Low-Level Perchlorate Analyses by LC/MS/MS

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EPA Method 314 Determination of Perchlorate in Drinking Water Using Ion Chromatography

- Method 314 employs conductivity detection.
- Conductivity is not specific to perchlorate.
- IC can yield false positive results at concentrations in the low-ppb range.

EPA 314
Performance Evaluation Study
October 2001

- Method 314 does not produce reliable results in environmental groundwaters at low-ppb levels.
- High bias and high false positive rates occurred with real groundwater samples at low-ppb levels.
- Consensus reached among LANL, GEL, DOE, and NMED-OB
  - MDL = 4 ppb
  - PQL = 12 ppb

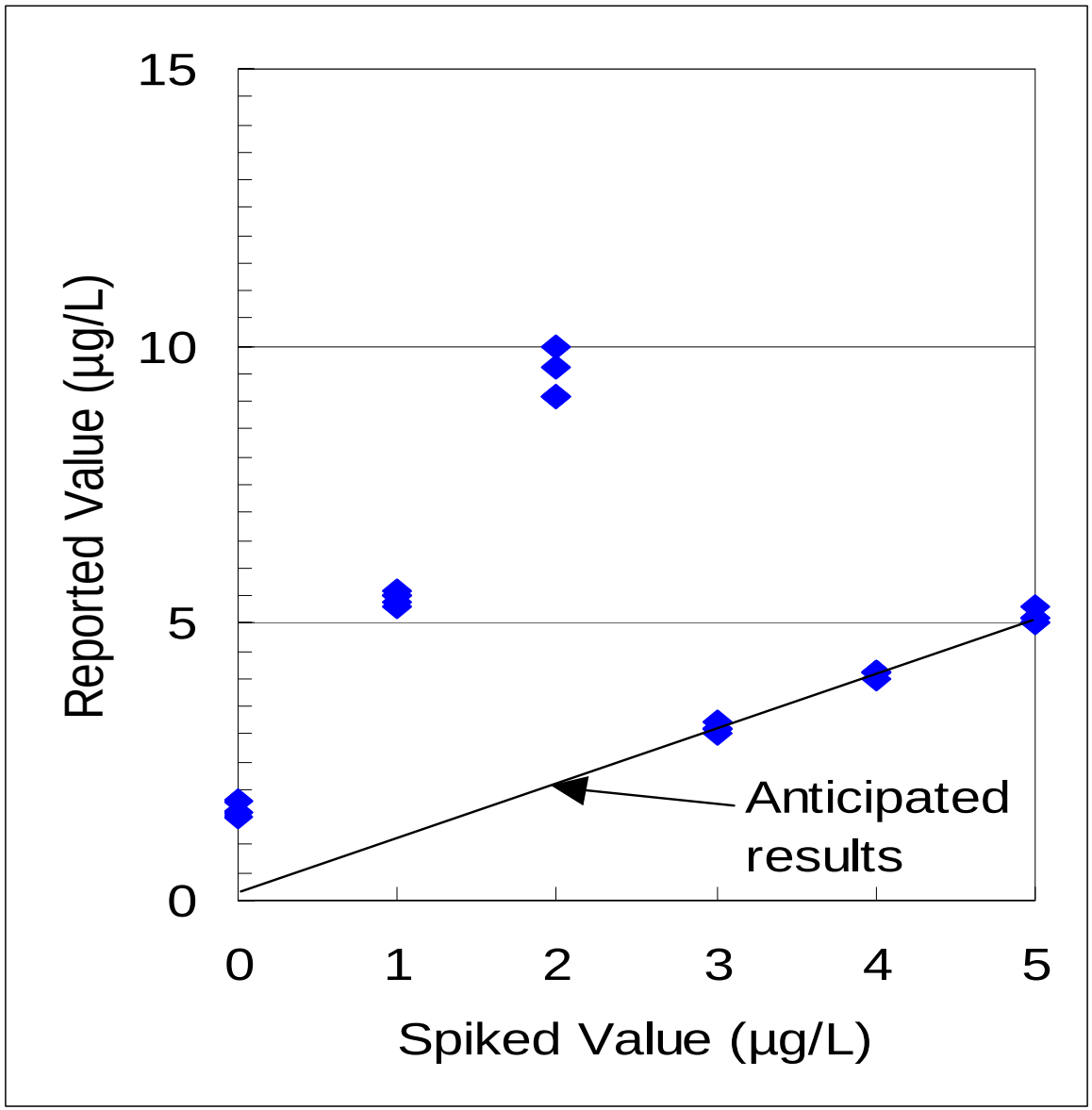
Liquid Chromatography / Mass Spectrometry / Mass Spectrometry (LC/MS/MS)

- Available in November 2001
- More perchlorate-specific than IC.
- Lower detection limits than IC.
- MDL = 0.25 ppb
- PQL = 0.5 ppb

LC/MS/MS
Performance Evaluation Study
November 2001

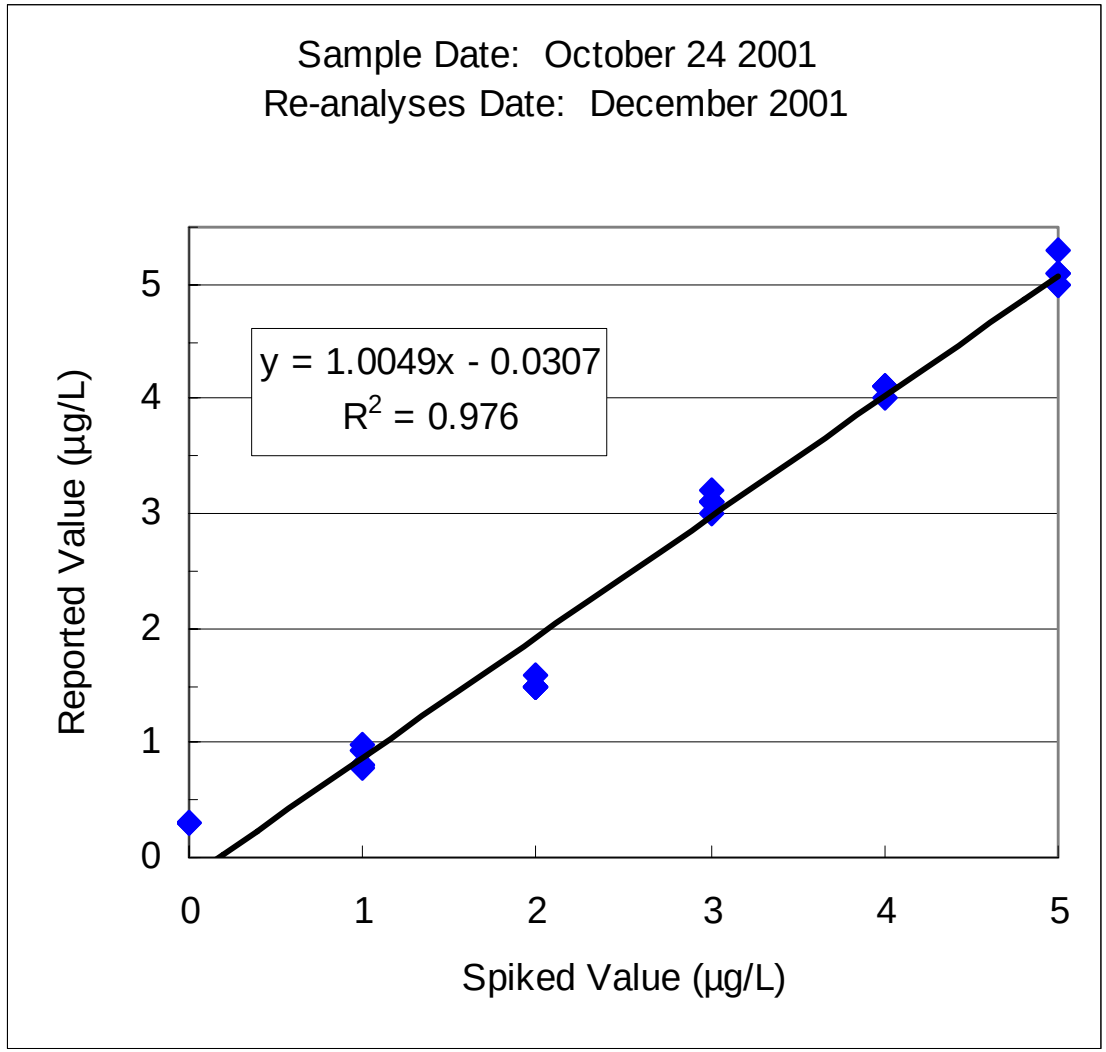
- Conducted at Acculabs, Inc. – Golden, CO.
- Environmental groundwaters from 3 sites submitted (Locations A, B, and C).
- Spike concentrations = 1, 2, 3, 4, and 5 ppb

Groundwater A



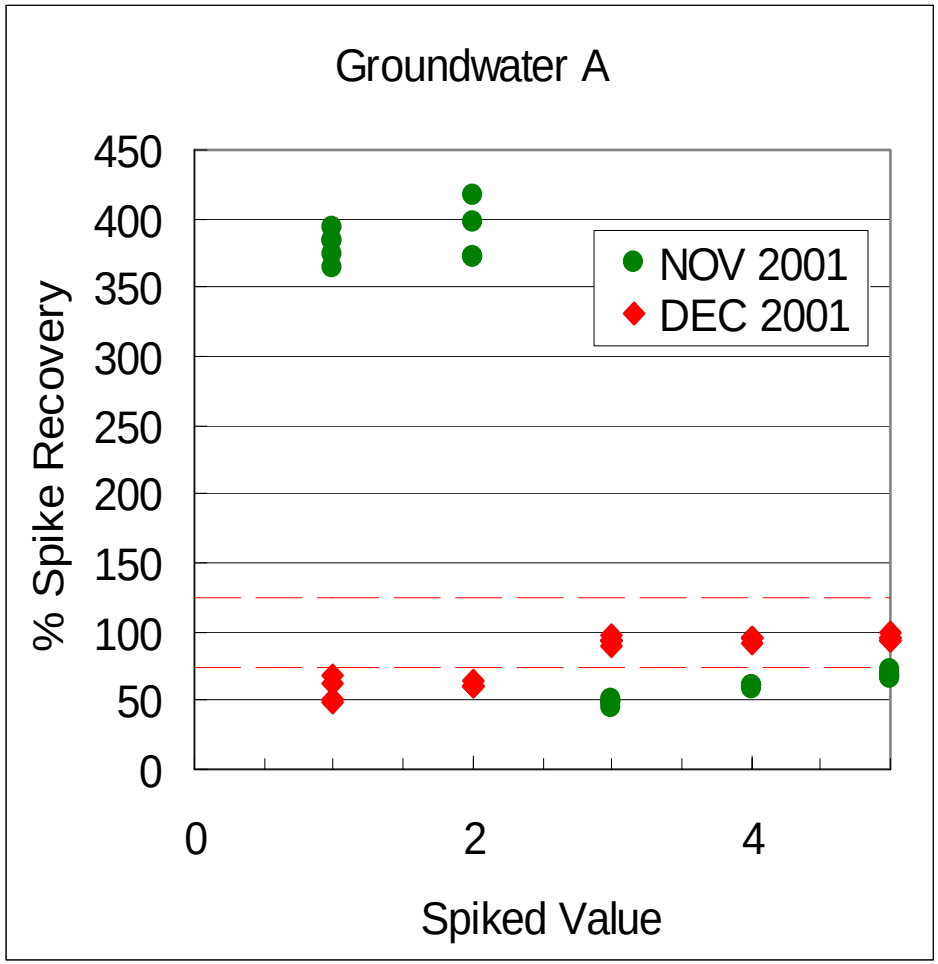
Groundwater A
Re-analyses – December 2001

A calibration standards discrepancy and an electronics problem and led to re-analyses.



Spike recovery was used to gauge accuracy in the PE study.

- Recovery control limits, = 75% to 125%.
- Orig. analyses recoveries = 45 % to 563 %.
- No recoveries within control limits.
- Re-analyses recoveries = 45% to 159 %
- 80% of the re-analyses within control limits.



LC/MS/MS
Performance Evaluation Study
May/June 2003

- Conducted at General Engineering Laboratories, Inc. (GEL) – Charleston, SC.
- MDL = 0.05 ppb
- PQL = 0.20 ppb
- Environmental groundwaters from 8 sites
- De-ionized water

Objectives

- Determine if the method works in environmental groundwater samples.
- Verify the method detection limit of 0.05 ppb
- Verify the method practical quantitation limit of 0.2 ppb
- Determine whether perchlorate is present in LANL area and regional groundwater samples.

Spike perchlorate concentrations for 2003 PE study

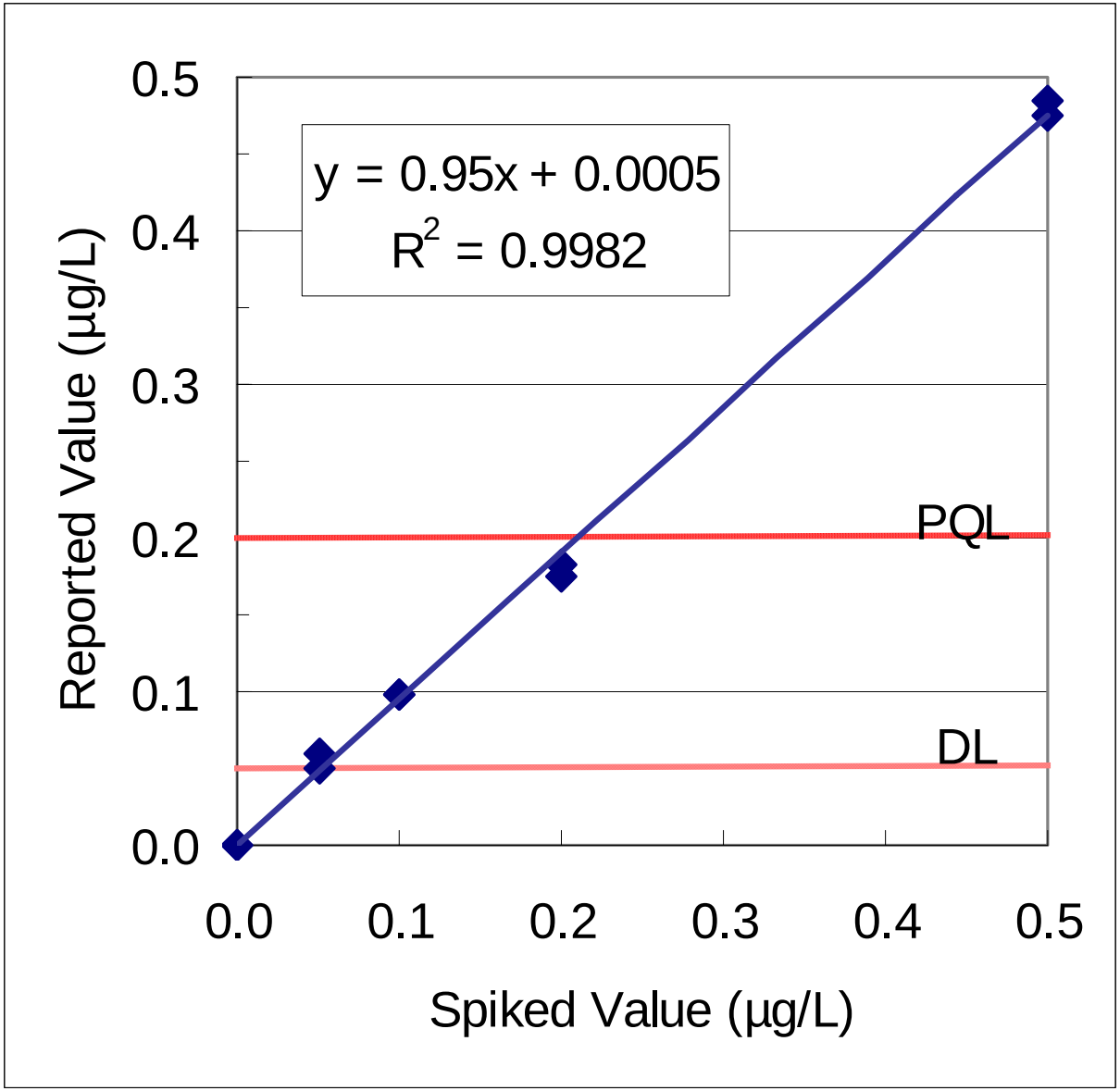
Objective	Spike concentration
Unspiked	0 ppb
~ MDL	0.05 ppb
> MDL and <PQL	0.10 ppb
~PQL	0.20 ppb
> PQL	0.50 ppb

Environmental groundwater samples submitted for PE Study

(samples spiked at ERA)

Source	Spiked perchlorate concentration (ppb)					Trip Blank collected	Field Blank collected	Equipment Blank collected
	0	0.05	0.1	0.2	0.5			
A	✓	✓	✓	✓	✓	✓	✓	✓
B	✓	✓	✓	✓	✓		✓	
D	✓	✓	✓	✓	✓	✓	✓	✓
E	✓	✓	✓	✓	✓	✓	✓	
F	✓	✓	✓	✓	✓	✓	✓	
G	✓	✓	✓	✓	✓		✓	
H	✓	✓	✓	✓	✓		✓	
I	✓	✓	✓	✓	✓	✓	✓	
DI water	✓	✓	✓	✓	✓			

Results of DI Water Samples



Results of 2003 PE Study

Source	Result (µg/L)	MDL	PQL	R^2	slope
DI water	0	0.05	0.2	0.998	0.95
A	0.32	0.05	0.2	0.97	0.99
B	0.28	0.05	0.2	0.98	0.98
D	0.66	0.05	0.2	0.98	0.94
E	0.21	0.05	0.2	0.96	0.86
F	0.12	0.05	0.2	0.99	0.75
G	0.17	0.1*	0.4*	0.89	0.76
H	0.23	0.1*	0.4*	0.93	0.94
I	0.17	0.05	0.2	0.95	0.86

*Samples were diluted, resulting in higher MDL and PQL

Results of QC Samples

Source	Trip Blank (ppb)	Field Blank (ppb)	Equipment Blank (ppb)
A	<0.05	<0.05	<0.05
B		<0.05	
D	<0.05	<0.05	<0.05
E	<0.05	<0.05	
F	<0.05	<0.05	
G		<0.05	
H		<0.05	
I	<0.05	<0.05	

Spike recoveries of environmental groundwaters (no DI water samples)

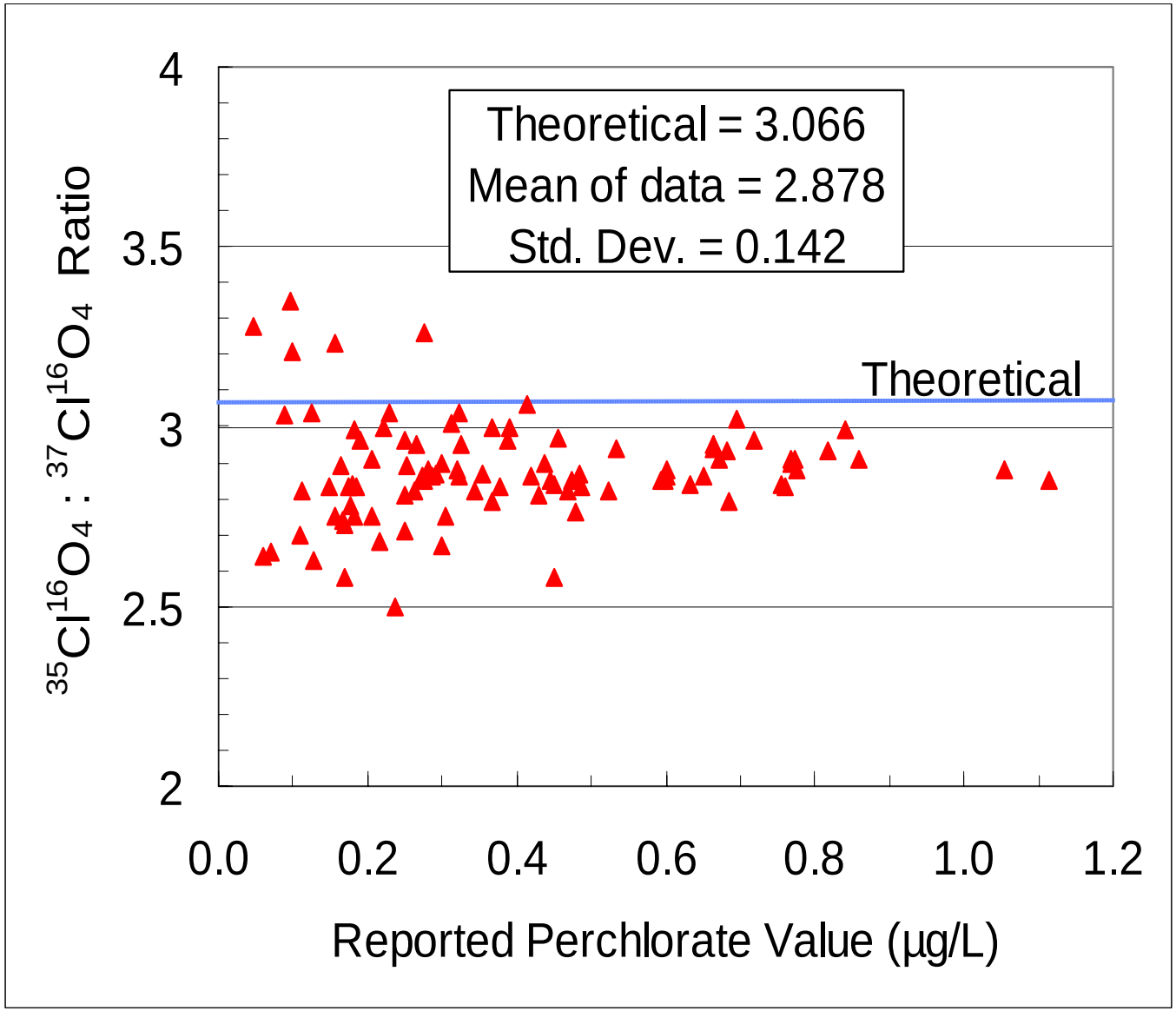
Spike Value	Within Control Limits	Outside Control Limits
<PQL	44%	56%
>PQL	87%	13%

Isotopic Ratios

- Chlorine exists in nature as ^{35}Cl and ^{37}Cl.
- Theoretical ^{35}Cl:^{37}Cl ratio = 3.066
- Perchlorate result based upon the sum of $^{35}ClO_4$ and $^{37}ClO_4$ measurements.

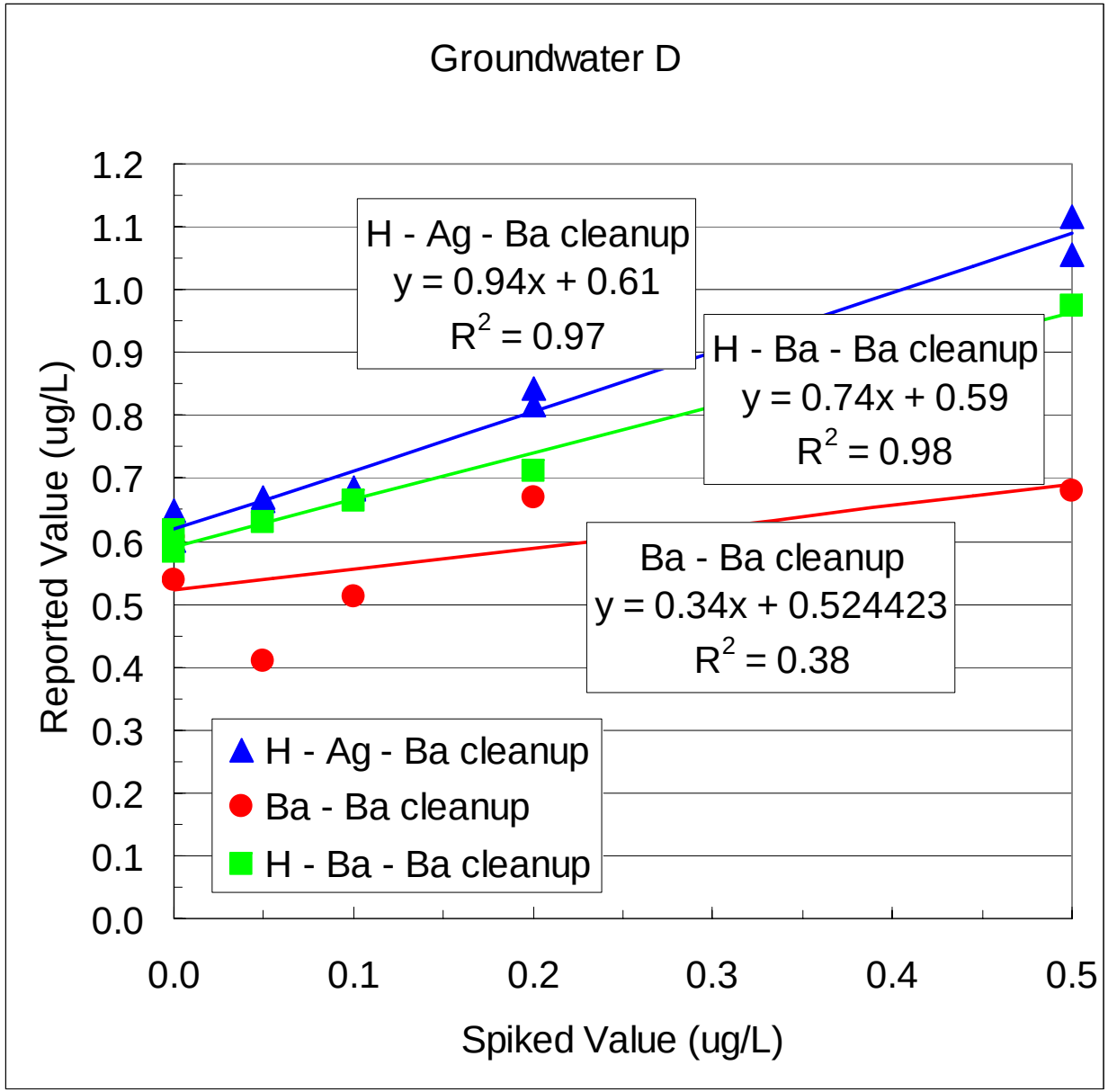
$^{37}ClO_4$ (ppb)	$^{35}ClO_4$ (ppb)	Reported ClO_4 (ppb)
ND	<0.15	
0.05 = MDL	0.15	0.20
0.20 = PQL	0.61	0.81
0.24	0.75 = upper range	0.99

Isotopic Ratio Results



Sample Preparation Cleanup Columns

- Hydrogen – Barium – Silver
- Barium – Barium
- Hydrogen – Barium – Barium



Historical LC/MS/MS data

Groundwater	Analytical Laboratory	Analysis Date	Reported Value (µg/L)
A	Acculabs	Dec-01	0.3
	Acculabs	Jan-02	<0.25
	Acculabs	Jan-02	<0.25
	Acculabs	Jan-02	0.3
	Acculabs	Jan-02	0.3
	GEL	Jun-03	0.3
	GEL	Jun-03	0.33
B	Acculabs	Dec-01	0.5
	Acculabs	Jan-02	<0.25
	GEL	Jun-03	0.49
	GEL	Jun-03	0.29
D	Acculabs	Dec-01	0.67
	GEL	Jun-03	0.60
	GEL	Jun-03	0.65
E	Acculabs	Dec-01	<0.25
	GEL	Jun-03	0.19
	GEL	Jun-03	0.12
DI Water	Acculabs	Dec-01	<0.25
	GEL	Jun-03	<0.05
	GEL	Jun-03	<0.05

Conclusions

- QC blanks results were all non-detect – indicates the method is generally free from contamination.
- Sample analytical preparation addresses some analytical interferences, but low bias persists.
- Chlorine isotopic data demonstrate that such data may provide a useful and accurate means to discriminate false positive signals from perchlorate signals. PE Study isotopic results have a low bias.
- Perchlorate appears to be ubiquitous.

Implementation of LC/MS/MS

Effective January 2004, all groundwater samples are analyzed for perchlorate by both EPA approved Method 314 and LC/MS/MS

Future Directions

(Spring 2004 – PES with synthetic groundwaters)

- Evaluate the potential for the LC-MS-MS to generate false positives (*this may happen by the formation of perchlorate from chloride ion or by other unidentified means*).

- Interferences still exist that result in low bias at increasing concentrations. Evaluate matrix suppression effects.