. Survey sampling of many additional wells within the ORFRC has exhibited lower and more typical H<sub>2</sub> concentrations. Even at waste sites impacted with fuels and waste solvents, published H<sub>2</sub> concentrations are typically less than 100 ppmv, that is, orders-of-magnitude lower than those observed at the ORFRC site. We are not aware of published reports of such high H<sub>2</sub> concentrations in groundwater or sediments in field settings.





**Figure 1.** Equilibrium gas concentrations in monitoring well FW010 at the ORFRC between October 2005 and August 2007 [4].

The  $\delta^2\text{H}$  value of natural  $\text{H}_2$  varies significantly, depending on their sources and production mechanisms. Near-surface atmospheric  $\text{H}_2$  has  $\delta^2\text{H}$  values, ranging from -300 to +100 ‰ [5]. For example,  $\text{H}_2$  from fossil-fuel and biomass burning has  $\delta^2\text{H}$  values of  $-200 \pm 10$  and  $-290 \pm 60$  ‰, respectively [6].  $\delta^2\text{H}$  values of microbial  $\text{H}_2$  are in the range of -700 to -800 ‰ [5], which are close to that in isotopic equilibrium with local groundwater due apparently to enzymatic activities. In contrary, experimentally produced radiolytic  $\text{H}_2$  has much higher  $\delta^2\text{H}$  values of -500 to -550 ‰ [7], reflecting kinetic isotope effects during radiolysis.

$\delta^2\text{H}$  values of dissolved  $\text{H}_2$  in groundwater were analyzed at two wells nearby the S-3 pond (FW106 and FW113-2) and one well (PTMW02) several hundred meters down-gradient. The  $\delta^2\text{H}$  values ranges from -586 to -493 ‰, except for the May 2008 sample at FW106 (-749 ‰). The former values are clearly out of isotopic equilibrium with the groundwater ( $\delta^2\text{H} = -37.6$  to  $-13.2$  ‰), and consistent with the radiolytic origin of the  $\text{H}_2$  gases (-500 to -550 ‰, [7]). In contrary, the depleted  $\delta^2\text{H}$  of the May 2008 sample at FW106 (-749 ‰) is very close to that in isotopic equilibrium with the groundwater. Microbial mediation of  $\text{H}_2$ , including by methanogens, is the most likely cause of the observed rapid isotopic exchange for the otherwise very slow reaction ( $10^3$ - $10^4$  years) [7].

Results of this study demonstrate for the first time that high concentrations (up to 14% ppmv) of  $\text{H}_2$  can be produced in the subsurface of radioactive-waste contaminated sites most likely by the radiolysis of water. However, unambiguous identifications of radiolytic sources of  $\text{H}_2$  in field could be challenging [8], because unique  $\delta^2\text{H}$  values (-500 to -600 ‰) of radiolytic  $\text{H}_2$  could be readily erased by microbial activities. The likely radiolytic source of the observed high  $\text{H}_2$  concentrations has far-reaching implications for abiotic organic synthesis and chemolithoautotrophy, both in terrestrial and extraterrestrial environments.

#### References:

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