



Evaluation of Perchlorate Soil Adsorption in Five Unique Soils Under Oxidic and Anoxic Conditions

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Perchlorate in Soil

Perchlorate (ClO_4^-)

- Used primarily as a solid rocket fuel
- Other sources include flares, fireworks, airbags, and some nitrate-based fertilizers
- Groundwater Contaminant
 - Competes with iodine in thyroid
 - Thought to move through soils with little, if any, adsorption occurring
 - Little literature evidence to support hypothesis





Perchlorate in Soil

Current method of detecting perchlorate is EPA method 314.0

- **Ion Chromatography Method**
 - **Method Issue - Relative high degree of false positive results**
 - **Method Issue - Lower detection limit level of 4 ppb**

- **State level advisory levels range from 1 ppb to 31 ppb**
 - **Low level action level is expected to be set**





Perchlorate in Soil

- **Design and conduct a series of experiments to test adsorption of perchlorate to soil.**
 - **Perchlorate has been detected many different states so a variety of soil types were chosen for studies investigating perchlorate adsorption to soil.**
- **Identify modifications to the analyte (perchlorate) and/or the medium (soil).**
- **Improve and/or develop new analytical methods for low level detection of perchlorate in environmental samples.**



Perchlorate in Soil

- Soils utilized in the project
 - Average Soil
 - Sandy Soil
 - High Iron Content Soil
 - High pH Soil
 - High Total Organic Content Soil

Soil Characteristic	Average Soil (WEB Reference)	Sandy Soil (Flaws Band)	High Fe Soil (Allison Loam)	High pH Soil (Prot Sandy Loam)	High TOC Soil
UCS Classification	Clay (CH), SP	SP	Sandy Clay (CL), Red	Sandy Clay (CH) Grey	
Total Ca (mg/kg)	1440	<20	416	59500	82
Total Fe (mg/kg)	21100	103	51600	13500	650
Total Mg (mg/kg)	2090	<25	1050	15000	170
TOC (mg/kg)	5320	13.85	6033	4746	27200
Percent sand	0.5	97.6	30.9	49.1	
Percent Fines	99.5	2.4	69.1	50.9	
pH of 20% Slurry	4.97	6.2	4.28	9.73	

From: Amery, 1996



➤ Experimental Conditions

- Oxidic
- Anoxic
- Controls
 - minus soil
 - minus perchlorate
 - abiotic



Perchlorate in Soil

➤ Experimental Design

- 30% w/w soil slurries, equilibrate for 1 week prior to addition of perchlorate
- Soil slurries exposed to 10 ppm perchlorate, with constant mixing for either 1 week or 1 month
- Soil slurries separated into an aqueous phase (with perchlorate spike) and a solid phase (soil)
 - The solid phase was rinsed twice, and after both rinses separated into an aqueous and solid phase
 - Rinse # 1: Deionized water (the method of choice to remove perchlorate from soil samples)
 - Rinse # 2: 50mM sodium hydroxide, which will remove any perchlorate that has adsorbed to soil particles





Perchlorate in Soil

Detection Methods

- **Primary Method - EPA method 314.0; modified in-house to purify and concentrate samples (ECB-Vicksburg, ECB-Omaha)**
- **Experimental Method - Ion Chromatography-Electrospray Ionization Mass Spectrometry (IC-ESI/MS) method; described in the EPA's solid waste test methods SW-846 Draft Method 314.2, again with in-house modifications (ECB-Omaha)**
- **Experimental Method - High Performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS) method; being developed in-house (ECB-Vicksburg)**





Perchlorate in Soil

- The TOC soil made a wonderful tea-like aqueous phase!



- **Sample Clean-up**
 - Filter Centrifugation
 - 5 kDa molecular weight cut-off
 - Acidification followed by centrifugation
 - nitric acid; <0.7% final concentration



Perchlorate in Soil



Acidification &



Centrifugation



Results of Acidification (IC Detection)

<u>Sample</u>	<u>ClO₄⁻ (ppm)</u>	<u>Acidified</u>	<u>Spiked</u>
TOC 1	5.512	No	No
TOC 1	4.148	Yes	No
TOC 1	10.167	Yes	Yes (5ppm)
TOC 2	5.936	Yes	No
TOC 3	5.399	Yes	No



Sample Analysis Report

Sample Name : 030404-004_H1996_CCV
Data File Name : C:\EAKNET\DATA\030404-01C\030404_019.D

Method File Name : c:\pednet\method\cig_r1041.mnt
Date Time Collected : 3/4/2004 6:43:38 PM
System Operator :

Peak Information: All Peaks

Peak #	Compound Name	Retention Time	Amount (pg)
1	perchlorate	9.27	20

Sample Analysis Report

Sample Name : M04090-016_Stand9
Data File Name : C:\EAKNET\DATA\030404-01C\030404_016A.DXD

Method File Name : c:\pednet\method\cig_r1041.mnt
Date Time Collected : 3/4/2004 6:00:41 PM
System Operator :

Peak Information: All Peaks

Peak #	Compound Name	Retention Time	Amount (pg)	Peak Area	Peak Height
1	perchlorate	9.22	10000.26	49243	1307

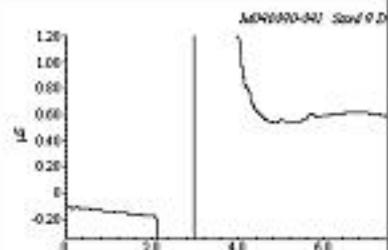
Sample Analysis Report

Sample Name : M04090-001_Stand9 B0
Data File Name : C:\EAKNET\DATA\030404-01C\030404_017A.D

Method File Name : c:\pednet\method\cig_r1041.mnt
Date Time Collected : 3/4/2004 6:15:00 PM
System Operator :

Peak Information: All Peaks

Peak #	Compound Name	Retention Time	Amount (pg)
1	perchlorate	9.25	927



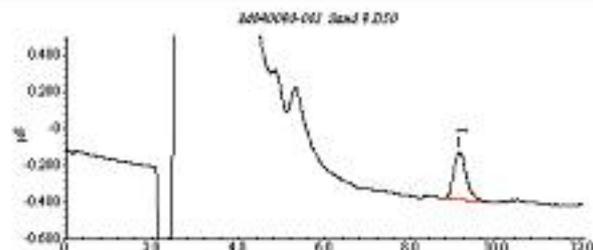
Sample Analysis Report

Sample Name : M04090-001_Stand9 B00
Data File Name : C:\EAKNET\DATA\030404-01C\030404_018A.DXD

Method File Name : c:\pednet\method\cig_r1041.mnt
Date Time Collected : 3/4/2004 6:25:31 PM
System Operator :

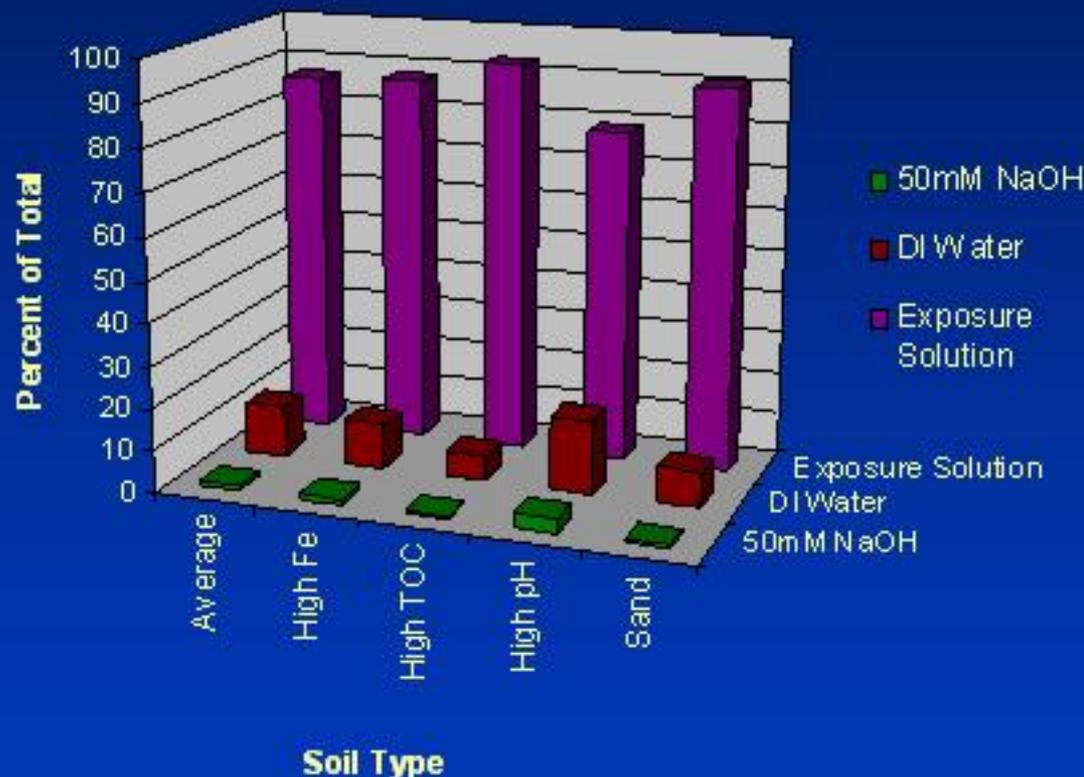
Peak Information: All Peaks

Peak #	Compound Name	Retention Time	Amount (pg)	Peak Area	Peak Height
1	perchlorate	9.10	85.11	32458	2564



Perchlorate in Soil

Perchlorate Distribution



Total (Perchlorate) = sum of the three different fractions

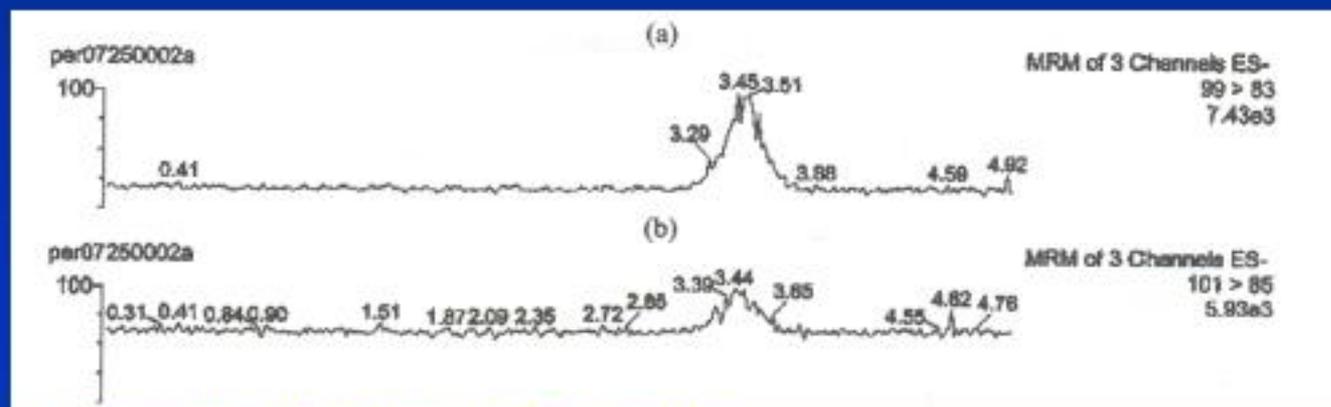
Preliminary Data (IC only)

- As expected, the majority of the perchlorate was recovered in the exposure solution, with only trace amounts detected in the final 50mM NaOH wash.
- There were no obvious differences between either soil type or oxygen conditions (oxic/anoxic).
- However, it is important to note that the values obtained have not been yet been corrected for any "carry-over" caused by the pore water that remains after centrifugation.

Perchlorate in Soil

IC-ESI-MS Method Development

- Expected MDL ≤ 0.1 ppb
 - MDL 0.05 ppb in recent article – Winkler *et al.*, 2004, *Anal Chem* 76(2): 469-73
- Monitor loss of oxygen ($\text{ClO}_4^- \rightarrow \text{ClO}_3^-$)
 - ^{35}Cl isotope is m/z 99 \rightarrow 83
 - ^{37}Cl isotope is m/z 101 \rightarrow 85



From: Winkler *et al.*, 2004, *Anal Chem* 76(2):469-73



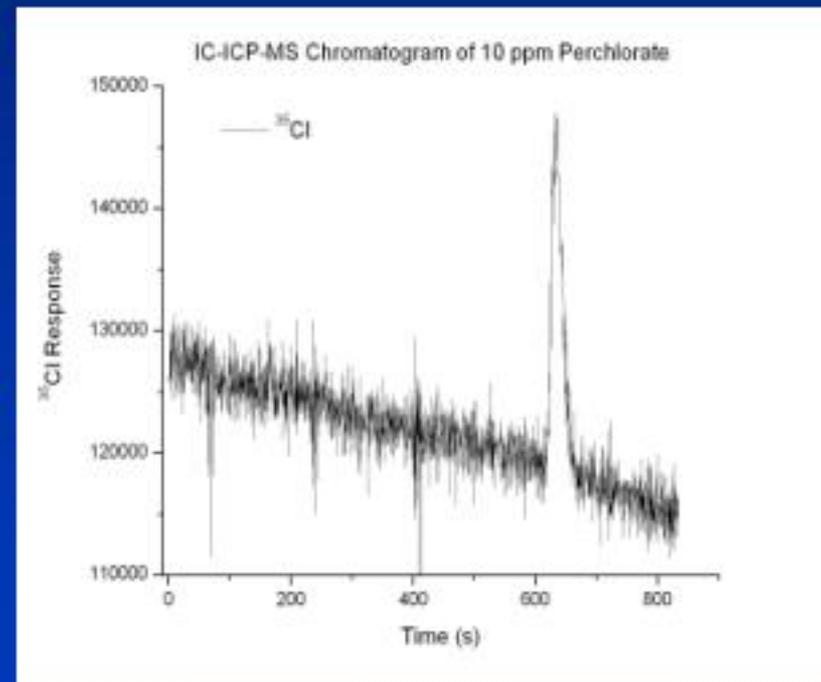
Perchlorate in Soil

HPLC-ICP-MS Method Development

➤ ICP-MS differs from ESI-MS because of 'complete' decomposition/ionization

➤ Although interferences and 'plasma loading' are a problem (100mM NaOH)

➤ Expected MDL 10's ppb





Perchlorate in Soil

Conclusions

- The majority of the perchlorate spike was recovered in the soil incubation solution.
- ClO_4^- soil adsorption did not appear to be affected by oxygen state (anoxic vs. oxic).
- Soil type does not appear to greatly affect ClO_4^- adsorption.
 - However, of the 5 soils tested, the high pH soil demonstrated the highest level of ClO_4^- in the final rinse solution.





Perchlorate in Soil

Method Development

- **The goal of the method development aspect of this project is to provide improved methods for ClO_4^- detection.**
 - **Reduce the occurrence of false positives**
 - **Lower the MDL (4 ppb with Method 314)**
- **The mass spectrometry techniques (ESI & HPLC-ICP) being investigated in conjunction with this ClO_4^- soil adsorption study should address the goals stated above.**



Perchlorate in Soil

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Perchlorate



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