General (Perchlorate, Groundwater)

Perchlorate Overview

for presentation to the

Los Alamos National Laboratory

Hydrogeologic Characterization Quarterly Meeting

Los Alamos National Laboratory
U.S. Department of Energy

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January 30, 2002 [redacted]

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Perchlorate --- Talk Outline

- Background information on perchlorate.

- Perchlorate analytical issues-
  - Most prior LANL perchlorate indications are non-detections due to matrix interference;
  - GEL detection limit probably too high.

- LANL spike study-
  - GEL detection limit in question;
  - Babcock performance seems reliable;
  - Acculabs accuracy in question.

- Summary of spring and Los Alamos water supply perchlorate results.

The Perchlorate Ion (ClO_4^{-1}) --- An Overview

- Highly soluble, mobile, and persistent.
- Appears as ammonium perchlorate (salts) and as perchloric acid.
- A strong oxidizer used in rocket fuel, fireworks, air bags, and analytical chemistry.
- Interferes with iodine uptake by the thyroid gland, affecting normal hormone production.
- California developed the current analytical method with a 4 ppb detection limit in 1997.
- Detected by EPA in ground water in 18 states, most extensively in CA.

Perchlorate --- Regulatory Standards

- No current state or federal drinking water standard.
- 1997 - California set a drinking water action level of 18 ppb.
- 1998 - EPA added to the SDWA Contaminant Candidate List.
- 2001- Texas set an interim drinking water level of 4 ppb.
- EPA has set provisional action levels of 4 ppb to 18 ppb.
- A federal standard awaits the completion of risk assessment studies.
- Current EPA MCL recommendation is 1 ppb.

Perchlorate --- LANL Sources

- Possible past discharges to Acid & Pueblo Canyons from TA-45 and to DP & Los Alamos Canyons from TA-21

- Current discharges from the RLWTF at TA-50 to Mortandad Canyon at NPDES Outfall 051.

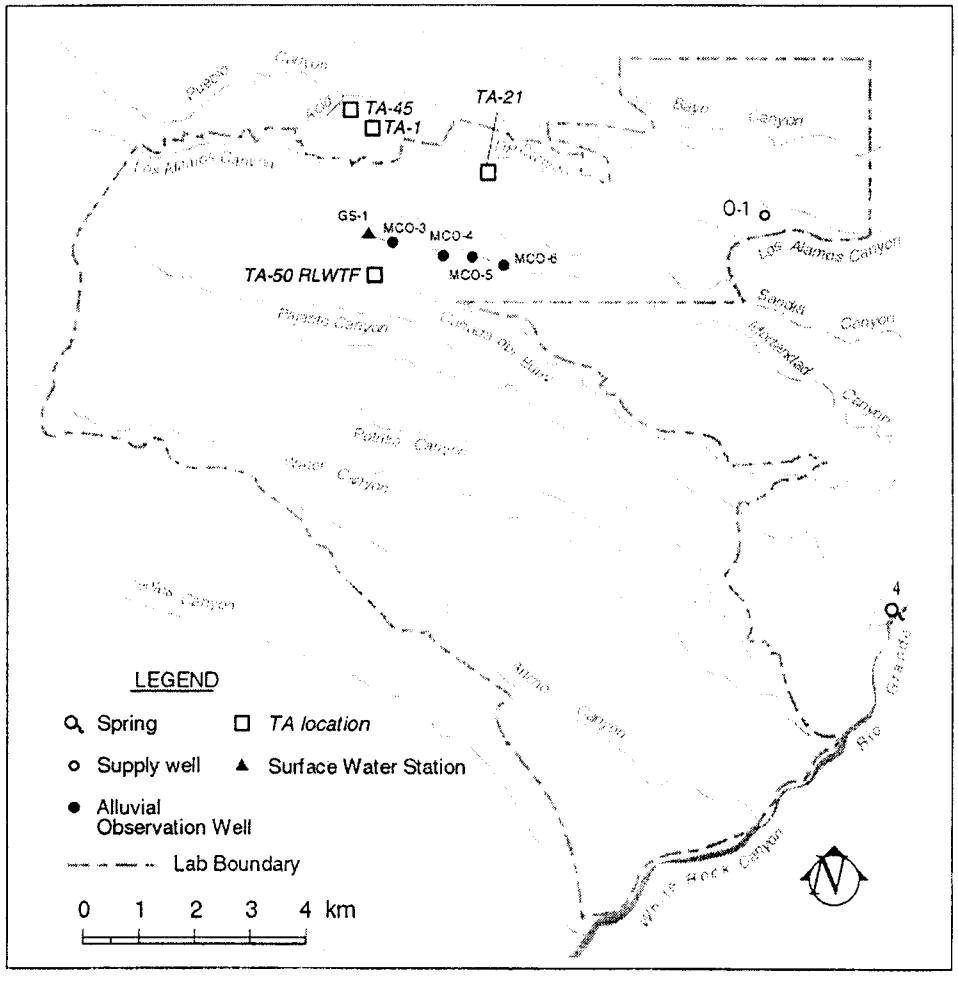
- Average RLWTF effluent concentration was about 250 ppb in 2000.

- RLWTF completed a perchlorate waste stream survey in 2000.

- Primary sources identified were duct wash-down water and process waste water.

- RLWTF has proposed a Waste Acceptance Criteria (WAC) of 500 ppb.

Perchlorate --- LANL Sources and Possible Detections



Locations of selected TAs, alluvial groundwater observation wells, springs, and surface water monitoring stations.

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Perchlorate --- Treatment at the RLWTF

- RLWTF conducted pilot scale tests using ion exchange resins selective for perchlorate.

- Pilot tests confirmed that treatment to below 4 ppb is achievable.

- All tubular ultrafilter (TUF) permeate will be treated by the ion exchange process.

- Ion exchange vessels and resin will be incinerated off site.

- Ion exchange treatment system is expected to be operational by March 31, 2002.

Perchlorate --- Analytical Issues

- EPA: "The need for a reporting limit of 4 ppb taxes the sensitivity and reproducibility of the current ion chromatography method."

- EPA is working to study existing methods and develop new techniques.

- The IC method relies on anion separation as the solution flows through a column. The detector response at a retention time characteristic of the anion is proportional to concentration.

- The elution time is the only parameter used to determine if the peak is perchlorate. If other anions are eluted at the same time the IC method can not tell the difference.

- If other anions are present, a false positive would result with no method to further separate perchlorate from the interfering species.

Perchlorate --- Analytical Issues

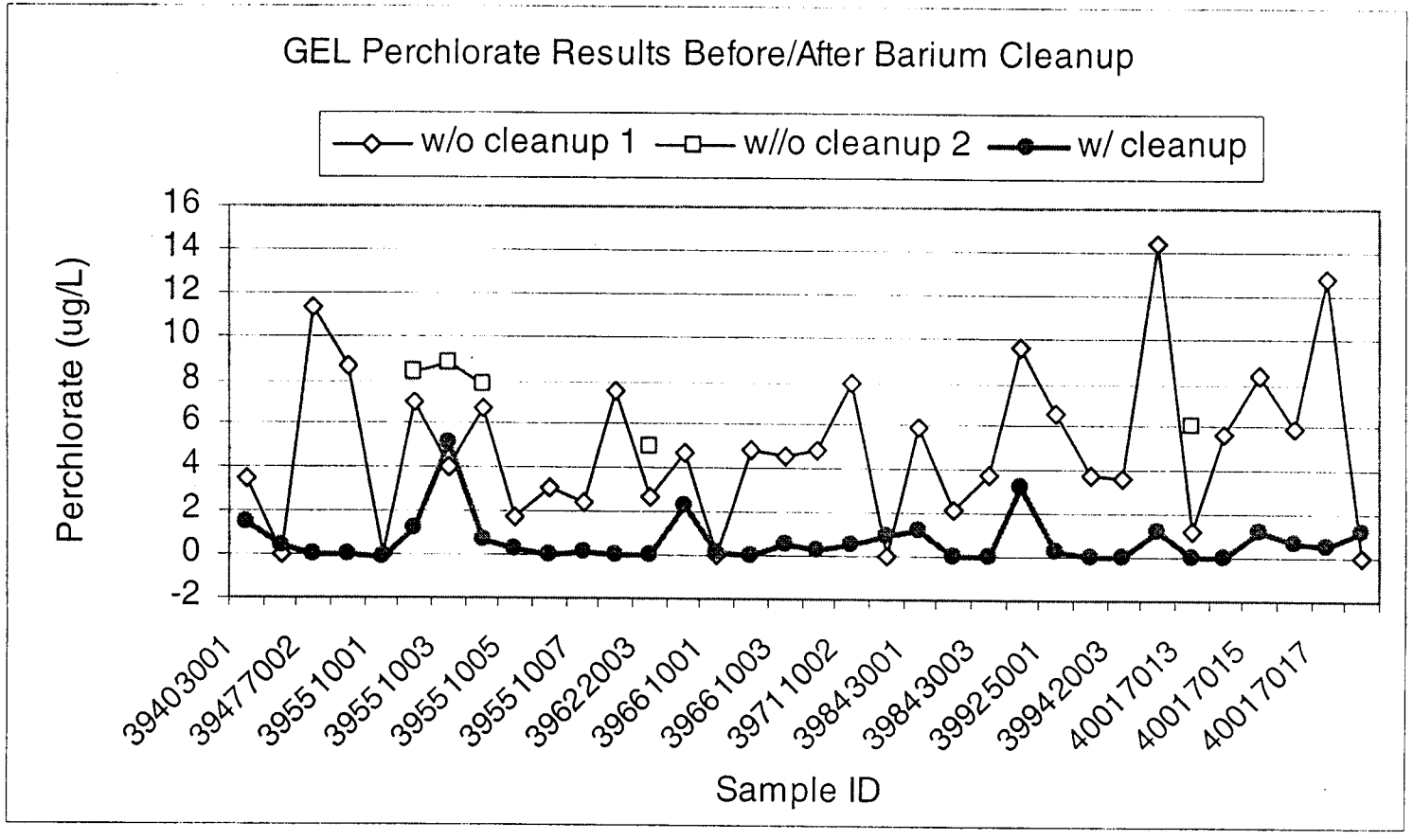
- A new method using liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) may distinguish between perchlorate and other anions.
- LC/MS/MS may yield lower detection limit.
- Analysis by LC/MS/MS offered by Acculabs.
- Acculabs' claimed MDL is 0.25 ppb; RL is 0.5 ppb.
- Results so far vary widely due to method and instrument problems; method precision and MDL need more evaluation.

Perchlorate --- GEL Analysis Issues

- GEL narrative for analysis of March 9, 2002 Spring 4B sample: "The original analyses for this batch indicated elevated concentrations that the laboratory believed were false positives. After investigating the cause it was determined to be matrix related and that an additional cleanup step using Barium was needed to reduce the potential matrix interference... The samples in this SDG were reanalyzed beyond using the cleanup techniques per EPA 314.0."

- GEL: "Prior to April 25, 2001 GEL had not been doing all clean-up methods including the Barium clean-up to remove sulfates, the silver clean-up to remove chlorides, and the hydrogen clean-up to remove excess silver, carbonates and other cations. Without these clean-ups the results could be questioned if false positives are present."

Perchlorate --- GEL Analysis Issues



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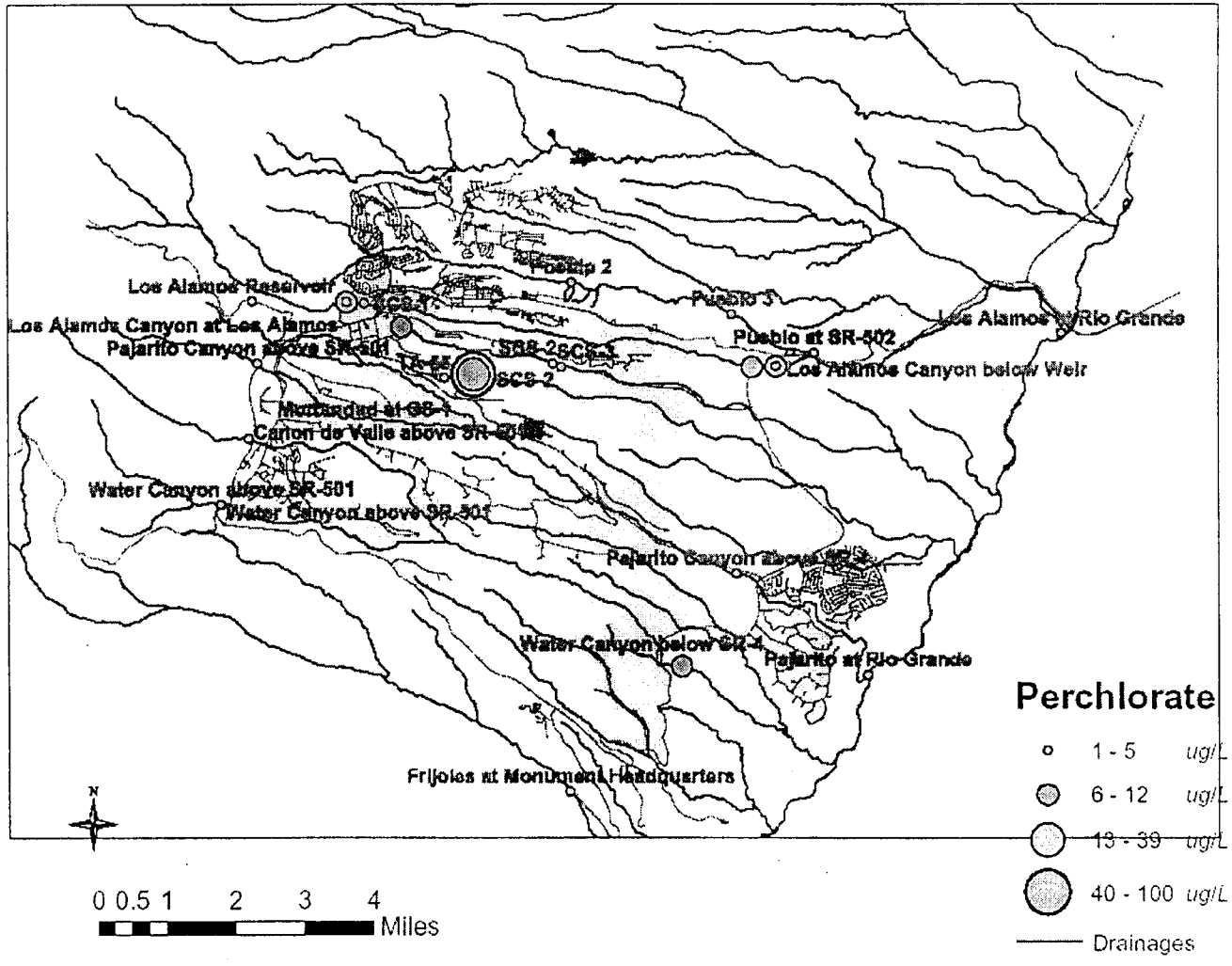
Perchlorate --- 2001 Surface Water Results Rejected



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Perchlorate --- Most GEL Detections Rejected

- As a result of GEL's method improvement-
  - "Detections" during 2000 are false positives;
  - "Detections" in Spring 4 area are false positives
  - Many surface water "detections" of perchlorate during early 2001 are false positives, lacking sufficient processing before analysis;

- The remaining surface water "detections" of perchlorate during early 2001 are non-detections based on validation- perchlorate was found in the blank.

- Perchlorate at LANL now reliably detected only at:
  - Otowi-1 water supply well;
  - Mortandad Canyon surface water;
  - Mortandad Canyon alluvial groundwater.

Perchlorate --- LANL Spike Study 9/5/01 --- Purpose

- Study goal: evaluate precision and reliability of laboratory analyses at ppb perchlorate levels.

- Submit spiked samples from water supply wells to each analytical laboratory as test case.

Perchlorate --- LANL Spike Study --- GEL IC Analysis

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Albuquerque, NM 87123
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Email: minteer@aol.com

To: Bob Beers, William Turney, and Ken Mullen (LANL ESH)
From: Mark Minteer (AQA/DOE-AL Analytical Management Program)
Date: 11/2/01
Re: ClO_4 detection limit study results

Background and Summary:

The method detection limit for perchlorate (ClO_4) by ion chromatography (IC), as calculated by GEL according to the specifications of 40 CFR 136, is 1 ppb. We have shown empirically that for ClO_4 by IC, as with previous results for some GC and HPLC techniques, the high precision attainable for low-level standards in clean (DI) water leads to calculated detection limits that are demonstrably lower than the limit of sensitivity of the instrument.

Pantex, LANL ESH, and LANL ER have all seen unexpected, random low-level hits for ClO_4 by IC. Matrix-specific MDL verification studies run for Pantex in late 2000 and early 2001 showed that ClO_4 can not be detected at the calculated 1 ppb MDL for IC when run in a real Ogallala aquifer groundwater matrix. Pantex adopted a 4 ppb MDL for ClO_4 after reviewing those data (see Attachment One). Additional data were recently acquired using groundwater from Los Alamos, with similar results. The data for groundwater matrices from both DOE-AL facilities show significant random variations in background (noise) that lead to frequent false positives. Based upon the data acquired in the new MDL verification studies, the GEL IC chemist (Bob Sosa) and DOE-AL Analytical Management Program staff recommend that LANL ESH also adopt an MDL level for ClO_4 run by IC that is no lower than 4 ppb.

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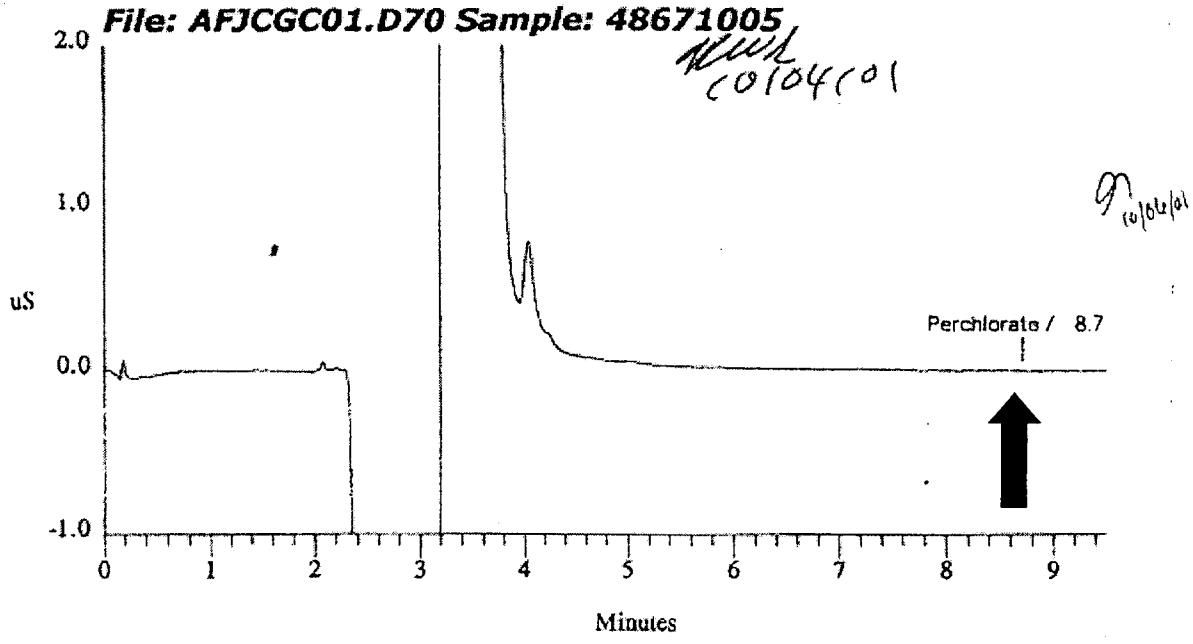
Perchlorate --- LANL Spike Study --- GEL IC Analysis

Pk. Num	Ret Time	Component Name	Concentration ug/l	Height	Area	Bl. Code	%Delta
1	8.71	Perchlorate	1.493	6310	45944	1	0.00
		Totals	1.493	6310	45944		



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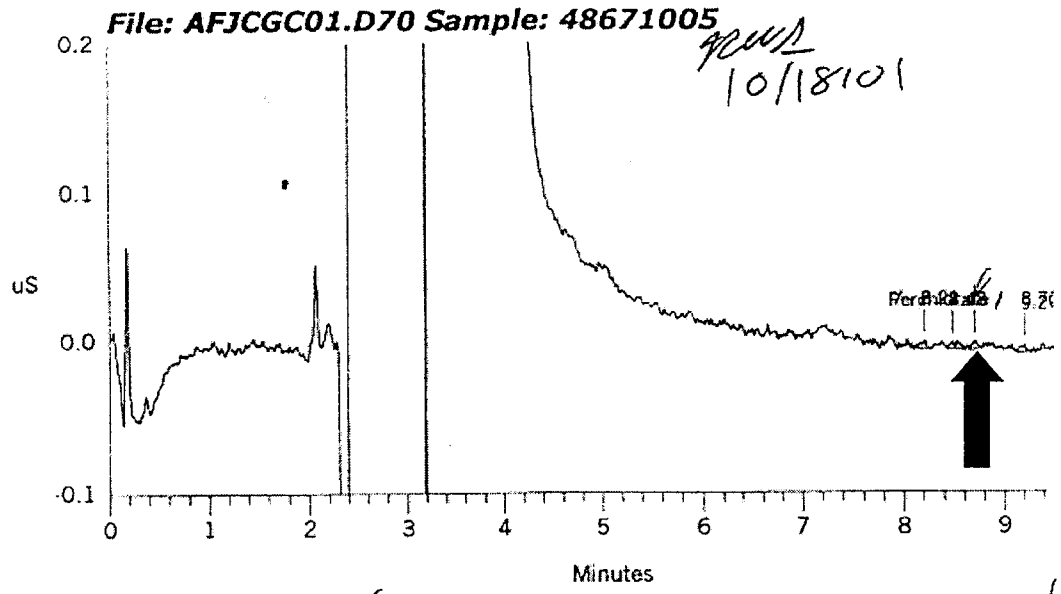
Perchlorate --- LANL Spike Study --- GEL IC Analysis

Pk. Num	Ret Time	Component Name	Concentration ug/l	Height	Area	Bl. Code	%Delta
3	8.70	Perchlorate	1.304	5304	19752	1	0.00
		Totals	1.304	5304	19752		



10/18/01

This chromatogram was reprocessed so the perchlorate could be more easily seen.

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Perchlorate --- LANL Spike Study 9/5/01 --- IC Analysis

Summary of Perchlorate Study Analytical Results. Sample Date: 9/5/2001. All units are ug/L (ppb).

	O-1		PM-3		PM-5		G-5A	
Sample Type	**Babcock**	**GEL**	**Babcock**	**GEL**	**Babcock**	**GEL**	**Babcock**	**GEL**
Initial Sample	<2	3.86	<2	<0.958	<2	2.05	<2	<0.958
Initial Sample Rerun #1	<2	3.24	<2	<0.958	<2	<0.958	<2	<0.958
Initial Sample Rerun #2	<2	2.55	<2	1.47	<2	1.493	<2	1.474
Initial Sample Rerun #3	NA	3.07	NA	<0.958	NA	1.663	NA	1.287
Initial Sample Rerun #4	NA	2.92	NA	1.62	NA	<0.958	NA	<0.958
Dupe Sample	<2	3.53	<2	2.56	<2	<0.958	<2	2.61
Unspiked Sample Mean	**<2**	**3.19**	**<2**	**1.42**	**<2**	**1.35**	**<2**	**1.37**
1 ppb Spike	NA	3.87	NA	3.49	NA	1.3	NA	<0.958
1 ppb Spike Rerun #1	NA	3.53	NA	1.86	NA	3.267	NA	1.88
1 ppb Spike Rerun #2	NA	3.88	NA	<0.958	NA	2.58	NA	3.026
1 ppb Spike Rerun #3	NA	3.77	NA	2.67	NA	1.505	NA	<0.958
1 ppb Spike Rerun #4	NA	3.87	NA	3.49	NA	1.295	NA	3.058
1 ppb Spike Mean		**3.78**		**2.49**		**1.99**		**1.98**
2 ppb Spike	2.7	4.22	<2	3.90	<2	2.3	3.1	3.24
2 ppb Spike Rerun #1	<2	4.52	<2	3.21	<2	3.525	<2	3.56
2 ppb Spike Rerun #2	<2	4.91	<2	3.57	<2	3.2	<2	3.269
2 ppb Spike Rerun #3	NA	4.56	NA	3.60	NA	3.37	NA	3.455
2 ppb Spike Rerun #4	NA	4.69	NA	3.00	NA	3.594	NA	3.015
2 ppb Spike Mean	**2.23**	**4.58**	**<2**	**3.45**	**<2**	**3.20**	**2.37**	**3.31**
4 ppb spike	6	6.59	4	4.16	4	3.72	5	6.19
6 ppb spike	7	7.56	6	5.72	7	6.88	7	5.42

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Perchlorate --- LANL Spike Study --- LC/MS/MS Analysis

Summary of Perchlorate Spike Study
Analytical Results from Acculabs.
Sample Date: 10/24/2001. All units are ug/L (ppl

	PM-3	
Sample Type	first run	rerun
Initial Sample	1.4	0.51
Initial Sample Rerun #1	1.6	0.57
Initial Sample Rerun #2	1.6	0.57
Initial Sample Rerun #3	1.7	0.58
Initial Sample Rerun #4	1.4	0.5J
Average of Detections	*1.5*	*0.5*
1 ppb Spike	5	1.5
1 ppb Spike Rerun #1	5.4	1.5
1 ppb Spike Rerun #2	5.7	1.6
1 ppb Spike Rerun #3	5.6	1.6
1 ppb Spike Rerun #4	5.6	1.6
Average	*5.5*	*1.6*
2 ppb Spike	8.5	2.6
2 ppb Spike Rerun #1	8.4	2.7
2 ppb Spike Rerun #2	8.3	2.7
2 ppb Spike Rerun #3	8.1	2.6
2 ppb Spike Rerun #4	8.1	2.7
Average	*8.3*	*2.7*
3 ppb Spike	9	3.7
3 ppb Spike Rerun #1	9.5	3.7
3 ppb Spike Rerun #2	9.7	3.7
3 ppb Spike Rerun #3	10	3.8
3 ppb Spike Rerun #4	10	3.7
Average	*9.6*	*3.7*
4 ppb Spike	10	5.1
4 ppb Spike Rerun #1	10	5.2
4 ppb Spike Rerun #2	12	6.2
4 ppb Spike Rerun #3	11	5.3
4 ppb Spike Rerun #4	11	5.2
Average	*10.8*	*5.4*
5 ppb Spike	11	8.5
5 ppb Spike Rerun #1	12	8.4
5 ppb Spike Rerun #2	11	7.8
5 ppb Spike Rerun #3	12	7.6
5 ppb Spike Rerun #4	13	5.1
Average	*11.8*	*7.5*

- Acculabs' first LC/MS/MS runs had errors of over 500% and over 8 ppb.
- Acculabs reran the samples only after LANL requested it.
- Acculabs case narrative for <u>first run</u>:

"The… results… are the first attempt to analyze… groundwater samples… by the technique."

"…the <u>precision is excellent over a wide range of concentrations</u> with the worst precision being at the… low concentration as expected."

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Perchlorate --- LANL Spike Study --- LC/MS/MS Analysis

Summary of Perchlorate Spike Study- Analytical Results from Acculabs.
Sample Date: 10/24/2001. All units are ug/L (ppb).

	PM-3		PM-5		G-1A	
Sample Type	**first run**	**rerun**	**first run**	**rerun**	**first run**	**rerun**
Initial Sample	1.4	0.51	1.6	<0.25	0.84	0.3J
Initial Sample Rerun #1	1.6	0.57	1.5	<0.25	0.98	0.62
Initial Sample Rerun #2	1.6	0.57	1.8	<0.25	0.8	0.5J
Initial Sample Rerun #3	1.7	0.58	1.6	0.3J	0.61	0.5J
Initial Sample Rerun #4	1.4	0.5J	1.8	0.3J	0.6	0.50
Average of Detections	*1.5*	*0.5*	*1.7*	*0.3*	*0.8*	*0.5*
1 ppb Spike	5	1.5	5.3	0.93	6.1	1.1
1 ppb Spike Rerun #1	5.4	1.5	5.5	0.98	6.4	1.1
1 ppb Spike Rerun #2	5.7	1.6	5.4	0.78	6.4	1.1
1 ppb Spike Rerun #3	5.6	1.6	5.6	0.81	6.2	1.1
1 ppb Spike Rerun #4	5.6	1.6	5.5	0.81	6.1	1.0
Average	*5.5*	*1.6*	*5.5*	*0.9*	*6.2*	*1.1*
2 ppb Spike	8.5	2.6	9.1	1.5	11	2.1
2 ppb Spike Rerun #1	8.4	2.7	10	1.5	11	2.0
2 ppb Spike Rerun #2	8.3	2.7	9.1	1.5	11	2.1
2 ppb Spike Rerun #3	8.1	2.6	9.1	1.5	12	1.9
2 ppb Spike Rerun #4	8.1	2.7	9.6	1.8	11	1.9
Average	*8.3*	*2.7*	*9.4*	*1.6*	*11.2*	*2.0*
3 ppb Spike	9	3.7	3.1	3.1	14	3.0
3 ppb Spike Rerun #1	9.5	3.7	3	3.0	14	2.9
3 ppb Spike Rerun #2	9.7	3.7	3.1	3.1	14	3.0
3 ppb Spike Rerun #3	10	3.8	3.1	3.1	15	3.2
3 ppb Spike Rerun #4	10	3.7	3.2	3.2	14	2.9
Average	*9.6*	*3.7*	*3.1*	*3.1*	*14.2*	*3.0*
4 ppb Spike	10	5.1	4	4.0	20	4.5
4 ppb Spike Rerun #1	10	5.2	4.1	4.1	19	4.2
4 ppb Spike Rerun #2	12	6.2	4.1	4.1	19	3.8
4 ppb Spike Rerun #3	11	5.3	4.1	4.1	19	3.9
4 ppb Spike Rerun #4	11	5.2	4.1	4.1	19	4.1
Average	*10.8*	*5.4*	*4.1*	*4.1*	*19.2*	*4.1*
5 ppb Spike	11	8.5	5.1	5.1	24	4.2
5 ppb Spike Rerun #1	12	8.4	5.1	5.1	23	4.2
5 ppb Spike Rerun #2	11	7.8	5.3	5.3	21	4.4
5 ppb Spike Rerun #3	12	7.6	5	5.0	23	4.8
5 ppb Spike Rerun #4	13	5.1	5	5.0	24	4.7
Average	*11.8*	*7.5*	*5.1*	*5.1*	*23.0*	*4.5*

- Spike accuracy is within 1%.
- Acculabs' first LC/MS/MS runs had errors of over 500% and over 8 ppb.
- Acculabs reran the samples only after LANL requested it.
- The second run still contains errors up to 70% or 3.5 ppb.

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Perchlorate --- LANL Spike Study 9/5/01 --- Conclusions

- GEL analytical results show considerable variation; MDL of 1 ppb and RL of 4 ppb in doubt.

- GEL: "Based on conversations with Pantex personnel in early May, MDLs and PQLs were raised to 4 and 12 ppb respectively. In fall of 2001 GEL submitted a proposal… as part of an audit finding to elevate the MDLs and PQLs of LANL projects as well."

- Babcock results more consistent; MDL of 2 ppb appears reliable.

- Acculab (LC/MS/MS) results lack repeatability; MDL of 0.25 ppb and RL of 0.5 ppb in doubt.

Perchlorate --- Overview of Water Supply Results

- Otowi 1 appears to have perchlorate, possibly at 2 ppb.

- No perchlorate detections in other water supply wells based on Babcock data.

- Possibly 33% estimated J-flagged "detections" in other water supply wells based on GEL data;
  - -this conclusion does not consider revised GEL MDL of 4 ppb.

Perchlorate --- Otowi 1 Results

- Two GEL detections of 5 ppb and 5.9 ppb.
- Thirty J-flagged (estimated) detections:
  - 10 of 13 samples from GEL
  - 20 of 27 samples from Babcock.
- Two Acculabs results of 2.0 and 5.9 (rerun was 2.1) ppb.

Perchlorate --- Spring 4 Results

- No perchlorate detected in any other White Rock Canyon springs.
- GEL result from 9/25/00 of 8.5 ppb- prior to GEL method revision.
- GEL result from 3/9/01 of 6.6 ppb (reanalysis using GEL method revision was non-detect).
- GEL results from 9/24-25/01 and 11/1/01 were non-detect or J-flagged.
- Acculabs results from 11/1/01 of 0.50 to 0.65 ppb- reliability of method and detection limit questionable at this level.

Perchlorate --- Results from Spring 4 Area

Location	Date	Sample Co	Analyte	Symbol	Std Result	Std Mdl	Std Uom	Qual Code	Lab Code
Spring 4	09/25/00	CS	ClO4		8.49	1.04	ug/L		GELC
Spring 4	09/24/01	CS	ClO4	<	0.96	0.96	ug/L	U	GELC
Spring 4	09/24/01	DUP	ClO4	<	0.96	0.96	ug/L	U	GELC
Spring 4	11/01/01	CS	ClO4		2.35	0.96	ug/L	J	GELC
Spring 4A	09/25/00	CS	ClO4	<	1.04	1.04	ug/L	U	GELC
Spring 4A	09/25/01	CS	ClO4	<	0.96	0.96	ug/L	U	GELC
Spring 4A	09/25/01	DUP	ClO4	<	0.96	0.96	ug/L	U	GELC
Spring 4A	11/01/01	CS	ClO4		1.71	0.96	ug/L	J	GELC
Spring 4AA	11/01/01	CS	ClO4		1.57	0.96	ug/L	J	GELC
Spring 4B	03/09/01	CS	ClO4		6.62	0.96	ug/L		GELC
Spring 4B	03/09/01	RE	ClO4	<	0.80	0.80	ug/L	U	GELC
Spring 4B	11/01/01	CS	ClO4		1.40	0.96	ug/L	J	GELC
Spring 4C	11/01/01	CS	ClO4		2.63	0.96	ug/L	J	GELC
Spring 4C	11/01/01	DUP	ClO4		2.50	0.96	ug/L	J	GELC
Spring 4	11/01/01	CS	ClO4		0.65	0.25	ug/L		ACCU
Spring 4A	11/01/01	CS	ClO4		0.50	0.25	ug/L		ACCU
Spring 4AA	11/01/01	CS	ClO4		0.55	0.25	ug/L		ACCU
Spring 4B	11/01/01	CS	ClO4		0.58	0.25	ug/L		ACCU
Spring 4B	11/01/01	DUP	ClO4	<	0.50	0.25	ug/L	B	ACCU
Spring 4C	11/01/01	CS	ClO4		0.67	0.25	ug/L		ACCU

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Perchlorate --- Summary

- Need for precision taxes reproducibility of current analytical methods .

- Due to GEL method modification, most prior LANL perchlorate results are now non-detections.

- GEL detection limit of 1 ppb is probably too low- GEL recommends 4 ppb.

- LANL spike study-
  - GEL detection limit and reproducibility in question.
  - Babcock performance seems reliable with 2 ppm MDL.
  - Acculabs accuracy and detection limit in question.

- Otowi 1 may have 2 ppb of perchlorate; Spring 4 has none.

Perchlorate --- Summary (continued)

- DOE Albuquerque is leading an effort to formally adopt a 4 ppb MDL for perchlorate by ion chromatography under 40 CFR 136.

- Even at an MDL of 4 ppb, we can expect 10 to 20% false positives from ion chromatography.

- DOE is leading an effort to get the LC/MS/MS (Acculabs) method approved by EPA.

Perchlorate --- LANL Path Forward

- Look for improved perchlorate analytical techniques and detection limits.
- Stay current on work done by other organizations on improved perchlorate analytical techniques.
- Evaluate possibility of matrix interference in perchlorate results.
- Continue to collect perchlorate monitoring data at LANL.
- Continue monitoring of Los Alamos water supply wells in cooperation with Los Alamos County.