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ITRC's Internet-based Training Program

Perchlorate: Overview of Issues, Status, and Remedial Options

Perchlorate: Overview of Issues, Status, and Remedial Options (PERC-1, 2005)

This training is co-sponsored by the EPA Office of Superfund Remediation and Technology Innovation

Presentation Overview:

Perchlorate is an inorganic chemical ion consisting of chlorine bonded to four oxygen atoms (ClO_4^-). It occurs both naturally and in manmade compounds. While it was once thought to occur naturally only in one location, ongoing study has found naturally occurring perchlorate in other locations as well. In manmade compounds, it has been manufactured since before the turn of the last century and has been manufactured primarily for use in defense activities and the aerospace industry. Highly soluble and mobile in water, perchlorate is also very stable. Most of the attention focused on perchlorate contamination concerns ground and surface water contamination. However, it can also contaminate soil and vegetation. In general, past management practices did not prevent the release of perchlorate to the environment because it was not recognized or regarded as a contaminant of concern. Improved analytical methodology has increased the known extent of perchlorate contamination in the U.S. A variety of remediation technologies are currently commercially available and being used for perchlorate remediation.

This training, based on ITRC's *Perchlorate: Overview of Issues, Status, and Remedial Options* (PERC-1, September 2005), explains why perchlorate is a hot topic in the environmental community today including up-to-date information on sources, occurrences, toxicity and exposure, regulatory status and remediation alternatives.

ITRC (Interstate Technology and Regulatory Council) www.itrcweb.org

Training Co-Sponsored by: EPA Office of Superfund Remediation and Technology Innovation (www.clu-in.org)

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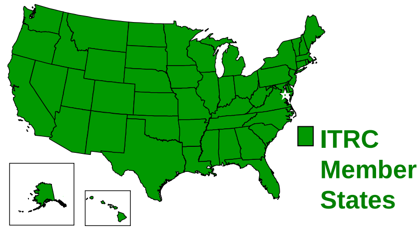

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The Interstate Technology and Regulatory Council (ITRC) is a state-led coalition of regulators, industry experts, citizen stakeholders, academia and federal partners that work to achieve regulatory acceptance of environmental technologies and innovative approaches. ITRC consists of 49 states (and the District of Columbia) that work to break down barriers and reduce compliance costs, making it easier to use new technologies and helping states maximize resources. ITRC brings together a diverse mix of environmental experts and stakeholders from both the public and private sectors to broaden and deepen technical knowledge and advance the regulatory acceptance of environmental technologies. Together, we're building the environmental community's ability to expedite quality decision making while protecting human health and the environment. With our network of organizations and individuals throughout the environmental community, ITRC is a unique catalyst for dialogue between regulators and the regulated community.

For a state to be a member of ITRC their environmental agency must designate a State Point of Contact. To find out who your State POC is check out the "contacts" section at www.itrcweb.org. Also, click on "membership" to learn how you can become a member of an ITRC Technical Team.

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Popular courses from 2007

- Characterization, Design, Construction, and Monitoring of Bioreactor Landfills
- Direct Push Well Technology for Long-term Monitoring
- Evaluate, Optimize, or End Post-Closure Care at MSW Landfills
- Perchlorate: Overview of Issues, Status and Remedial Options
- Performance-based Environmental Management
- Planning & Promoting Ecological Re-use of Remediated Sites
- Protocol for Use of Five Passive Samplers
- Real-Time Measurement of Radionuclides in Soil
- Remediation Process Optimization Advanced Training
- Risk Assessment and Risk Management
- Vapor Intrusion Pathway: A Practical Guideline

New in 2008

- Bioremediation of DNAPLs
- Decontamination and Decommissioning of Radiologically-Contaminated Facilities
- Enhanced Attenuation: Chlorinated Solvents
- Phytotechnology
- Quality Consideration for Munitions Response
- Remediation Technologies for Perchlorate Contamination in Groundwater and Drinking Water
- Sensors
- Survey of Munitions Response Technologies
- More in development…

More details and schedules are available from www.itrcweb.org under “Internet-based Training.”

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Perchlorate Overview

Logistical Reminders

- Phone line audience
  - ✓ Keep phone on mute
  - ✓ "*6" to mute, "*7" to un-mute to ask question during designated periods
  - ✓ Do NOT put call on hold
- Simulcast audience
  - ✓ Use ? at the top of each slide to submit questions
- Course time = 2¼ hours

Presentation Overview

- **Introduction to perchlorate**
- **Sources and uses**
- **Analytical methodologies**
- **Toxicity, exposure, risk**
- Questions and answers
- **Remediation options**
- Links to additional resources
- Your feedback
- Questions and answers

No associated notes.

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Meet the ITRC Instructors

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H. Eric Nuttall, Ph.D., is a professor emeritus of Chemical/Nuclear Engineering at the University of New Mexico (UNM) in Albuquerque. He has worked for UNM since 1973. He has over 200 publications/presentations and directs graduate student research on in situ bioremediation as well as teaches an annual course on bioremediation. At UNM, Eric developed and managed a very successful field site for in situ treatment of nitrate-contaminated groundwater. He has been an active member of ITRC since 1996 working with several different teams that create guidance documents and training related to in situ bioremediation, technology verification, chemical oxidation, enhanced attenuation: chlorinated organics, and perchlorate. He also has developed an in situ process to immobilized uranium and heavy metals which is being tested both by U.S. Department of Energy at an Uranium Mill Tailings Remedial Action (UMTRA) site and in Germany through WISMUT. Eric earned a bachelor's degree in chemical engineering from University of Utah in Salt Lake City in 1966, a master's degree in 1968 and a doctoral degree in 1971 both in chemical engineering from University of Arizona in Tucson.

Dr. Lee Lippincott, Ph.D., is a Research Scientist 1 with the New Jersey DEP Division of Science, Research, and Technology. He is also an assistant professor of Chemistry at TCNJ and MCCC. Lee is in charge of managing the state's A-280 safe drinking water research program as project manager and the results of his research are published in many technical journals. His primary research is focused on emerging contaminants in New Jersey's ground and surface water supplies that are used as sources for drinking water. Lee is the ITRC Perchlorate Team Leader. Lee is a former chairman of the New Jersey AWWA Research and Technology Transfer Committee and participates in the New Jersey Drinking Water Quality Institute as a technical resource on the testing and treatment subcommittees.

Tony Lieberman is the Bioremediation Program Manager and Senior Environmental Scientist with Solutions-IES in Raleigh, North Carolina. Mr. Lieberman has a B.S. in Biology from St. Lawrence University and an M.S. in Microbiology from Penn State University. With over 30 years of academic and industrial research and environmental consulting experience, Tony leads Solutions-IES' efforts on many industrial, Brownfields, and DoD sites, using biological and non-biological approaches to address complex environmental conditions. He has prepared over 45 publications and presentations for scientific journals, trade magazines, and symposium proceedings and is a contributing member of the ITRC Perchlorate Team. Tony is currently serving as Project Manager for an ESTCP contract evaluating the technical viability and cost-effectiveness of emulsified oil substrate as a permeable reactive barrier and source area remediation technology for biodegradation of chlorinated solvents and perchlorate and is Principle Investigator for Solutions-IES' ESTCP-funded study of the potential for the monitored natural attenuation of perchlorate.

Dr. Ian Osgerby, Ph.D., is the senior chemical engineer and innovative technology advocate for the New England District of the US Army Corps of Engineers, based in Concord, MA. He has presented papers in many symposia and conferences on subjects as diverse as thermal desorption, bioattenuation, chemical oxidation, electric resistive heating, groundwater treatment including perchlorate treatment technologies. He represents the government on domestic and international committees on remediation and chemical oxidation in particular, including SERDP/ESTCP, ITRC, and EPA TIO. He was responsible for the assembly and production of the EPA TIO web based ISCO collection of vendor case studies and continues to encourage development of the state of the art in ISCO through personal involvement with vendor applications of chemical oxidants.

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What You Will Learn…

- What perchlorate is and why it is a contaminant of concern
- How the sources and uses of perchlorate relate to perchlorate contamination
- What analytical methods can be used to detect perchlorate in the environment
- About the toxicity, risk, and acceptable exposure levels of perchlorate
- The latest information on the regulatory status of perchlorate
- What proven remediation technologies are commercially available
- What emerging remediation technologies may be commercially available in the future
- Where to go for more information

No associated notes.

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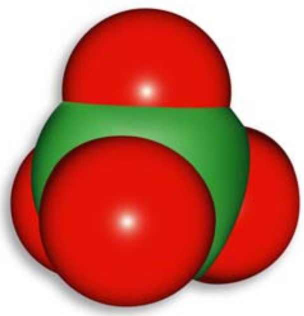
What is Perchlorate?

- Inorganic chemical ion consisting of chlorine bonded to four oxygen atoms
- Usually found as the anion component of a salt, usually with one cation
  - Ammonium (NH_4ClO_4)
  - Sodium ($NaClO_4$)
  - Potassium ($KClO_4$)
- Also found in
  - Perchloric acid ($HClO_4$)



ClO_4^-

The physical properties of the common perchlorate ions are listed in Table 1-1 of the Overview document. Perchlorate exhibits the characteristics of high solubility and mobility in water, as well as being very stable. These characteristics lead to the formation of long and persistent contaminant plumes when released into either groundwater or surface water. Like the water contaminant nitrate, perchlorate is not attenuated to any great degree by soil surface chemistry. However, it can be broken down by naturally occurring bacteria in the environment.

Perchlorate occurs both naturally and as a manufactured ion. Knowing the sources of perchlorate and the variety of uses it has served will help to guide perchlorate investigations.

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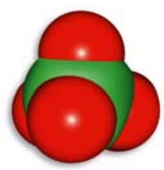
Why Do We Care About Perchlorate?

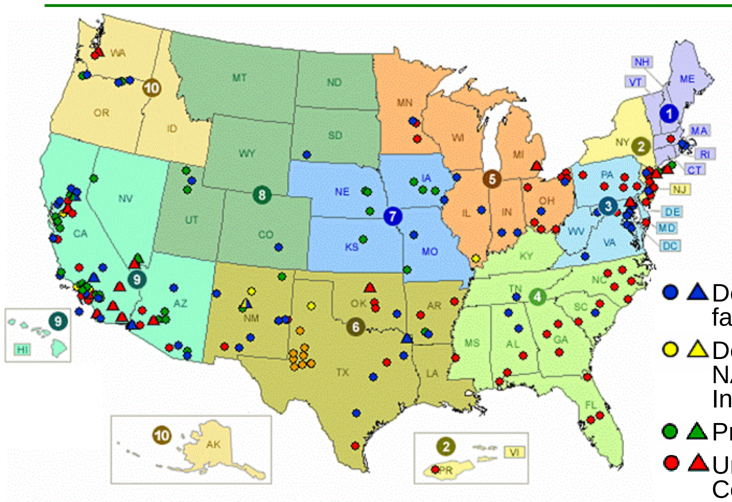


- Perchlorate
  - Soluble
  - Mobile
  - Stable
- Perchlorate in ground or surface water plumes
  - Extensive
  - Persistent
- Perchlorate can contaminate
  - Drinking water sources
  - Food supplies
- Presents a human health concern

Because of solubility, mobility and stability, perchlorate can form extensive and persistent contaminant plumes when released into either ground or surface water. Perchlorate can contaminate drinking water sources and food supplies and therefore present a human health concern.

Perchlorate is one of several compounds that can interfere with the thyroid's uptake of iodide, an essential component of thyroid hormones. Iodide uptake inhibition is considered the mode of action (MOA) for perchlorate (see Figure 4-1 in the document). The mode of action also identifies that perchlorate has a threshold for effects and that the degree of effects are dependent on the dosage.

Where Has Perchlorate Been Found?



Legend

- One site (circle)
- Multiple sites (triangle)
- (blue) Dept. of Defense (DOD) facilities
- (yellow) Dept. of Energy (DOE), NASA, and Dept. of the Interior (DOI)
- (green) Privately-owned
- (red) Unregulated Contaminant Monitoring Rule (UCMR) detections
- (orange) Texas Tech University – West Texas study detections

Map source: EPA

EPA Perchlorate Detection information as of September 2004: http://www.epa.gov/fedfac/documents/perchlorate_map/nationalmap.htm

Increased monitoring, improved analytical methods = increased # of detections of perchlorate

State regulators may be involved in perchlorate monitoring, remediation or regulatory status review. Perchlorate contamination of drinking water has been a primary concern with this contamination.

While a variety of sites where perchlorate contamination is known to occur have already been identified, it can be assumed that further sites will be discovered as more geographical areas are tested and additional information becomes available.

Detailed legend:

Perchlorate detections at:

(blue) Department of Defense (DOD) facilities

(yellow) other federal agency facilities: Department of Energy (DOE), National Aeronautics and Space Agency (NASA), and Department of the Interior (DOI)

(green) privately-owned sites

(red) Unregulated Contaminant Monitoring Rule (UCMR) detections

(orange) Texas Tech University – West Texas study detections

(circle) point contains one site

(triangle) point contains multiple sites

Colors in states represent EPA regions

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Why Are We Detecting Perchlorate Everywhere?

- More natural sources than originally thought
- More widely used in industry than originally thought
- Detecting at lower levels with improved analytical methodologies

No associated notes.

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Sources and Uses of Perchlorate

Naturally occurring

Widely manufactured

- **Knowing sources and uses guides perchlorate investigations**

This section of our Internet-based training introduces the range of perchlorate sources known at this time. It is important to point out that there are both natural and man made sources. However, the nature sources from Chilean fertilizers usually results in very low groundwater perchlorate concentrations. The major sources seem to have come from industrial or military related manufacturing or operations.

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Natural Sources of Perchlorate

- Most natural sources limited to arid environments
- Natural sources include
  - Chilean nitrate
  - Evaporite deposits
  - Atmospheric formation

When the source of groundwater contamination is Chilean fertilizer, the concentration values are generally low due the distributed nature of the application. Exceptions can be storage and distribution locations.

Most natural sources appear to be geographically limited to arid environments.

Arid environments can include environments that were more arid in the past, such as in west Texas; see also Orris, G.J. 2004. “Perchlorate in Natural Minerals and Materials,” USGS Quarterly Report (April) and Orris, G.J., G.J. Harvey, D. T. Tsui, and J. E. Eldrige. 2003. Preliminary Analyses for Perchlorate in Selected Natural Materials and their Derivative Products. Open-File Report 03-314. U.S. Geological Survey.

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Man-made Sources of Perchlorate

- Early 1900's – first manufacturing
- 1940's – production increased dramatically

- 99% of manufactured perchlorate consists of four compounds
  - Ammonium perchlorate (NH_4ClO_4)
  - Sodium perchlorate ($NaClO_4$)
  - Potassium perchlorate ($KClO_4$)
  - Perchloric acid ($HClO_4$)

USEPA has compiled information on known or suspected users or manufactures who have shipped more than 500 pounds of perchlorate in any one year. American Pacific Corporation manufactures ammonium perchlorate in Cedar City, Utah, and is currently the sole domestic manufacturer of commercial quantities of propellant-grade ammonium perchlorate.

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Uses of Perchlorate

- Prior to WWII
  - Fireworks
  - Flares

- After WWII, additional uses
  - Oxidizing agent for solid propellant rockets and missiles

Interestingly, fireworks and signal flares are often identified as potential sources. In rockets and missiles, first potassium perchlorate then ammonium perchlorate used as oxidizing agent for solid propellant rockets and missiles; perchlorate from solid propellant is perhaps the most common source of perchlorate contamination in soils and groundwater.

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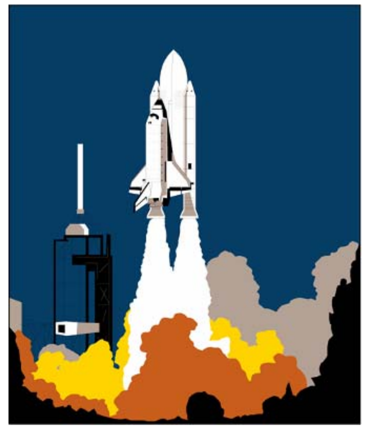
Solid Propellants

- Largest proportion by volume of U.S. production of perchlorate
- Used in
  - Missiles
  - Rockets
  - Launch vehicles
    - NASA's space shuttle
    - Commercial satellite vehicles



Solid propellants constitute the largest application of perchlorate.

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Uses of Perchlorate

- Munitions
  - Simulators, smokes, pyrotechnics, grenades, signals and flares, fuses, etc.
- Commercial explosives
- Fireworks
- Safety or hazard flares
- Car airbags
- etc.

Mortar Fuze

Weapons systems may contain perchlorate in varying amounts

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Uses of Perchlorate (continued)

- Matches
- Industry
- Laboratories
- Contaminant of agricultural fertilizer
- Medical and pharmaceutical
- Water and wastewater treatment
- Sodium chlorate manufacture and use

No associated notes.

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Perchlorate Releases – Past Practices

- Disposal of solid propellant, explosives, and munitions
  - Open burn and open detonation
  - Hydraulic wash out (hog-out)
- Manufacturing practices
  - Wastewater storage
  - Disposal and storage practices
  - Testing
- Landfills

Past practices have lead to much of the groundwater perchlorate contamination. The disposal methods listed above have proven to be the cause for many perchlorate contaminations.

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Potential Perchlorate Releases

- Fireworks
- Explosives use, such as blasting sites
- Impurities in agricultural chemicals
- Sodium hypochlorite used in water and wastewater treatment
- Sodium chlorate manufacture and use

Current uses continue to contribute to perchlorate contamination in the environment. However with growing awareness, the negative practices are being mitigated.

Environmental Fate and Transport

- Released as salts
- Movement in soil depends on water
- In groundwater
  - Perchlorate characteristics
    - High solubility
    - Low sorption
    - Lack of degradation
  - Plumes
    - Large
    - Persistent

Perchlorate may be released into the environment in the form of a number of different salts. Movement of perchlorate in soil depends on the amount of water present. Once in groundwater, the combination of high solubility, low sorption, and lack of degradation tends to create large and persistent plumes.

Since perchlorate is negatively charged anion, it readily migrates through aquifers following the water pathway and leading often to very sizeable plumes on the order of miles in length.

Because of its high solubility, perchlorate is washed from the soil and into the groundwater below by recharge water. In thick vadose zones, the perchlorate may persist for long periods and continue to be a source term for groundwater contamination.

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Detecting Perchlorate in the Environment

- Improved analytical methodologies resulted in increased detection
  - 1997
    - 4 ppb quantitation level
  - Today
    - 1 ppb and lower quantitation level

I would like to introduce myself, I'm Dr. Robert Lee Lippincott. I've worked for the New Jersey Department of Environmental Protection's Division of Science, Research, and Technology as a research scientist 1 for the past 15 years. One of my responsibilities is to assess analytical capability for the groundwater, surface water, and drinking water emerging contaminants in New Jersey

There are two reasons why we are finding perchlorate in more places than we had expected; one has to do with improved analytical methodologies that allow for detection at lower levels, and the second reason is that perchlorate is being found to occur naturally in more environments than originally thought. The next set of slides concerns the analytical methodologies that have allowed for the improvements in detection capabilities.

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Analytical Laboratory Methods

- Ion chromatography (IC)
- Liquid chromatography (LC)
- IC or LC can be paired with a mass spectrometer (MS) or tandem mass spectrometer (MS/MS):
  - IC/MS, IC/MS/MS
  - LC/MS, LC/MS/MS

The currently available regulatory and research analytical methods for perchlorate are listed here, they include

Ion Chromatography

Ion Chromatography separates ions in solution by pressurized liquid column chromatography and then detects ions by utilizing a very sensitive conductivity detector As you would suspect, any dissolved ions in solution other than perchlorate has the potential to effect the sample results. Typically, ion chromatography mobile phases are more acidic and/or basic than the polar mobile phases utilized in liquid chromatographic separation methods.

Liquid chromatography (LC) is an analytical chromatographic technique that is useful for separating ions or molecules that are dissolved in a solvent. If the sample solution is in contact with a second solid or liquid phase, the different solutes will interact with the other phase to differing degrees due to differences in adsorption, ion-exchange, partitioning, or size.

Most of the data that has been collected from drinking water sources has used ion chromatography with a conductivity detector. The newer methods that are being used and develop use a mass spectrometer or two mass spectrometers in series called tandem mass spectrometry. These detectors can not only quantify the amount of perchlorate present, they can positively identify them by mass.

This greatly reduces the probability of false positive reporting of perchlorate.

By the way, in tandem mass spectroscopy techniques, the first mass spectrometer is utilized as a filter to improve signal to noise ratios and increase the sensitivity for perchlorate detection and quantification.

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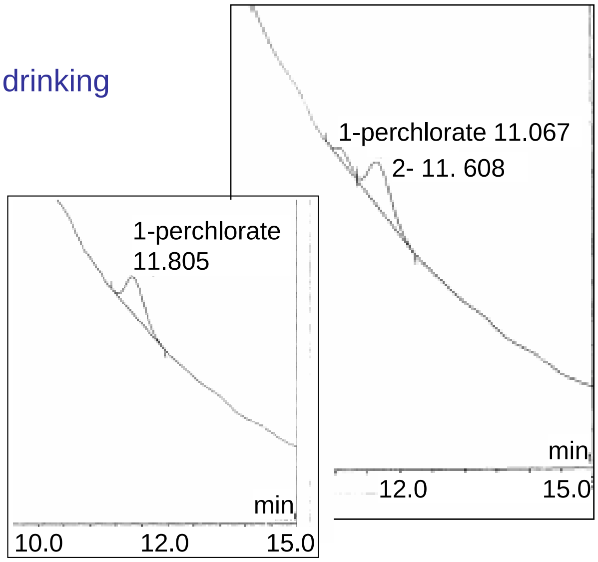
Ion Chromatography USEPA Method 314.0

- Designed to monitor drinking water for perchlorate
- Can be subject to false positives
- Inappropriate for use in samples with high total dissolved solids



Ion chromatograph results for perchlorate analysis

The ion chromatography method that has been used by USEPA for the nation wide occurrence study has been method 314.0. Method 314.0 analyzes for the ion perchlorate in a drinking water matrix by sensing its conductivity in solution.

Looking at the left ion chromatograms in the lower right hand corner of the slide, you can see that the baseline is not horizontal. This means that there is a significant background response by the detector and therefore false negative reporting by the laboratory has been a concern with this method due to contributions to the signal from other conductive interfering species present in the sample.

There is also a high probability for false positive reporting for this method.

If the samples contain high dissolved solids and/or conductivity, this method can yield misleading information as in the chromatogram on the right.

There are two peaks in this chromatogram, the one at 11.067 minutes is the small perchlorate peak, and the second at 11.688 minutes is a contaminant.

If perchlorate was not present, the laboratory technician could misidentify the contaminant peak as perchlorate and report a false positive determination.

Method 314.0 is not a determinative method meaning that the signal is not exclusively unique to the perchlorate molecule.

To confirm the presence of perchlorate in an environmental sample, it is preferable to use the analytical technique mass spectrometry (MS), which confirms the chemical composition of unknown ions by their molecular weight (mass-to-charge ratio).

Other methods that are being developed improve upon Method 314.0. See Chapter 3 of the perchlorate overview document and Table 3-1 for a comparison of analytical laboratory methods.

Improved Analytical Methodologies

Several methods improve upon EPA Method 314.0

Published EPA methods	Link
EPA 314.1 inline enrichment/ cleanup and dual column verification	http://www.epa.gov/ogwdw000/methods/pdfs/method_314_1.pdf
EPA 331: LC/MS	http://www.epa.gov/ogwdw/methods/sourcalt.html
EPA 332: IC/MS	http://www.epa.gov/nerlcwww/ordmeth.htm

There are several methods that have been published or are in development to improve upon EPA Method 314.0 The ITRC Perchlorate Overview Document covers these developments in more detail.

• Drinking water method 314.1 utilizes dual column - ion chromatography and in-line column concentrator/counter ion cleanup. This method is currently under consideration for certification by the state of New Jersey's primacy health laboratory.

• USEPA methods that have recently been published are EPA 331 and 332. These two methods use the determinative mass spectrometer detector to identify and quantify perchlorate by mass.

Method 331 is a liquid chromatography/mass spectroscopy "LC/MS" method and

332 is a ion chromatography/mass spectroscopy IC/MS method. I have listed their internet addresses so that you may learn more about the published methods.

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Improved Analytical Methodologies Under Development

Ongoing development of improved methods, including

- SW9058
  - Perchlorate using ion chromatography with chemical suppression conductivity detection
- SW6850
  - Perchlorate by LC/MS or LC/MS/MS
  - Similar to Method 331
- SW6860
  - Perchlorate by IC/MS or IC/MS/MS
  - Similar to Method 332
- US Food and Drug Administration (FDA) Method

• There are many other methods under development by several different organizations including EPA, Federal Bureau of Investigation, US Air Force, and Food and Drug Administration (FDA).

The information presented includes projects that are under development in the Office of Solid Waste like the SW6800 series methods. As you can see, the SW methods are similar to the USEPA Office of Water methods because they utilize LC/MS and IC/MS in single or tandem configurations.

You may want to consider these methods for site investigation because they have procedures that can handle more robust matrices.

Food and Drug Administration (FDA) methods are available for analyzing food products.

•These various techniques could be used for challenging solid or aqueous samples.

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Sensitivity and Cost Comparison

Method	Detection Level	Estimated Cost Range
USEPA 314.0: IC	4 µg/L	$ 65-150
USEPA 314.1: IC	0.5-1 µg/L	$120-230
EPA 331: LC/MS LC/MS/MS	0.1 µg/L 0.02 µg/L	$ 85-200 $150-260
EPA 332: IC/MS IC/MS/MS	0.1 µg/L 0.01 µg/L	$ 90-200 $150-260
SW6850: LC/MS LC/MS/MS	0.1 µg/L 0.02 µg/L	$ 85-200 $150-260
SW6860: IC/MS IC/MS/MS	0.1 µg/L 0.01 µg/L	$ 90-200 $150-260
SW9058: IC	0.5-1 µg/L	$120-230
FDA Method	0.5 µg/L	$100-200

No associated notes.

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Considerations for Choosing an Analytical Methodology

- Regulatory acceptance of method
- State and US EPA certification of laboratory
  - If required by the state or the program
- Sensitivity
- Selectivity

When choosing an analytical method that is appropriate for your site specific needs, you want to consider

1. The regulatory acceptance of method,
2. state/USEPA certification of laboratory (if required by the state or the program),
3. sensitivity that you require to characterize the extent of contamination, and
4. selectivity for natural and/or synthetic perchlorate contamination.

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Example Analytical Strategy

- Strategy used in California for drinking water
- Starts with EPA Method 314.0
- If perchlorate is detected and
  - If analytical results agree with site hydrology models, then
    - Method 314.0 is acceptable for identification
  - If analytical results do not agree with projections, either
    - Pretreat and run again
    - Use a determinative method

On this slide, we give you a hypothetical example of an analytical strategy that you may want to utilize on your site.

The strategy starts with the promulgated USEPA method 314.0. This approach is for drinking water samples that have conductivity below the Maximum Conductivity Threshold determination for the analytical method.

If Perchlorate is Detected and:

•Analytical results from the 314.0 agree with site hydrogeology models, then Method 314.0 is acceptable as a method for identifying perchlorate in the medium being analyzed, assuming that the sampling grid for the contaminated site is representative of the actual condition.

•Analytical results don't agree with projections either pretreat and run again or use a determinative method (LC/MS which is liquid chromatography Mass Spectrometry or IC/MS which is Ion Chromatography Mass Spectrometry)

An example that is used for groundwater contamination in illustrated in Figure 3-1 in the Overview Document.

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Example Analytical Strategy (continued)

- If perchlorate is NOT detected and
  - If analytical results from the EPA Method 314.0 are non detect without dilution, then
    - Method 314.0 results are acceptable as is
  - If samples require dilution to the calibration range, then
    - New reporting limit must be acceptable
    - If the result is still non detect and high reporting limit is not acceptable, then
      - Analyze by mass spectrometry

If Perchlorate is NOT Detected and:

• Analytical results from the 314.0 are non detect without dilution, then Method 314.0 results are acceptable as is

• If samples require dilution to the calibration range the new reporting limit (RL) must be acceptable

•If the result is still Non Detect and high Reporting Limit in not acceptable, then analyze by one of the determinative Mass Spectrometric methods.

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Forensic Techniques

- Used for the systematic investigation of a contaminated site or event
- Techniques
  - Traditional source identification and concentration profiling
  - Association with affiliated chemicals
  - Isotopic analysis

The example of the analytical strategy is only one component of the environmental forensic “big picture” for site evaluation

Environmental forensics is the systematic investigation of a contaminated site or event

The focus of a forensic investigation is on defensibly allocating liability for the contamination.

Forensic investigative approaches for soil or groundwater include;

1.traditional source identification and concentration profiling,

2.association with affiliated chemicals, and

3.isotopic analysis.

Isotope analysis research is focusing on the ability to distinguish between naturally occurring and synthetic perchlorate contamination.

The detection and use of associated chemicals is often of more forensic value in identifying and allocating sources than for the contaminant of concern. For example

When identifying perchlorate associated with highway road flares, you look for a distribution of strontium nitrate, which often composes up to 70% of a road flare.

Other co-contaminant analysis may also lead a site investigator to suspect perchlorate contamination.

Perchlorate in the Environment: The Concern

- Most of the available research focused on determining effects of human exposure
- Perchlorate may have deleterious effects on other species throughout the environment; subject of on-going research

The concern for perchlorate in the environment is show in this slide

Most of the available research on perchlorate has focused on determining effects of human exposure BUT

Perchlorate may have deleterious effects on other species throughout the environment; this is the subject of on-going research

33

Primary Routes of Perchlorate Exposure to Humans

- Drinking water
  - Public water systems
  - Private wells
- Food
  - Leafy vegetables
  - Milk
  - Some other food products
- US Food and Drug Administration (FDA) data
  - http://www.cfsan.fda.gov/~dms/clo4data.html

On this slide, we talk about routes of human exposure scenarios, there are primary and secondary routes of exposure.

For Example: In New Jersey the Bureau of Safe Drinking water utilized a modification of USEPA Method to allow detection down to 1 ppb and found perchlorate at 30 well locations with background levels at about 0.5 ppb.

Perchlorate is also a concern in food

A recent study by the FDA discovered that Leafy vegetables can be as high as 12 ppb, milk can contain as much as 6 ppb, they also investigate some other food products

The results of this investigation can be viewed at the URL that is shown on the slide

http://www.cfsan.fda.gov/~dms/clo4data.html#table2

J. Agric. Food Chem 2005, 53, 369-373 "Perchlorate Accumulation in Forage and Edible Vegetation, Jackson W. Andrew. Kansas

cucumber 0.77 mg/kg (ppm)

cantaloupe 1.6 mg/kg (ppm)

tomato 0.22 mg/kg (ppm)

ES&T Vol. 39, # 24, 2005 "Perchlorate and Nitrate in Leafy Vegetables of North America", Sanchez, C.A.

Maximum perchlorate conc.

Spinach 0.628 mg/kg (ppm)

baby mix lettuce 0.370 mg/kg (ppm)

green leaf lettuce 0.195 mg/kg (ppm)

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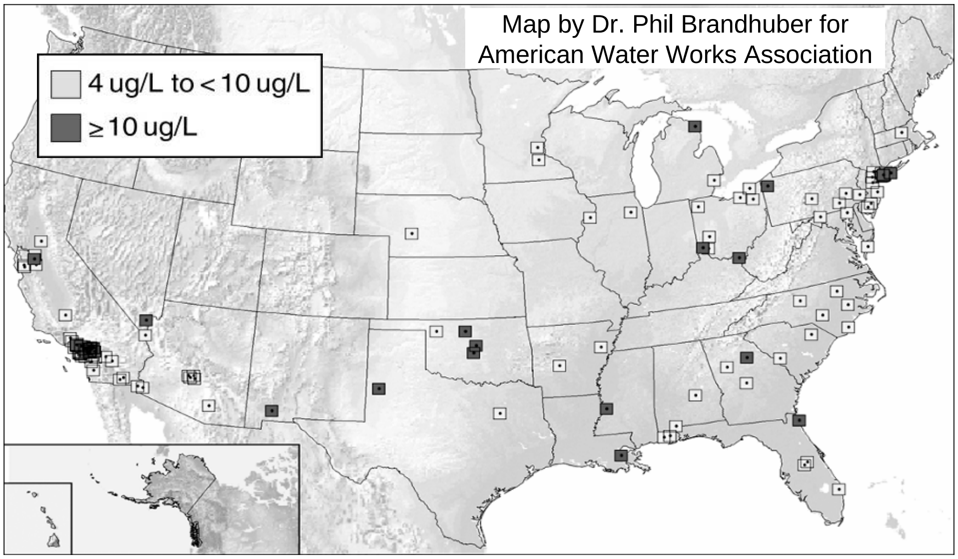
Drinking Water: A Primary Route of Exposure

Large public water systems with detectable perchlorate (≥4 μg/L)



As of 2004, perchlorate contamination and perchlorate releases have been documented in 35 states by EPA (USEPA, 2004). USEPA monitored for perchlorate in drinking water through the Unregulated Contaminant Monitoring Rule (UCMR) Program.

As of January 2005, perchlorate had been detected in 153 public water systems and 25 states across the United States. The majority of detections in drinking water have not been associated with USEPA-identified perchlorate releases and most detections have been below 12 ppb.

In California, perchlorate has been found in more than 350 of the approximately 6,700 public drinking water sources (CA DHS, 2005).

The lower Colorado River, a major source of irrigation and drinking water for southern California, also contain levels of perchlorate.

The Texas Commission on Environmental Quality has detected perchlorate concentrations in an area exceeding 30,000 square miles in western Texas

Extensive testing of New Jersey's and Massachusetts' public water supplies has shown several drinking water sources to have perchlorate.

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Secondary Routes of Exposure

- Can impact sensitive receptors
- Fetal exposure
  - Perchlorate can pass through placenta and enter fetal bloodstream
- Infant exposure
  - May be exposed to perchlorate from human milk

The secondary routes of exposure shown in this slide consider impacts to sensitive receptors from a human developmental approach.

•Secondary exposure of the fetus can occur from perchlorate passed through the placental when the mother is hypothyroid.

•Secondary neonatal exposure can come form human breast milk

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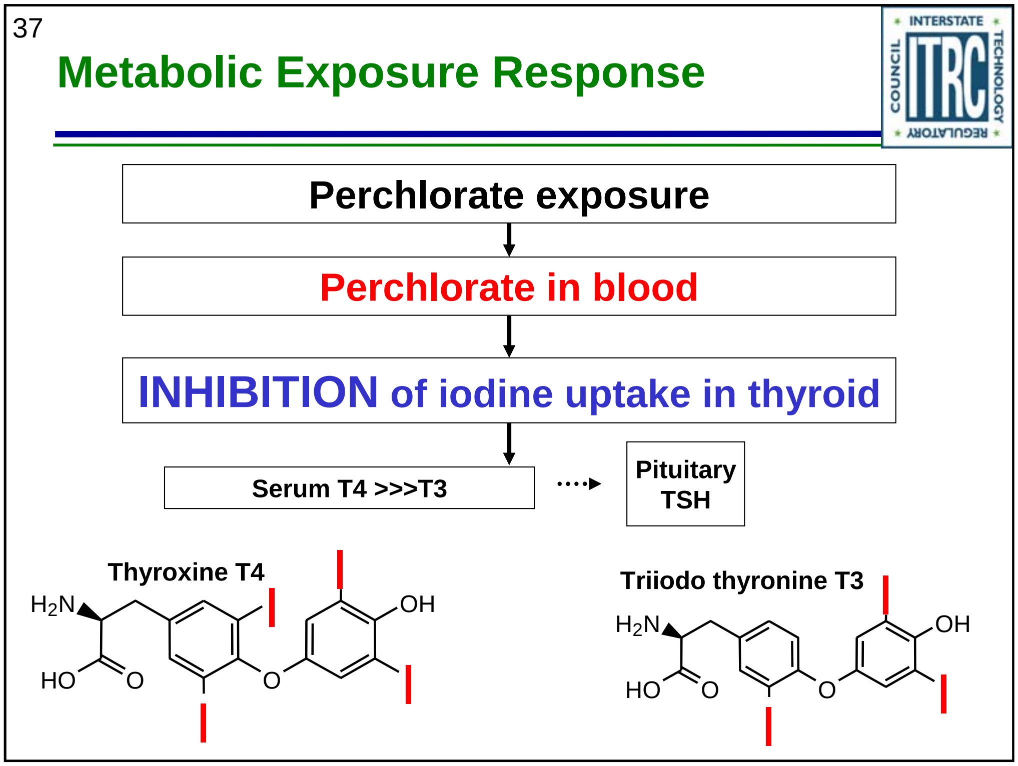
Perchlorate Toxicity

- Perchlorate is one of several compounds that competitively interfere with iodide uptake in the thyroid. Examples of other interfering chemicals are
  - Nitrates
  - Thiocyanates
- Perchlorate is **NOT** a known human carcinogen

Perchlorate is one of several compounds that competitively interfere with iodide uptake in the thyroid. Examples of other interfering chemicals are

Nitrates and thiocyanates which also inhibit iodine uptake

The risk assessment for perchlorate has been complicated by the fact that perchlorate is not a known human carcinogen, in fact it has been used therapeutically.



On this slide, we discuss the mode of action associated with perchlorate exposure

Perchlorate dissolves in the blood and inhibits the natural uptake of iodine

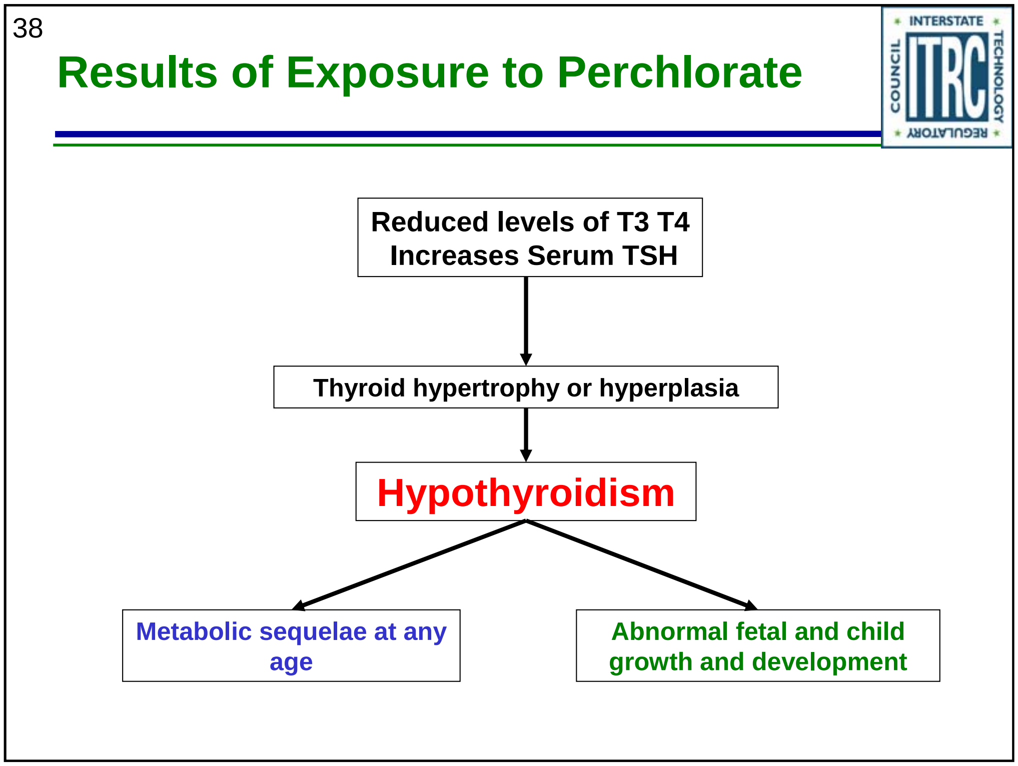
A normal diet contains about 400-500 µg of iodine, of which the gland takes up about 80(+)µg.

Once dietary intake of iodide is consistently under 100 µg per day for a period of about three months, hypothyroidism will progressively become apparent.

Iodine deficiency is said to be a public health problem for about 30% of the world population, for example, there are villages in Zaire where everyone is hypothyroid! We don't know the extent of exposure due to competitive inhibitors like nitrate, thiocyanate, and perchlorate.

It is best to regard T4 as a prohormone, a precursor of T3

And as you can see any interference with iodine absorption directly effects the production of T3 and T4 serum proteins because each molecule contains several iodine atoms. This indirectly disturbs the production of thyroid stimulating hormone (TSH) in the pituitary gland



Reduced levels cause a condition doctors call hypertrophy or hyperplasia.

This may lead to hypothyroidism and can have metabolic effects in humans at any age, but is primarily of concern for abnormal fetal and infant growth and development.

These effects have not been identified in humans as a result of perchlorate exposure and are difficult to estimate from animal data due to the large amount of uncertainty in extrapolation of effect dosages from species to species,

This is due to differences in hormone physiology.

By the way, Metabolic sequelae simply means effects on metabolic endpoints

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Human Health Risk Assessment

- Primary concern
  - Fetal and neonatal neurodevelopment
- Most sensitive subpopulation
  - Developing fetus in a mother who is hypothyroid
- Other populations of concern
  - Nursing infants
  - Children
  - Postmenopausal women
  - Hypothyroid individuals

On this slide, we show some of the elements of the current human health risk assessments.

There is General agreement that fetal and neonatal neurodevelopment is the primary concern for human health risk assessment.

Based on available laboratory animal studies, the most sensitive subpopulation is the developing fetus in a mother who is hypothyroid

Other populations of concern include nursing infants, children, postmenopausal women and hypothyroid individuals

Thyroid hormones are critical for both the fetus and neonate.

Although the periods of development that are most sensitive to thyroid perturbations are known, our understanding is limited by lack of data on perchlorate dose-response, making it difficult to predict the potential effects of perchlorate.

Some Risk assessors believe that hypothyroid pregnant women may not have sufficient compensatory mechanisms to manage reduced iodide uptake due to perchlorate competitive inhibition.

There is still uncertainty in the dose-response relationship and the human epidemiological data do not support this hypothesis.

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Reference Dose Calculation

- Analysis to determine the dose where there is no observed adverse effect and in some cases, the lowest dose corresponding to an adverse effect
- Analysis of studies to determine adverse effects in order to calculate a reference dose (RfD)
- Uncertainty factors used to ensure that RfD adequately protects human health

An oral RfD is an estimate, (to within an order of magnitude), of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects during a lifetime.

A high-confidence RfD is based on data that address all potentially critical life stages.

Although there is a standard process for risk assessment, its application on a site-specific basis can be complex.

Many elements complicate a risk assessment, there is;

1.The difficulty of site characterization,

2.the likelihood of exposure under different scenarios, and

3.the ongoing scientific debate over toxicity

This uncertainty result in a range of different outcomes and risk evaluations.

These difficulties are evident in the site-specific risk assessments for most chemicals, including perchlorate.

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National Research Council Findings

- National Academy of Sciences National Research Council committee reviewed existing studies
- Recommended an RfD
  - 0.0007 mg/kg/day
- Summary of findings available on-line
  - http://www.nap.edu/html/perchlorate/perchlorate-brief.pdf

National Academy of Sciences National Research Council committee reviewed existing studies

They recommended an RfD 0.0007 mg/kg/day

Summary of findings available on-line

http://www.nap.edu/html/perchlorate/perchlorate-brief.pdf

The important thing to remember is that this RfD is based on a biochemical precursor effect

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Drinking Water Equivalent Levels (DWEL)

- Not a regulatory level
- RfD EPA posted on Integrated Risk Information System (IRIS) – www.epa.gov/iris
  - 0.0007 mg/kg/day
  - Equates to a DWEL of 24.5 ppb
- Based on the assumption that 100% of perchlorate ingestion is from drinking water
  - There may be many other sources
- Its sole utility is in making rough comparisons among different reference doses

DWEL is Not a regulatory level

EPA posted this reference dose on their Integrated Risk Information System (IRIS)

This reference dose equates to a DWEL of 24.5 ppb

Humans may also be exposed to perchlorate by ingestion from sources other than public drinking water supplies.

These include;

1.lettuce, and other leafy vegetables,

2.human and dairy milk and

3.bottled water.

If there is exposure to perchlorate from sources other than water then the daily allowable amount in drinking water needs to be reduced to some concentration lower than the Drinking Water Equivalent Level (or DWEL) of 24.5 ppb.

Integrated Risk Information System Website is available at www.epa.gov/iris

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Regulatory Status

- EPA adopted the National Research Council's RfD of 0.0007 mg/kg/day in February 2005
  - EPA posted this value on the Integrated Risk Information System (IRIS)
  - No current maximum contaminant level (MCL) for perchlorate, but EPA is beginning process to determine if an MCL should be established
- California Prop 65 list – Insufficient evidence to list as a developmental or reproductive toxicant

So for the current regulatory status

USEPA utilizes a three step approach to developing MCL levels for all contaminants;

The first step is to determine levels of human health concern

EPA has done this by publishing the National Research Council's Reference dose in IRIS, but has not promulgated an MCL

The second is to determine if the parameter of interest can be reliably detected and quantified in the environment

EPA's Office of Research and Development has developed several low level methods that we discussed earlier

And third is the determination of Best Available Treatment Technology

We are about to discuss this topic in the next presentation made by Tony Lieberman after the question and answer period.

The California Developmental and Reproductive Toxicant (DART) Identification Committee is a panel of independent scientists.

This committee, which is administered by the California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA), concluded that available scientific information on perchlorate was not sufficient for placing the substance on the Proposition 65 list.

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Individual States Establish Cleanup Standards and Health-based Goals

- Nevada adopted EPA's advisory level of 18 ppb as a cleanup standard
- Some states established their own health-based goals
  - Texas – 17 ppb
  - Arizona – 14 ppb
  - California – 6 ppb
  - New Jersey – 5 ppb
  - Kansas – considering 4 ppb
- California established a cleanup standard of 4 ppb in the Record of Decision (ROD) for Aerojet facility
- Massachusetts has adopted a drinking water and waste site cleanup standard (MMCL) of 2 ppb

Some states have adopted advisory levels for perchlorate in drinking water, while a few are considering or are in the process of promulgating state levels in lieu of a Federal standard. Although States evaluate the same toxicological data used by the EPA and the National Academy of Sciences to determine the RfD of 0.0007 mg/kg/day, they may evaluate that information differently, apply different uncertainty factors, or considered relative source contribution differently.

States as well as the Federal EPA may also consider site-specific risked-based cleanup standards such as a Superfund Record of Decision (ROD). An example is the Aerojet facility in Rancho Cordova, CA.

Additionally, based on EPA acceptance of the National Academy of Science Jan 05 report identifying 24.5 ppb as the Drinking Water Equivalent Level (DWEL) for perchlorate, the US Department of Defense issued its 26 Jan 06 perchlorate policy (Policy on DoD Required Actions Related to Perchlorate). This policy establishes 24 ppb as the current level of concern for managing perchlorate across DoD and that it will comply with that level of concern or any more stringent applicable state or federal promulgated standards, once established. DoD is willing to conduct necessary cleanups under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), when a site-specific risk assessment demonstrates risks to human health exists.

A link to the Policy on DoD Required Actions Related to Perchlorate is available from the U.S. EPA Federal Facilities Restoration and Reuse's Perchlorate Links page at http://www.epa.gov/fedfac/documents/perchlorate_links.htm

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Risk Management Strategies

- Pollution prevention
  - Source reduction and/or substitution
  - Best management practices
- Recycling
- Risk reduction
  - Alternative water supplies
  - Blending
  - Treatment prior to use
  - Plume and source remediation

Risk management involves evaluation of several different factors to decide how best to eliminate or minimize risks due to contaminants at a site.

Traditionally Risk management involves implementing remedial activities that reduce contaminant concentrations to acceptable risk-based levels that are established during a risk assessment

Other measures may be taken to prevent completion of exposure pathways

or the best strategy for your site may involve a combination of these approaches.

Because of site- and location-specific factors, risk management strategies may not be consistently applied across site and programmatic boundaries.

After a Q&A break, Tony Lieberman is going to discuss various innovative treatment systems that can be used in diverse risk management strategies.

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Questions and Answers

No associated notes.

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Remediation Options Considerations

- Where is the perchlorate?
  - Soil, groundwater, surface water, drinking water or wastewater
  - Perchlorate accessibility (deep vs. shallow)
- What is the objective of the remediation?
  - Protect or treat drinking water supply
  - Treat source or control plume

There are a number of remediation technologies available that are applicable to any number of perchlorate situations. As with any cleanup effort, there are several questions that need to be answered when considering the remediation options that are available. First, what matrix is the perchlorate in and how do I best access the perchlorate, and second, what is the objective of my remediation?

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Remediation Options Considerations (continued)

- What is the regulatory goal and can it be attained?
  - Cleanup goals and timing
  - Discharge limits
- What is the prevailing geology and hydrogeology?
  - In situ or ex situ treatment

Having established the objectives, then we can look at what the regulatory goal is and how aggressive we need to be with the treatment approach that is selected. Based on that information, you can decide whether an in situ or ex situ approach best suits the needs of the project.

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Factors in the Selection and Success of Treatment Technologies

- Factors in the selection and success of treatment technologies
  - Perchlorate concentration (high, low, trace)
  - Scale of the treatment needed
  - Water quality parameters
    - pH and alkalinity
    - Total dissolved solids (TDS)
    - Metals concentration
    - Anions
    - Dissolved organic carbon
    - Dissolved oxygen and oxidation-reduction potential

Factor 1 - Perchlorate concentration: The choice of technology is somewhat dependent on the relative starting concentration. The technology of choice for treating a public drinking water supply that contains 1 – 10 µg/L may be very different from the treatment approach for a groundwater plume that contains 5,000 – 10,000 µg/L.

Factor 2 – The scale, magnitude or extent of the problem can also influence the treatment approach taken. For example, a small, defined groundwater plume that is clearly delineated may be treated in its entirety using one of several in situ approaches, while a mile-wide and mile-long plume threatening a drinking water reservoir may lend itself to a technology that intercepts further plume spread and provides hydraulic control.

Factor 3 – Water Quality Parameters: Biological approaches for treating perchlorate can be sensitive to water quality extremes (low pH, high dissolved oxygen, high oxidation-reduction potential, elevated metals) much more than non-biological systems. However, non-biological systems can be more sensitive to some conditions including high dissolved solids (TDS).

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Factors in the Selection and Success of Treatment Technologies (continued)

- Presence and concentrations of co-contaminants
  - Petroleum and chlorinated solvents, energetics, nitrate
  - Different microbial populations metabolize different compounds at different degradation rates
  - Different compounds have different absorption or ion exchange capacities
  - Ex situ – may require treatment trains to address all constituents
  - In situ – all designs do not address all contaminants equally
- More detailed discussion in forthcoming Tech-Reg document

Factor 4 - Co-contaminants are not usually a problem in drinking water situations. But, on commercial and military installations, perchlorate is frequently found co-mingled with other chlorinated solvents such as PCE, TCE and TCA, petroleum solvents such at BTEX, and sometimes explosives such as RDX, HMX and TNT. The populations of microorganisms that can biodegrade perchlorate are very different than those capable of degrading other co-contaminants and the conditions for optimal removal of perchlorate may be opposite of the conditions optimal for supporting biodegradation of the co-contaminant. However, in some situations, the presence of co-contaminants may actually promote conditions ultimately favorable for perchlorate degradation. Co-contaminants can also affect the selection of abiotic treatment approaches. Different contaminants may have different affinities for ion exchange resins, or carbon sites, causing interference with the treatment of the perchlorate. Wherever possible, these possible interactions should be evaluated in lab microcosms, bench tests or field pilot tests before committing to a full-scale implementation.

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Technology Availability

- Proven and commercially available
- Emerging
- State of the technology (see Remediation Technology Applicability Matrix in Appendix F)
  - Different projects summarized
    - Full scale systems
    - Treatment units

The ITRC Perchlorate Overview document provides summaries, with some details, of the proven and commercially available technologies currently employed. In Appendix F of the ITRC Overview document, there is a matrix that summarizes different projects that are actively treating perchlorate. Some projects employing emerging technologies are also described.

ITRC does not endorse any particular products or vendors. The Applicability Matrix provides site locations, summarizes site conditions, identifies the technology that is being used, and offers a summary of the progress to date. Readers can use the matrix to identify consultants, vendors, practitioners, and products that are currently involved in perchlorate cleanups.

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Commercially Available Technologies

- Physical and chemical technologies
  - Ex situ technologies
  - Primarily ion exchange
- Biological processes
  - Ex situ and in situ technologies
  - Perchlorate-reducing bacteria appear to be widespread in the environment

Ion exchange is only an ex situ treatment technology for aqueous media. It is applied to extracted groundwater or surface water pumped to the treatment station. Anion exchange is the most commonly used physical treatment process for ground or surface water and leachate.

Biological processes may be used in situ and ex situ and may be applied to both soil and aqueous media. There are a number of genera of bacteria that have been shown to have the enzymatic capability to biodegrade perchlorate. Under conditions that are relatively easy to establish both in situ or ex situ, these microorganisms can very effectively carry out the desired biotransformation.

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Ion Exchange Reaction Mechanism

- Equilibrium process
- Perchlorate ($Cl0_4^-$) is exchanged with another anion, typically chloride (Cl^-)
- Medium consists of an ion exchange resin containing a positively charged functional group (R_4N^+) with a strong affinity to the perchlorate ion

$$R_4N^+Cl^- + ClO_4^- \Leftrightarrow R_4N^+ClO_4^- + Cl^-$$

The exchange resin can be made from natural or synthetic organic, inorganic or polymeric material that contains functional ionic groups. A typical ion exchange system consists of small resin beads that form a resin bed in a cylindrical vessel, that contains millions of beads. A number of full-scale systems for treatment of contaminated groundwater for drinking water and remediation have been implemented in California and in other states.

A second emerging approach is under development. This involves the use of bi-functional anion exchange resins that are very highly selective for perchlorate. These resins are commercially available and the cost is coming down.

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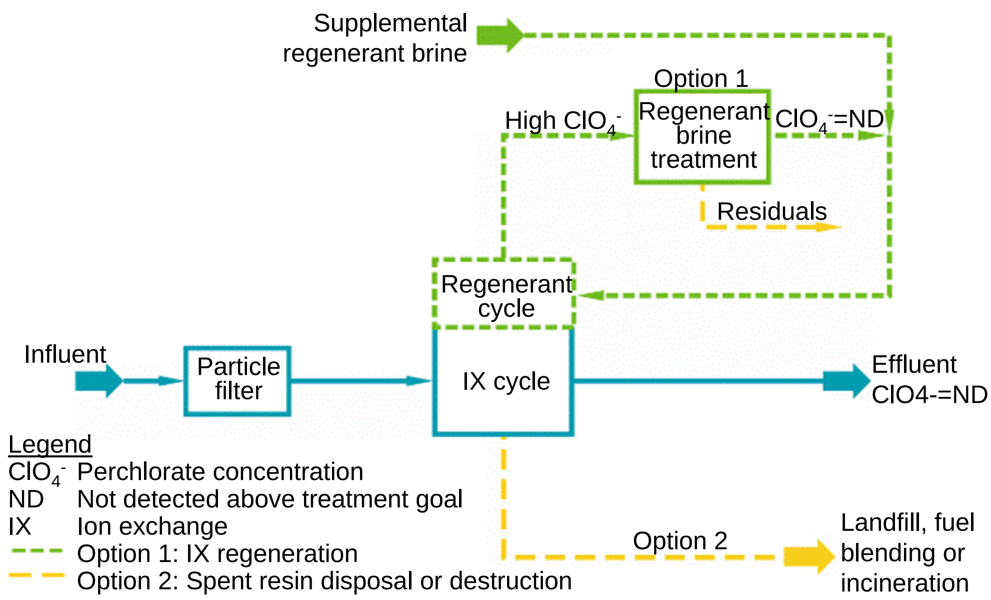
General Schematic of Ion Exchange



This schematic covers the two options that are currently being employed. In either case, perchlorate-contaminated water is pumped to the treatment system and enters the ion exchange bed (IX cycle). The treated water, after perchlorate is removed, is then discharged. The commercially available options are related to how the resin is handled. Option 1 shows a regenerable system in which the resin is cleaned and re-used multiple times. In Option 2, the resin is disposed of and is therefore called a non-regenerable system.

The regenerable process consists of at least three distinct steps:

1. Absorption or loading - Contaminated water is pumped through the system where the exchange takes place. The rate of absorption depends on many factors (e.g., resin selectivity, perchlorate concentration, competing ions in the waste stream, flow, size of the resin beads, and diffusion within the porous structure of the beads.)

2. Regeneration - A regenerant brine solution is used to displace the concentrated contaminant ions that are absorbed on the exchange resin.

3. Rinse - The regenerant solution is rinsed from the exchange resin before the next exchange cycle. Thorough rinsing prolongs resin life.

The non-regenerable uses the resin one time. After the active resin exchange sites reach saturation, the resin is removed and replaced with new material. The spent resin is disposed of in a landfill, by fuel blending or incineration.

Example Ion Exchange System

No associated notes.

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Ion Exchange Systems

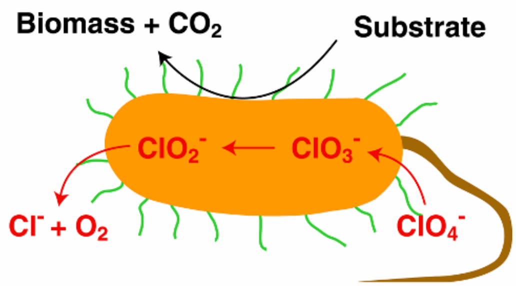
- Advantages
  - Treats to <4 µg/L
  - Fast reaction times allows for high flows
  - Regulatory acceptance
  - Continuing research and development should reduce costs
- Disadvantages
  - Sensitive to incoming water chemistry
  - High total suspended solids can clog resin bed
  - Competitive uptake by other anions (high total dissolved solids)
  - Waste brine high in perchlorate and total dissolved solids requires treatment and disposal
  - Non-selective resins require frequent replacement and disposal

No associated notes.

57

Biological Processes

- A variety of perchlorate-reducing bacteria have been isolated
- Biological perchlorate reduction is typically limited by aerobic conditions
- A variety of electron donors (substrates) have been shown to promote the biological reduction of perchlorate



Although a variety of perchlorate-reducing bacteria are present in soil and groundwater, the conditions conducive to natural attenuation have not been fully identified and are currently being studied. Under typical aerobic groundwater conditions, perchlorate tends to persist despite the presence of many bacteria that have the potential to degrade it.

Multiple genera and species have been isolated that can partially or fully degrade perchlorate. All are anaerobes or facultative anaerobes. (Facultative anaerobes are microorganisms that can use aerobic respiration in the presence of oxygen, but can employ fermentation if no free oxygen is present in their environment.) Perchlorate reductases describe a category of enzymes that can sequentially remove oxygen atoms from the perchlorate anion. The rate limiting step is the degradation of perchlorate to chlorate. Perchlorate (ClO_4^-) reductase enzymes then catalyze reduction of chlorate (ClO_3^-) to chlorite (ClO_2^-). Chlorite dismutase is one enzyme that has been shown to be specific for carrying out the last stage of reaction from chlorite to chloride (Cl^-) and oxygen (O_2).

Lactate, acetate, non-specific available dissolved organic carbon, ethanol, vegetable oils and others serve as electron donors and promote anaerobic bioremediation.

Ex Situ Bioremediation

- Aqueous waste streams
  - Continuous-flow stirred tank reactors
  - Fluidized bed reactors
  - Packed bed reactors

No associated notes.

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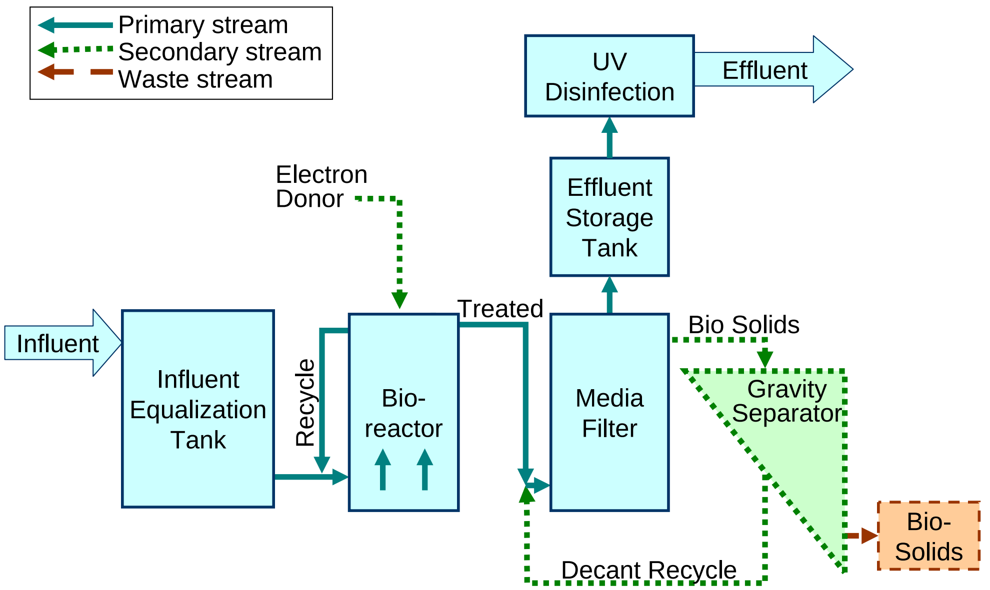
Ex Situ Bioremediation Schematic



Process flow diagram illustrates the overall concept for treating aqueous perchlorate-contaminated waste streams. To achieve high perchlorate removal rates, a soluble electron donor substrate (e.g., ethanol, acetate) is typically fed into the reactor. Controlling the growth of biosolids and managing excess biosolids is an issue that must be addressed for any bioreactor application.

The steps illustrated on the right half of the diagram (i.e., after the word “treated”) are specifically applicable to providing clean drinking water. If the bioreactor effluent is to be discharged to some other permitted receiving stream, the additional cleanup steps may not be required. There is still some debate regarding acceptance of biological reactor approach for treating public drinking water supplies, but it has been approved in a few localities.

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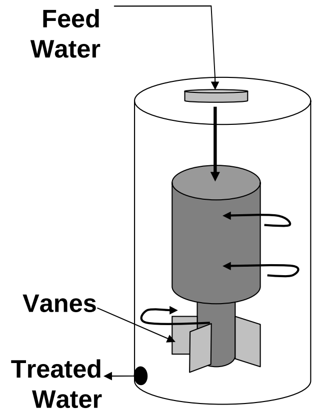
Continuous-Flow Stirred-Tank Reactors (CSTRs)

- Suspended-growth reactor with continuous influent and effluent flow
- Most commonly applied to the treatment of industrial wastewaters
- Generally best suited for low-flow, high-strength waste streams



General schematic of Continuous-Flow Stirred-Tank Reactors (CSTRs)

No associated notes.

61

Fluidized Bed Reactors (FBRs)

- Uses solid media, often sand or granular activated carbon to support microbial biofilms
- Applicable for wide range of perchlorate concentrations
  - 10 ppb to >500 ppm
- Can treat some co-contaminants, such as nitrate
- Permittable for drinking water treatment in California

Fluidized Bed Reactors at Longhorn Army Ammunition Plant, TX

No associated notes.

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Full Scale Fluidized Bed Reactors System in Henderson, Nevada

Fluidized Bed Reactor for Perchlorate Treatment System

Applicable to aqueous perchlorate contamination.

Still some debate regarding acceptance of biological reactor approach for treating public drinking water supplies.

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Packed Bed Reactors (PBRs)

- Fixed-film bioreactor that uses a solid media to support biodegradative organisms
- No full-scale PBRs, but pilot testing has shown that this reactor design can effectively remove perchlorate and nitrate in groundwater
- Permittable for drinking water treatment in California

Pilot-Scale PBR Tested at Redlands, California

Fixed-film or packed bed reactors are well-used in many wastewater applications. Trickling filters at wastewater treatment plants are an example of packed bed reactors. The can be effective for treating high-strength wastewaters as high microbial population densities grow in biofilms on the medium.

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In Situ Bioremediation

- In situ bioremediation applied to the saturated zone below the water table
- Perchlorate-reducing bacteria can often be stimulated to degrade perchlorate to below detection by adding a microbial growth substrate
- Two general strategies for groundwater
  - Permeable reactive barriers
  - Mobile soluble amendments

In situ bioremediation is generally applied to the saturated zone below the water table.

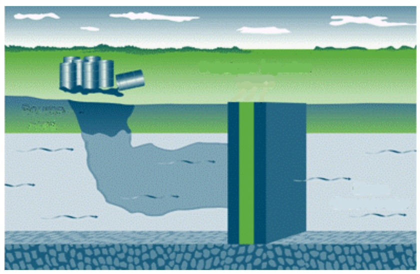
Permeable reactive barriers are typically used to intercept contaminant migration downgradient of the source. Several barriers can be installed in closer proximity to one another forming a grid to achieve continuous treatment that might be used to treat a source zone.

Mobile soluble amendments are generally fast-acting, but do not remain as long in the aquifer.

65

Permeable Reactive Biobarriers (PRBs)

- Permeable reactive biobarriers
- Solid substrates placed in trenches or low viscosity amendments injected across the flow path of the contaminated groundwater
- Water flows to, through, and past the fixed treatment zone



More information available in documents from ITRC's Permeable Reactive Barriers Team at www.itrcweb.org under "Guidance Documents"

Trenching depths may limit depth of application of solid amendments (e.g., mulch walls) compared to injectables that can be introduced at specific (and greater) depths via direct push or injection wells. To form the PRB, the injectable substrate has to be able to generally stay in the engineered radius of influence around each point.

Advantages of PRB:

1) Limited source area delineation needed.

2) Lower construction costs because not trying to impact entire plume.

3) Essentially no O&M after installation.

4) Width of treatment zone (contact time) can be engineered.

Disadvantages:

1) Does not address the source.

2) May need to be re-generated at some future date.

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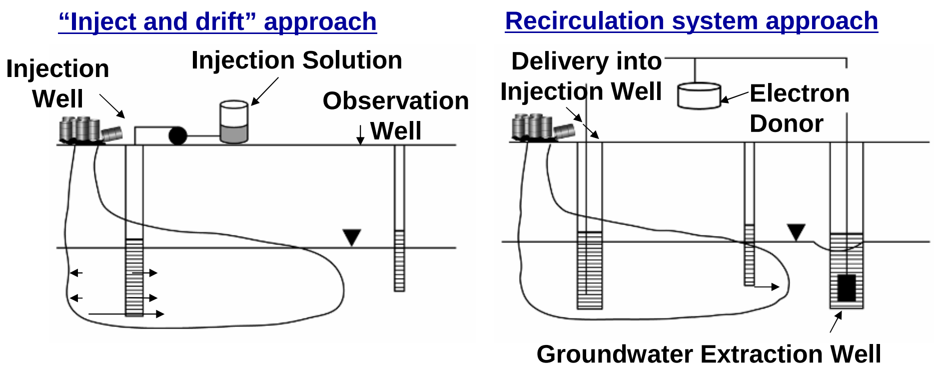
Mobile Amendments

- Inject water-soluble or miscible amendments with low viscosity into the upgradient portion of the plume or source area
  - Passive or active design creates impact zone



Passive (inject & drift) approach: Inject the amendment into the contaminated groundwater zone. Rely on groundwater flow to distribute the organic carbon (electron donor) downgradient away from the injection points thereby expanding the zone of influence. Injection performed under low pressure (soluble amendments and low-viscosity miscible amendments) or high pressure (high-viscosity amendments). May be chased with water to provide wider, immediate radius of influence.

Active (recirculation) approach: Set up recirculation system to help draw the soluble injected donor amendment through the aquifer to form a smear zone. Continuous recirculation used with low molecular weight soluble substrates such as lactate, ethanol, acetate, dilute molasses because substrate is rapidly consumed in the subsurface. High energy substrate can result in biofouling of equipment over time.

Temporary recirculation systems employed with vegetable oil emulsions to help spread the amendment and form a smear zone. Not subject to biofouling of equipment.

Biofouling potential of the subsurface should be monitored for continuous recirculating systems.

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Examples of In Situ Bioremediation Amendments

- PRBs
  - Bark mulch
  - Soybean oil
  - Emulsified soybean oil
  - Chitin
- Mobile amendments
  - Lactate
  - Polymerized lactate
  - Molasses
  - Ethanol
  - Acetate

Permeable reactive barriers are formed by filling a trench with a solid material with high organic content such as bark mulch or chitin. Alternatively, PRBs can be established by injecting substrates such as edible oils or edible oil emulsions that can be distributed away from the injection point to form a bioactive front that groundwater must pass through.

Mobile amendments can be used effectively in either the “inject-and-drift” or recirculation designs.

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Amendment Injection Approaches

Photo on the left shows installation of a PRB prepared using emulsified oil substrate. The emulsified oil substrate is injected under low pressure via a manifold into multiple wells simultaneously forming overlapping impact zones around each injection point. The length of the PRB can be extended by the number of injection points installed perpendicular to the direction of groundwater flow. The vertical depth of the zone of influence can be designed by adjusting the screen intervals for the injection.

Photo on the right shows high pressure grout pump injecting viscous amendment into the subsurface through a drive rod. Distribution of the amendment beyond the immediate injection zone relies on groundwater flow and the solubility of the amendment.

More information is available about injection approaches in the Tri-Services document entitled Principles and Practices for the Use of Oils in Groundwater Remediation. It can be found on the AFCEE web site.

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Soil Bioremediation

- In situ soil bioremediation
  - Carbon source as biological substrate
    - Tested at several sites with near-surface contamination
- Ex situ bioremediation
  - Carbon sources, water, and in some cases bulking agents blended with contaminated soils
    - Large scale demonstration conducted and completed at Naval Weapons Industrial Reserve Plant (NWIRP) McGregor

No associated notes.

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Emerging Processes

Bioremediation

- Vapor-phase electron donor injection
- Membrane bioreactors
- Monitored natural attenuation
- Phytoremediation
- Constructed wetlands

ITRC offers documents and training on these general topics at www.itrcweb.org under "Guidance Documents" and "Internet-based Training"

Physical and chemical

- Nanoscale bimetallic particles
- Titanium +3 chemical reduction
- Zero-valent reduction under UV light
- Electrochemical reduction
- Capacitive deionization
- Reverse osmosis
- Electrodialysis
- Nanofiltration and ultrafiltration
- Catalytic gas membrane
- Thermal treatment of soil

Emerging Processes can be divided into biological and physical/chemical processes.

The conditions supporting monitored natural attenuation (MNA) are been evaluated and the lines of evidence are being determined. As with all contamination scenarios, this has a high probability of substantially reducing remediation costs, while remaining protective of human and environmental health.

Phytoremediation and constructed wetlands rely on biological processes for uptake and transformation of the perchlorate. Some plants and trees have been shown to take up perchlorate; other studies show that rhizobacteria are responsible for the biodegradation that is observed. Concentrations <2 ppb can be achieved.

Vapor phase electron donor injection is being evaluated for stimulating vadose zone bioactivity.

The chemical processes all promote active and rapid breakdown of the perchlorate molecule.

Reverse osmosis (RO), electrodialysis and filtration technologies are physical separation technologies being studied.

New exchange media are being developed. One is based on coating (tailoring) the inner pores of granular activated carbon (GAC) with a functional group that participates in an ion exchange with perchlorate, potentially increasing the bed volume capacity of conventional GAC by many orders of magnitude. The process essentially converts GAC (a cheap substrate) from a VOC/SVOC adsorber to an ion exchange medium. This material is being tested at one site in the Los Angeles area, so is really considered an emerging approach.

A successful thermal project using a rotary kiln operated at 950 ºF followed by a cyclone at >1450 ºF was recently completed at Massachusetts Military Reservation, Cape Cod, treating approximately 65,000 tons of perchlorate and explosive powder contaminated soils. The use of a thermal method was unique in destroying an inorganic compound (Perchlorate) to less than 1 ppb (compliance originally 4 ppb) while simultaneously destroying RDX/HMX and polychlorinated naphthalenes. Treated soils were returned as backfill.

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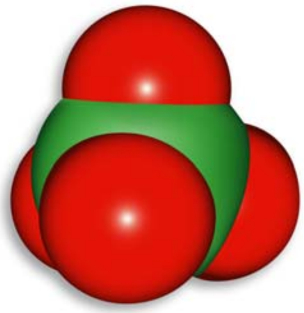
Summary – General

- Perchlorate is an emerging contaminant of concern
- Increased monitoring, improved analytical methods = increased number of known sites
- Long and persistent contaminant plumes when released into either ground or surface water
- Drinking water has been the primary focus of concern



ClO_4^-

The Overview Document and the Internet Training represent the **CURRENT STATUS** of the understanding about the sources, extent, analytical methods, health impacts and risks, regulatory climate and remediation options. This field is very active and new information is becoming available all the time. The ITRC “Tech Reg” document which will serve as a follow up to the current “Overview Document” will provide additional depth and detail.

Drinking water has been the primary focus of concern, but as other impacted areas are identified and characterized, they too are being recognized as areas of concern. One such example is irrigation water.

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Summary – Sources

- Perchlorate is both naturally occurring and widely manufactured
- Knowing the sources of perchlorate and the variety of its uses will help guide perchlorate investigations

Naturally-occurring perchlorate is found in arid and semi-arid environmental and very persistent with oxygenated water.

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Summary – Analytical Methodologies

- USEPA Method 314.0 used for monitoring of drinking water under the Unregulated Contaminant Monitoring Rule (UCMR) Program
- Improved analytical methodologies developed more recently

No associated notes.

Summary – Toxicity, Exposure, Risk

- Perchlorate is one of several substances that competitively interfere with iodide uptake in the thyroid
- General agreement that fetal and neonatal neurodevelopment is the primary concern for human health risk assessment
- No federal maximum contaminant level (MCL) for perchlorate, but EPA has set a reference dose (RfD)
- Some states have advisory and cleanup levels, two states are currently promulgating standards

No associated notes.

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Summary – Regulatory Status

- Some states established their own health-based goals or adopted EPA's advisory level
  - Nevada – 18 ppb
  - Texas – 17 ppb for Residential PCL
  - Arizona – 14 ppb
  - California – 6 ppb
  - New Jersey – 5 ppb
  - Kansas – considering 4 ppb

  http://www.epa.gov/fedfac/pdf/stateadvisorylevels.pdf
- Massachusetts has adopted a drinking water and waste site cleanup standard (MMCL) of 2 ppb

http://www.mass.gov/dep/service/regulations/310cmr40.pdf

No associated notes.

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Summary – Remediation Options

- There are existing remediation technologies commercially available and in use
- To date, most remediation technologies have been used to treat drinking water sources
- A variety of considerations are involved in selecting a remediation technology
- A variety of emerging technologies are under development and study

Reminder: the Applicability Matrix in the Overview document provides site locations, summarizes site conditions, identifies the technology that is being used and offers a summary of the progress to date. Readers can use the matrix to identify consultants, vendors, practitioners and products that are currently involved in perchlorate cleanups.

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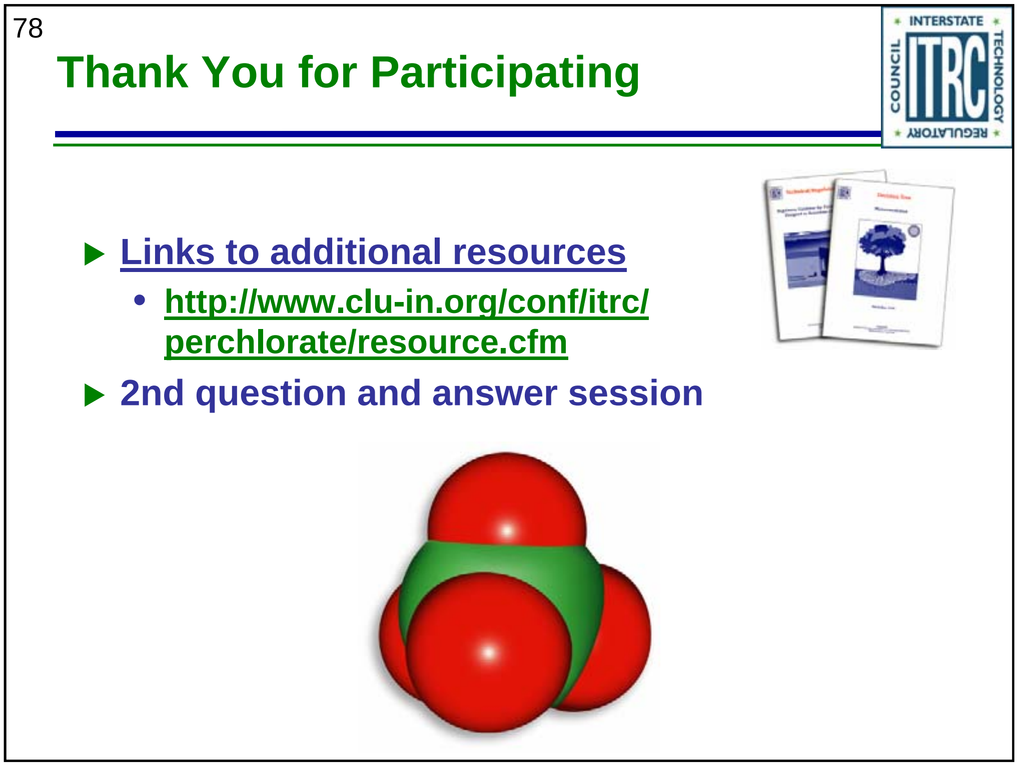
Upcoming ITRC Guidance

- New document entitled

  "ITRC Technical and Regulatory Guidance for Remediation of Perchlorate"

- Electronic compendium of perchlorate information

No associated notes.



Links to additional resources:

http://www.clu-in.org/conf/itrc/perchlorate/resource.cfm

Your feedback is important – please fill out the form at:

http://www.clu-in.org/conf/itrc/perchlorate/

The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants include:

Helping regulators build their knowledge base and raise their confidence about new environmental technologies

Helping regulators save time and money when evaluating environmental technologies

Guiding technology developers in the collection of performance data to satisfy the requirements of multiple states

Helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations

Providing a reliable network among members of the environmental community to focus on innovative environmental technologies

How you can get involved with ITRC:

Join an ITRC Team – with just 10% of your time you can have a positive impact on the regulatory process and acceptance of innovative technologies and approaches

Sponsor ITRC's technical team and other activities

Be an official state member by appointing a POC (State Point of Contact) to the State Engagement Team

Use ITRC products and attend training courses

Submit proposals for new technical teams and projects