

Environmental Remediation Sciences Program

Major Fixed Gaseous Microbial Metabolites (CO₂ H₂ CH₄ N₂O and CO) Are Abundant in FRC Groundwater

Brian Spalding and David Watson



Needs Driving Development of Fixed Gas Analytical Capabilities

ORNL procured a state-of-the-art hydrogen analyzer gas chromatograph to support microbial studies and to perform groundwater tracer tests with noble gases (He and Ne).

Justification:

Hydrogen gas is an important indicator metabolite for in situ microbial processes related to contaminant degradation and immobilization.

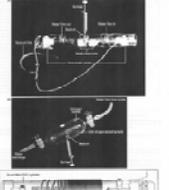
Groundwater tracer tests using He and Ne under natural hydraulic gradients are needed for contaminant migration assessment (direction, rates, dispersion).

Previous research on hydrogen gas in anoxic sediments, found low concentrations (0.1-20 ppmv) requiring a challenging sampling and analytical protocol

Hydrogen Concentration Ranges:

Terminal Electron Accepting Process	Hydrogen (H ₂) Concentration (nM)	Hydrogen (H ₂) Concentration (ppmv)
Denitrification	<0.1	<0.12
Iron Reduction	0.2-0.8	0.2-1.0
Sulfate Reduction	1-4	1.2-5
Reductive Dechlorination	>1	>1.2
Mathanogenesis	5-20	6-25

Hydrogen Sampling Tools:



Lovely & Goodwin, 1988. *Geochim Cosmochim Acta* 52: 2993-3003.

And many others

To Support FRC Investigators and Site Characterization Needs, We Procured a Gas Chromatograph To Analyze Hydrogen, and Helium, and Neon and ...



SRI "Blue Collar" GC with interchangeable components:

Manual or rotary sampling valve injection on column with two detectors in series

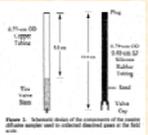
1. Thermal Conductivity
2. Reductive Gas (HgO)

How to Use the FRC GC Effectively: Our Decision

1. Manually inject 0.5 mL with gas-tight syringe from stripped bubbles.



2. Passive Sampler for He & Ne Tracers: Sanford & Solomon, 1996. *Water Resources Res.* 32:1635.



3. Hybrid Passive Sampler & Syringe:



Hydrogen Sampling By the Bubble Stripping Method Cannot Be Used at FRC



Well	Released Gas	During Pumping		
		Bubble Stripped Gas	Avg CO ₂ (ppm)	Avg H ₂ (%)
FW115-1	38	64.3	1271	3.0
FW113-1	128	98.8	361	1.0
FW010	63	95.2	3272	1.6
FW106	7	46.5	204	2.2
FW115-2	124	85.5	1450	1.5
FW112	117	98.5	1759	1.3

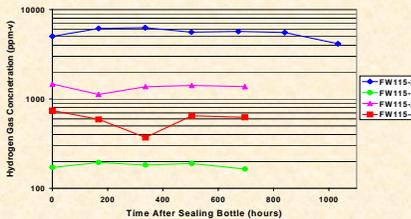


Problems: Out-gassing of CO₂ as pressurized groundwater is brought to the surface dilutes the H₂ in the "bubble".

If the "bubble" gas is analyzed anyway, it can be an order-of-magnitude too low in H₂. There is a lot of CO₂ in FRC groundwater!

Hydrogen Gas Is Rather Stable in FRC Groundwater

Hydrogen in Sealed Bottles of Groundwater From Wells FW115



Hydrogen Appears To Originate From the S-3 Ponds via biogenesis and/or radiolysis. Is Hydrogen From the S-3 Ponds/Parking Lot Safe?



One Conceptual Model of S3 Ponds

Is This Model of S3 Ponds Helpful or Useful?

Is it 4-acre dome with a good 2-ft of compacted clay (@10⁻⁷ cm/sec) plus a geomembrane liner and no vents?

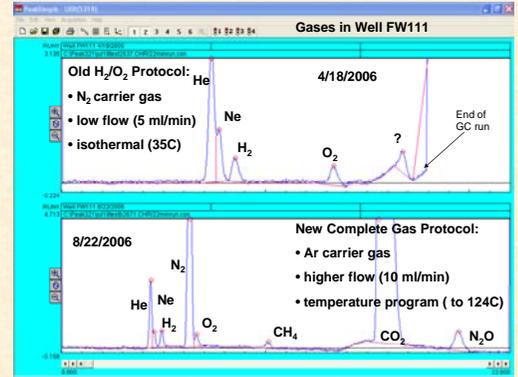


We have developed a new rapid method to analyze a suite of gases in one GC run (H₂ O₂ N₂ N₂O CO₂ CO CH₄ He & Ne)

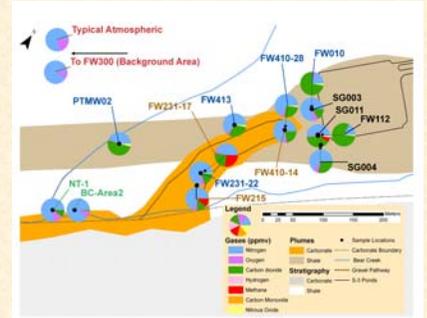
- Metabolic gases present and persistent
- Source under S-3 Ponds and Tanks?
- All gases present in significant quantities are being quantified

Well	N ₂ (ppmv)	O ₂ (ppmv)	CO ₂ (ppmv)	H ₂ (ppmv)	CH ₄ (ppmv)	CO (ppmv)	N ₂ O (ppmv)	Sum Gases (ppmv)
FW231-1	7.62E+05	5.93E+04	1.86E+05	4.46E+00	ND	8.50E+00	1.37E+04	1.02E+06
FW231-2	4.08E+05	3.40E+04	2.44E+05	6.05E+00	2.50E+05	1.35E+01	3.52E+02	9.36E+05
FW215	7.02E+05	4.83E+04	1.28E+05	1.29E+00	1.18E+05	7.43E+00	ND	9.96E+05
FW410-1	6.28E+05	4.03E+04	2.37E+05	1.60E+03	1.63E+03	1.53E+02	2.25E+04	9.32E+05
FW413	5.59E+05	3.70E+04	2.72E+05	6.17E+02	3.98E+02	8.99E+01	2.73E+04	9.10E+05
PTMW02	4.39E+05	1.80E+04	4.43E+05	1.41E+02	ND	5.13E+01	3.36E+04	9.34E+05
SG11	4.54E+05	1.82E+04	3.57E+05	7.10E+00	5.31E+04	2.18E+00	2.14E+04	9.04E+05

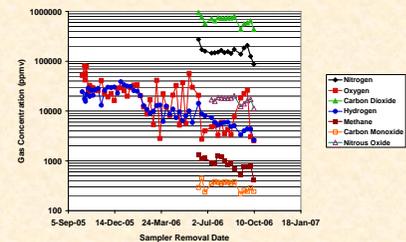
Gas Chromatograms for Fixed Gases



Distribution of Fixed Gases at FRC



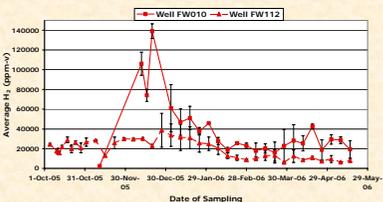
When Hydrogen Peaks Again This Winter, How Will Other Fixed Gases Behave?



Hydrogen At the FRC - Summary

- Hydrogen gas is easier and quicker to sample and to analyze more accurately than ever before.
- There is a lot more hydrogen gas in FRC and surrounding groundwater than we or anyone expected.
- Hydrogen gas is remarkably stable in FRC groundwater
- Potential hydrogen sources, sinks, and contaminant effects and interactions abound at the FRC (and elsewhere).
- Our findings are published this week in *Environmental Science & Technology ASAP*, "Measurement of dissolved H₂, O₂, and CO₂ in groundwater using passive samplers for gas chromatographic analyses."

Hydrogen Concentrations Peak in Monitoring Wells Near S-3 Ponds in December 2005



OAK RIDGE NATIONAL LABORATORY

Contact: David Watson, FRC Manager, (865) 241-4749, watsondb@ornl.gov

<http://www.esd.ornl.gov/nabirfrc>