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

Dr. Shana R. Dalton, PhD, CEERD-EP-C

Dr. Denise K. MacMillan, PhD, CEERD-EP-C

Dr. Anthony Bednar, PhD, CEERD-EP-C

Mr. Scott Waisner, CEERD-EP-E

USACE - ERDC

DoD Environmental Monitoring and Data Quality

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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

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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

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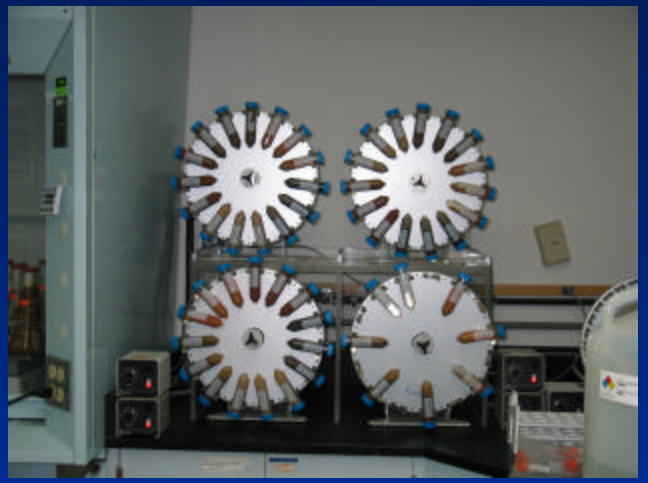
- Soils utilized in the project
  - Average Soil
  - Sandy Soil
  - High Iron Content Soil
  - High pH Soil
  - High Total Organic Content Soil

Soil Characteristic	Average Soil [WES Reference]	Sandy Soil [Ottawa Sand]	High Fe Soil [Telleco Loam]	High pH Soil [Crot Sandy Loam]	High TOC Soil
UCS Classification	Clay (CH), Brown	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	690
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
  - Oxic
  - 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)

Sample	ClO_4^- (ppm)	Acidified	Spiked
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

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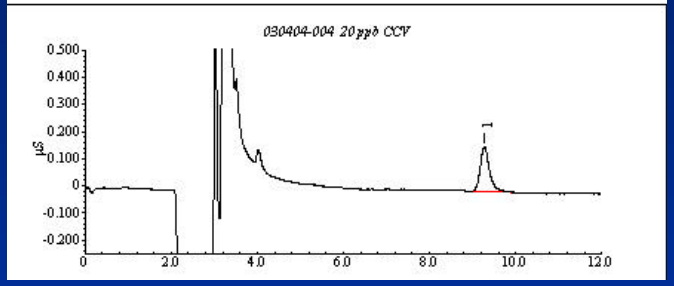
Perchlorate in Soil

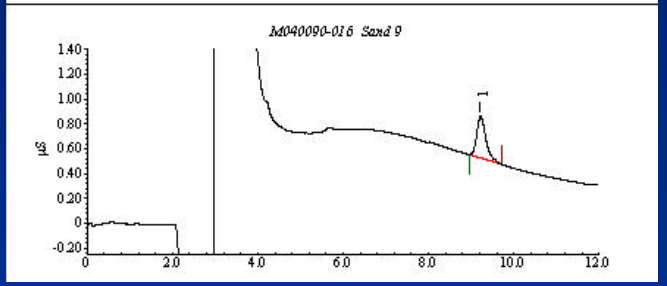
Peak Information : All Peaks

Peak #	Component Name	Retention Time	Amount (ppb)	Peak Area	Peak Height
1	perchlorate	9.27	20.17	24245	1614



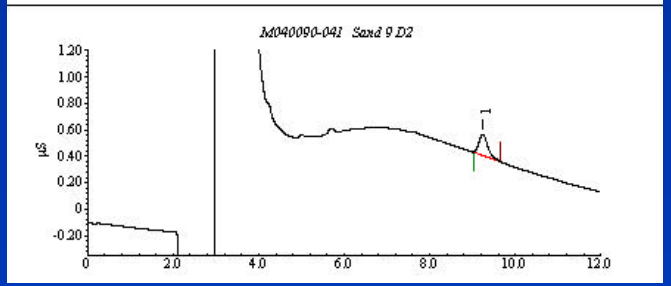
Peak Information : All Peaks

Peak #	Component Name	Retention Time	Amount (ppb)	Peak Area	Peak Height
1	perchlorate	9.22	1000036	49240	3307



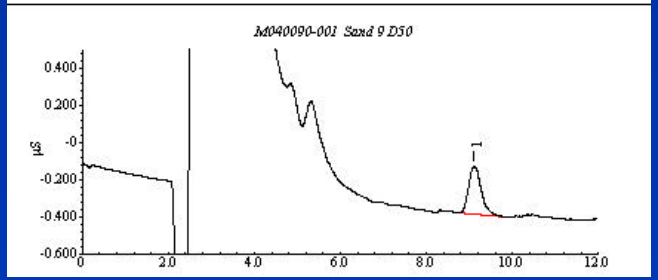
Peak Information : All Peaks

Peak #	Component Name	Retention Time	Amount (ppb)	Peak Area	Peak Height
1	perchlorate	9.23	927.99	22218	1565



Peak Information : All Peaks

Peak #	Component Name	Retention Time	Amount (ppb)	Peak Area	Peak Height
1	perchlorate	9.10	85.11	52458	2564



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Perchlorate in Soil

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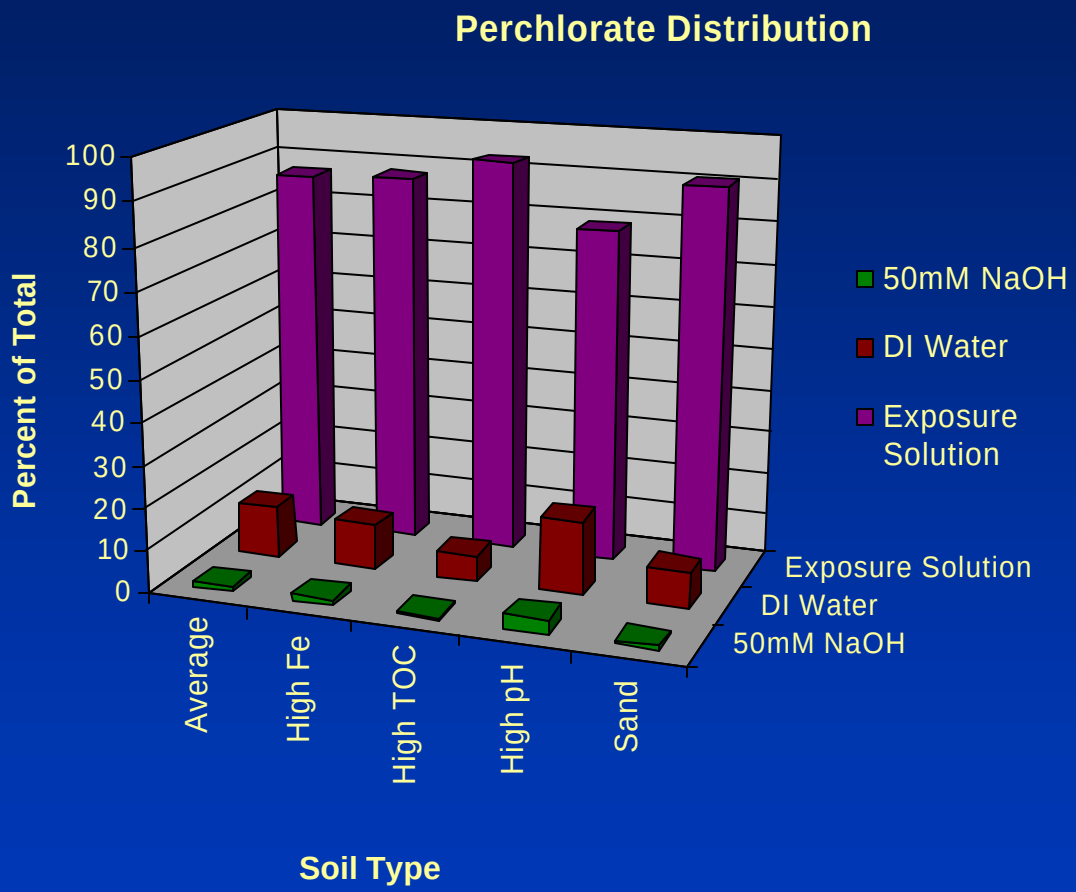

Total (Perchlorate) = sum of the three different fractions

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

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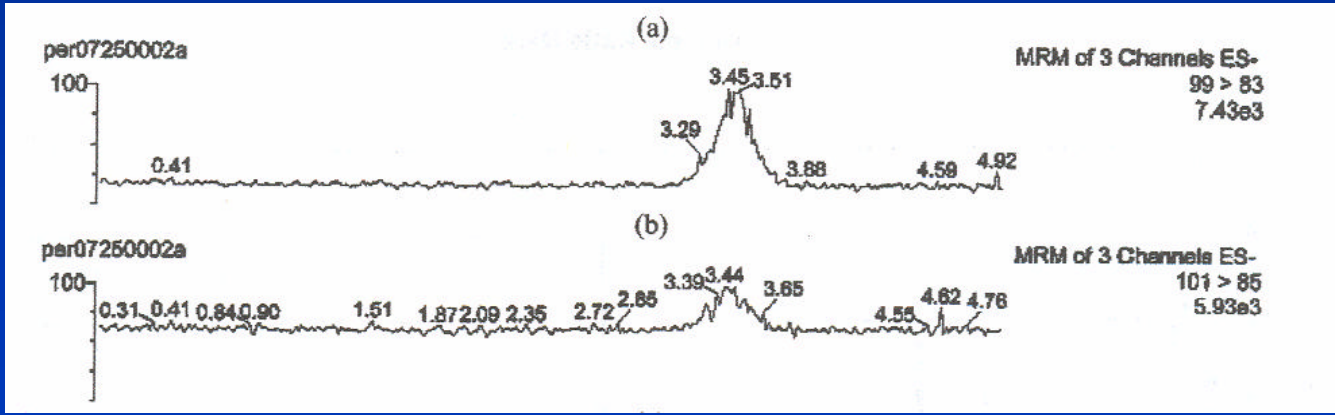
IC-ESI-MS Method Development

- 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 ($ClO_4^- \longrightarrow ClO_3^-$)
  - ^{35}Cl isotope is m/z 99 → 83
  - ^{37}Cl isotope is m/z 101 → 85



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

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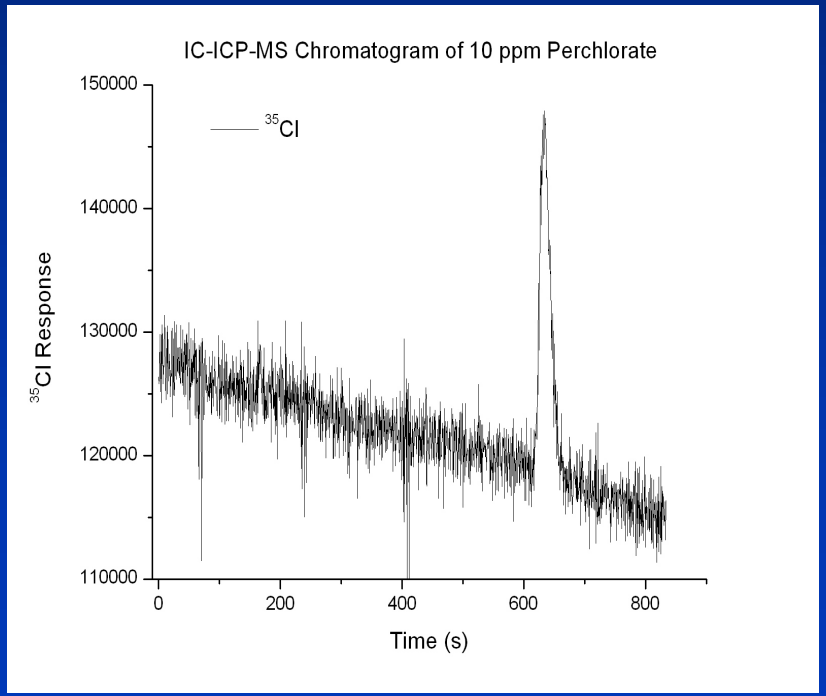
HPLC-ICP-MS Method Development

- 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 affect 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.

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