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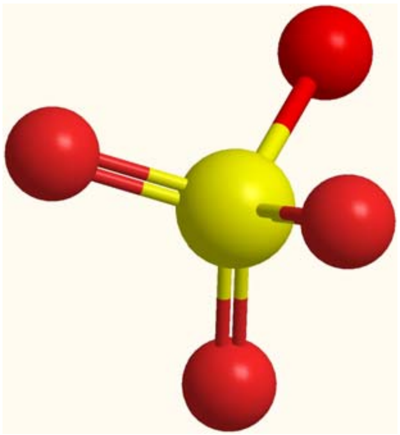
Perchlorate: an emerging contaminant



WaterTech 2008

April 18, 2008

Presented by: Erik J. Martin, Ph.D.

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Outline of Presentation

1. Perchlorate Background
2. Health Effects
3. Exposure Assessment
4. Drinking Water Standards
5. Remediation Technologies
6. Environmental Forensics

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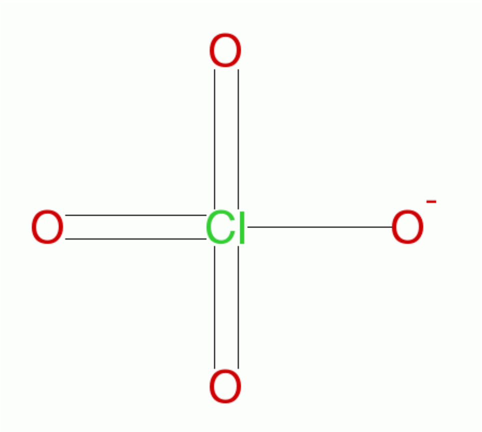
PERCHLORATE BACKGROUND

Perchlorate

What is Perchlorate?

Perchlorate (ClO_4^-), the dissociated anion of perchlorate salts such as potassium perchlorate and ammonium perchlorate, is used in the manufacture of:

- Solid propellants for rockets and missiles
- fireworks
- road flares
- blasting agents
- automobile air bags



perchlorate

Why is Perchlorate Important?

- Due to past disposal practices, extensive contamination of surface water and groundwater has been reported in many states in the US – MA, TX, CA
- Combination of high solubility, low sorption, and lack of degradation creates plumes that are large, persistent, and difficult to remediate
- Migrates at rates approximating the velocity of groundwater

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HEALTH EFFECTS

Perchlorate – Mechanism of Toxicity

- Human health concerns associated with exposures to perchlorate relate to its ability to reduce iodide transport into the thyroid gland
- Iodide is actively transported into thyroid cells via a transmembrane protein known as the sodium–iodide symporter (NIS)

- Because perchlorate has similar physicochemical properties as iodide, it competitively inhibits iodide transport into the thyroid by binding to the NIS

Perchlorate – Health Effects

- Thyroid requires iodide to synthesize thyroxine (T_4) and triiodothyronine (T_3) - hormones important in a number of physiological and developmental processes, including regulation of cell respiration, and growth & maturation of body tissues (neural and skeletal)
- Perchlorate-induced iodide deficiency, if severe, can cause hypothyroidism (↓ thyroid hormone production), which can result in clinical disorders, such as goiter and developmental defects in fetuses



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EXPOSURE ASSESSMENT

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Exposure Assessment

- Concern has been raised regarding the uncertainties in conducting human health risk assessments for perchlorate
- Example - contribution of diet to the daily perchlorate dose
- In the general population, it is anticipated that exposures to perchlorate will primarily occur as a result of ingestion of contaminated water and foods
- To conduct an accurate and meaningful risk assessment for perchlorate one must understand the contribution of diet to the daily perchlorate dose

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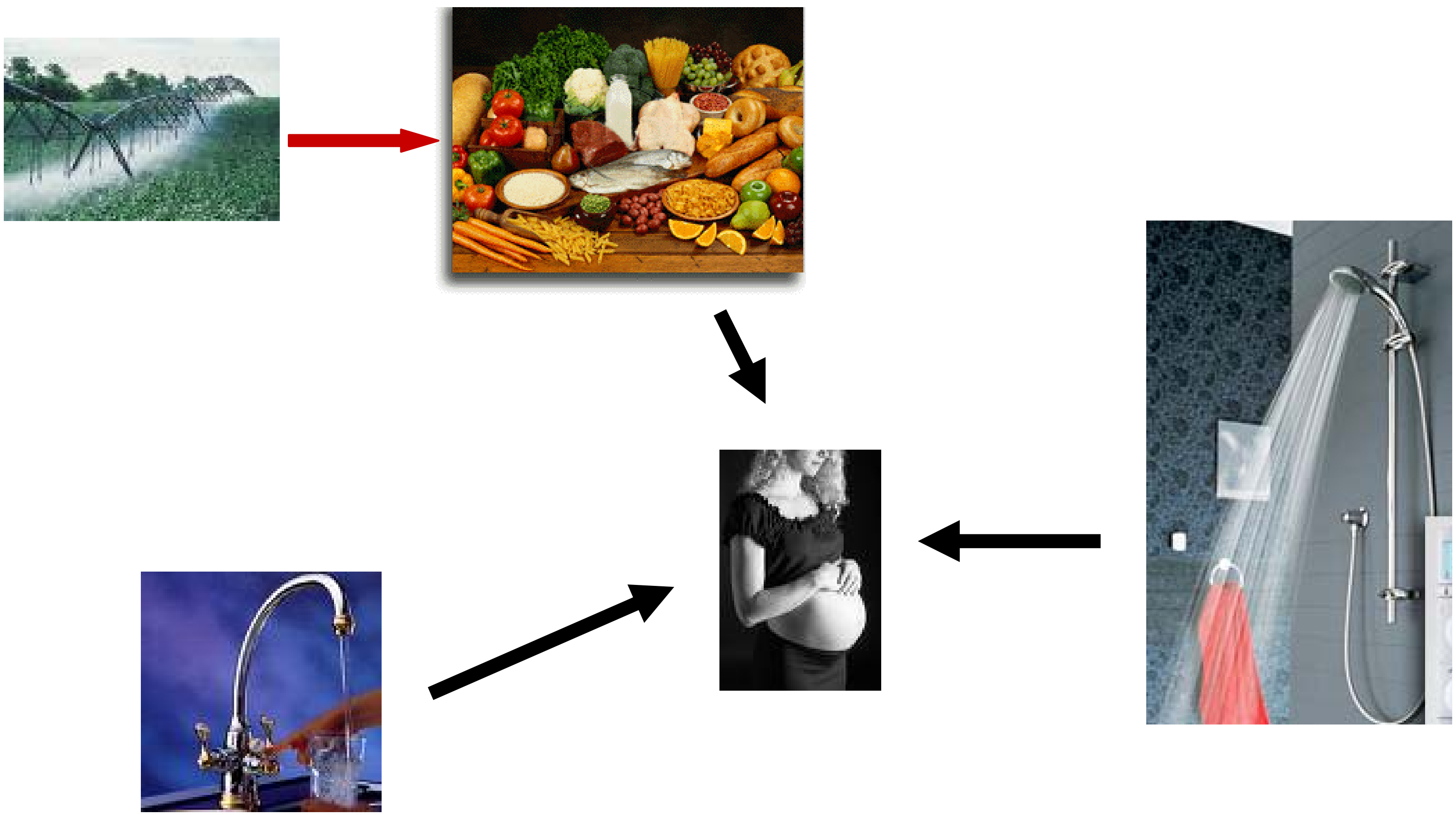
Risk Assessment Conceptual Model



Study Objective

To calculate a practical daily perchlorate dose from ingestion of foods that can be used for human health risk assessments

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Methodology

- Used US FDA exploratory survey data and parameters from the Dietary Guidelines for Americans at the 1200, 2000 and 2800 calorie levels
- Three separate daily doses were calculated for perchlorate at each calorie level by utilizing: the mean (low value), the 95% upper confidence limit of the mean (middle value), and the 90^{th}-percentile (high value) of perchlorate concentrations in food items
- For each food group, daily perchlorate doses were calculated by deriving the quantity of perchlorate consumed per serving and multiplying this value by the number of servings consumed per day
- Final perchlorate doses were calculated by dividing the daily doses by the appropriate body weight

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Daily Perchlorate Doses for a Child and Adult Receptor from Consumption of a 1200, 2000 or 2800 Calorie Diet, and Comparision of Adult Values to the MDEP Reference Dose

	1,200 calorie diet			2,000 calorie diet			2,800 calorie diet			
	Perchlorate Dose (□g/kg-day)			**Perchlorate Dose** (□g/kg-day)			**Perchlorate Dose** (□g/kg-day)			**MDEP RfD** (□g/kg-day)
Receptor (weight)	Mean	95% UCL	90th Percent	Mean	95% UCL	90th Percent	Mean	95% UCL	90th Percent	
Child (14.3 kg)	0.42	0.60	0.79	0.69	1.01	1.32	na	na	na	
Adult (70 kg)	0.09	0.12	0.16	0.14	0.21	0.27	0.17	0.25	0.33	0.07
Magnitude of Exceedance	1.3x	1.7x	2.3x	2x	3x	3.9x	2.4x	3.6x	4.7x	

Notes:

Child weight is the mean weight of a 2 to 3 year old male or female[4]

CDPH RfD is 0.37 □g/kg-day. All calculated perchlorate doses are below this \

DRINKING WATER STANDARDS

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Drinking Water Standards

- Can be established by state or federal (i.e., US EPA) agencies
- In general, a drinking water standard (DWS) is the maximum permissible level of a contaminant in water which is delivered to any user of a public water system
- DWSs are **enforceable** standards that are derived through consideration of public health and such factors as the best available technology, treatment techniques, and cost

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Regulatory Levels for Perchlorate

State	Health-Based Goal	Drinking Water Standard
Arizona	14	-
California	6	6
Massachusetts	1	2
Maryland	1	-
New York	-	-
Texas	-	-
US EPA[1]	24.5	-

Current as of September, 2005

All units are parts per billion (ppb) or µg/L

- Indicates that a value has not been established

[1] US EPA value is a Drinking Water Equivalent Level

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Development of Drinking Water Standards

The US EPA promulgates legally-enforceable drinking water standards termed maximum contaminant levels (MCL) - highest level of a contaminant permitted in drinking water that is anticipated to pose no risk to human health. MCLs can also be derived by state authorities though these values must be at least as stringent as those derived by the US EPA. MCLs are developed through a four-step process:

1. Derivation of an oral reference dose (RfD)
2. Calculation of the drinking water equivalent level (DWEL)
3. Adjustment of the DWEL by the relative source contribution (RSC)
4. Consideration of analytical methodologies, treatment technologies and costs, economic impacts, and regulatory impacts

1. Derivation of an Oral RfD

Oral Reference Dose (RfD)

The dose below which no adverse non-carcinogenic health effects should result from a lifetime of oral exposure

- Usually based on a subchronic or chronic animal study
- Identify NOAEL or LOAEL from appropriate study
- Calculate RfD by dividing the NOAEL or LOAEL by an uncertainty factor (UF) – e.g., intra- or interspecies variability
- UF serves to introduce a margin of safety into RfD development

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The RfD is calculated as follows:

$$\textbf{RfD} = \frac{\text{NOAEL (or LOAEL)}}{\text{UF}}$$

Where:

RfD	-	oral reference dose (mg/kg-day)
NOAEL	-	no-observed-adverse-effect-level (mg/kg)
LOAEL	-	lowest-observed-adverse-effect-level (mg/kg)
UF	-	uncertainty factor

2. Calculation of the DWEL

Drinking Water Equivalent Level (DWEL)

Lifetime exposure concentration protective of adverse, non-cancer health effects, that assumes all of the exposure to a contaminant is from drinking water.

The DWEL is calculated as follows:

$$\textbf{DWEL} = RfD \times (BW/WC)$$

Where:

DWEL - drinking water equivalent level (mg/L)

RfD - oral reference dose (mg/kg-day)

BW - body weight (kg)

WC - water consumption rate (L/day)

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3. Adjustment of the DWEL

The DWEL is adjusted by the relative source contribution (RSC), which is the proportion of exposure believed to result from drinking water compared to other sources (e.g., food, air).

$$\textbf{MCL} = RfD \times (BW/WC) \times RSC$$

Where:

MCL	-	maximum contaminant level (mg/L)
RfD	-	oral reference dose (mg/kg-day)
BW	-	body weight (kg)
WC	-	water consumption rate (L/day)
RSC	-	relative source contribution

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4. Consideration of Additional Factors

Must consider such factors as:

1. the availability and feasibility of analytical methodologies and treatment technologies
2. clean-up costs
3. economic and regulatory impacts

These factors may cause regulatory authorities to adjust the MCL upward or downward.

MCL

MCL

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Development of Regulatory Levels for Perchlorate

- The following slides present the approaches used by the US EPA, California Environmental Protection Agency (CalEPA), and Massachusetts Department of Environmental Protection (MDEP) in deriving a regulatory level for perchlorate
- Each organization calculated an oral RfD based on a study by Greer et al. (2002)
- Due to differences in methodology and scientific opinion, each has derived a different RfD and consequently distinct drinking water standards

United States Environmental Protection Agency

California Environmental Protection Agency

Massachusetts Department of Environmental Protection

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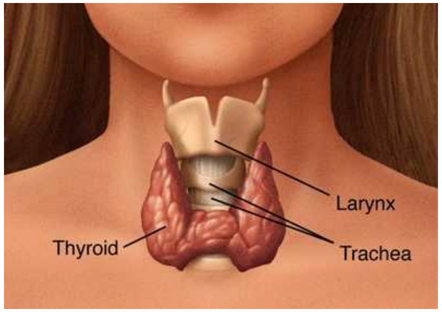
Greer et al., 2002

Study Design

- Thirty-seven healthy adults were assigned to four separate exposure groups: 0.007, 0.02, 0.1 or 0.5 mg potassium perchlorate / kg body weight per day
- Subjects were exposed to perchlorate for 14 consecutive days
- Thyroid uptake of radioiodide was measured at 8- and 24-hours after radioiodide administration: at baseline, on days 2 and 14 of perchlorate administration, and 15 days after dosing



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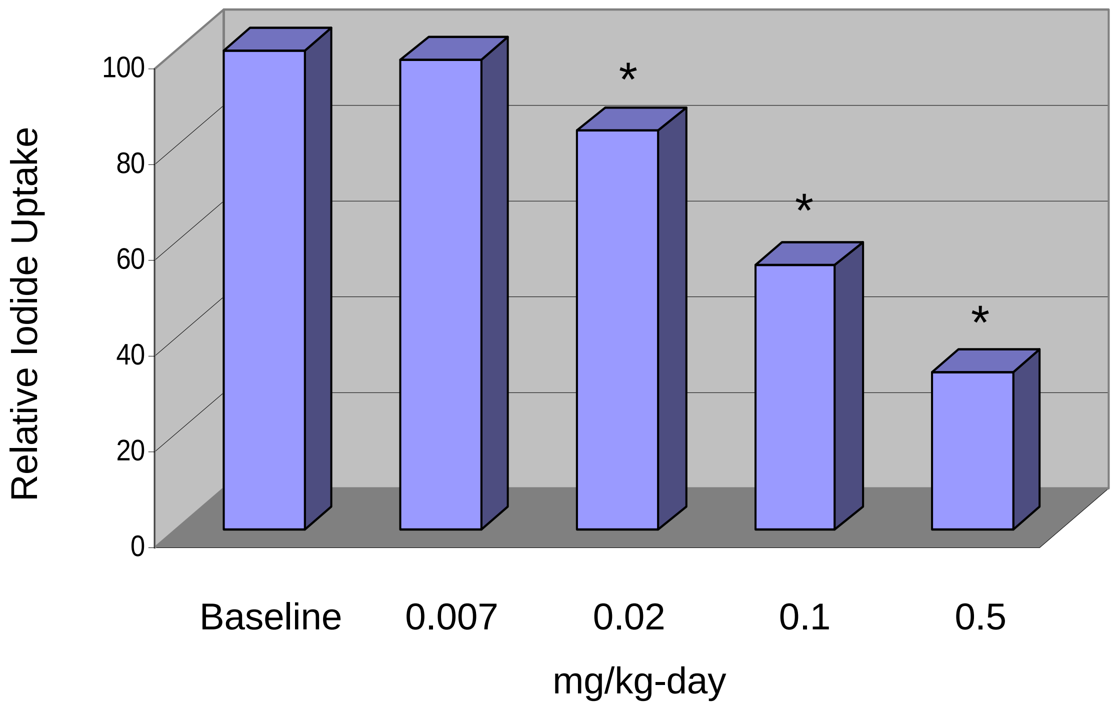
Results from Greer et al.

On day 14 of perchlorate administration, thyroid iodide uptake was significantly decreased with respect to the baselines for the three highest doses, while the low dose group was not significantly decreased.



* Significantly different than respective baseline mean

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Conclusion from Greer et al.

Because the low dose group was not significantly decreased from its respective baseline mean, Greer et al. designated this dose (i.e., 0.007 mg/kg-day) as a NOEL (no-observed-effect-level).

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Derivation of Regulatory Levels for Perchlorate

United States Environmental Protection Agency

To date, the US EPA has only developed a DWEL for perchlorate as regulators are awaiting further research regarding public exposures before selecting a RSC value

DWEL = RfD x (BW/WC)

= 0.0007 mg/kg-day x (35 kg/day/L)

= 0.0245 mg/L (or **24.5 ppb**)

RfD - NOEL from Greer et al. (2002) and an UF of 10 to account for intraspecies variability

BW/WC - 70-kg adult consuming 2 L of water per day

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California Environmental Protection Agency

The California Department of Health Services establishing a drinking water standard (MCL) that is effective as of January, 2008.

MCL = RfD x RSC x (BW/WC)

= 0.00037 mg/kg-day x 0.6 x (25.2 kg/day/L)

= 0.0056 mg/L (rounded to **6 ppb**)

RfD - Applied benchmark dose (BMD) modeling to data from Greer et al. to derive a NOEL and used a UF of 10

BW/WC - 95th percentile of the pregnant woman population (i.e., 61.2-kg woman consuming 2.4 L of water per day)

RSC - 0.6, due to detection in foods such as milk

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Massachusetts Department of Environmental Protection

Massachusetts disseminated a drinking water standard (MCL) for perchlorate in March, 2006. Prior to establishing a MCL, MDEP developed health-based drinking water limits for adults and formula-fed infants:

Adults

C = RfD x RSC x (BW/WC)

= 0.00007 mg/kg-day x 0.2 x (35 kg/day/L)

= 0.00049 mg/L (rounded to **0.5 ppb**)

Formula-Fed Infants

C = RfD x RSC x (BW/WC)

= 0.00007 mg/kg-day x 1.0 x (6.25 kg/day/L)

= 0.0004375 mg/L (rounded to **0.44 ppb**)

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RfD	- Considered low dose from Greer et al. (2002) a LOAEL and applied a UF of 100 to account for intraspecies variability, uncertainty in using LOAEL, and insufficiency of the database
BW/WC	- Adults: 70-kg adult consuming 2 L of water per day
	- Infants: 4-kg infant consuming 0.64 L of water per day
RSC	- Adults: 0.2, default US EPA value
	- Infants: 1, drinking water for formula

MCL of **2.0 ppb** was believed to provide the best overall protection of public health while retaining a margin of safety to account for uncertainties in the data

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Perspective

MDEP

Allowable daily dose

= RfD x BW

= 0.07 μg/kg-day x 70 kg

= 4.9 μg/day

Potential dose from water consumption

= MCL x WC

= 2 μg/L x 2 L

= 4 μg

∴ **0.9** μg remaining for other exposures

Daily Perchlorate Doses from Consumption of a 1200, 2000 or 2800 Calorie Diet

	1,200 calorie diet			2,000 calorie diet			2,800 calorie diet		
	Perchlorate Dose (µg/day)			**Perchlorate Dose** (µg/day)			**Perchlorate Dose** (µg/day)		
Food Group (serving size)	Mean	95% UCL	90th Percent	Mean	95% UCL	90th Percent	Mean	95% UCL	90th Percent
Meat & Beans (1 ounce)	0.81	1.84	2.07	1.49	3.37	3.79	1.89	4.29	4.82
Milk (1 cup)	2.72	2.90	4.12	4.09	4.35	6.18	4.08	4.35	6.18
Grain (1 ounce)	0.35	0.48	0.77	0.53	0.72	1.15	0.88	1.20	1.92
Fruit (½ cup)	0.70	1.16	1.59	1.41	2.32	3.17	1.76	2.90	3.97
Vegetable (½ or 1 cup)	1.38	2.18	2.78	2.30	3.63	4.64	3.21	5.08	6.50
Total Dose	**5.96**	**8.55**	**11.32**	**9.80**	**14.39**	**18.93**	**11.82**	**17.81**	**23.38**

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REMEDIATION TECHNOLOGIES

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Perchlorate Treatment Technologies

1. Ion Exchange
2. Bioreactors
3. In situ Anaerobic Remediation
4. Permeable Reactive Barriers
5. Phytoremediation
6. Soil Biotreatment

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Ion Exchange

- Used for treatment of groundwater, surface water, and leachate
- Mechanism: captures perchlorate anions on a positively charged resin and releases a harmless chloride ion in its place
- Exchange resin made of natural or synthetic organic, inorganic, or polymeric material that contain functional ionic groups

Process consists of at least three distinct steps:

1. Adsorption or Loading - contaminated water is pumped through the system where exchange takes place
2. Regeneration - a regenerant solution is used to displace the contaminant ions that are adsorbed on the exchange resin
3. Rinse - resins are rinsed to remove regenerant solution

Ion Exchange

Advantages

- Proven ability to remove perchlorate to below 4 ppb
- Fast reaction and simple operation
- Can be operated at a high flow rate
- Regulatory acceptance
- Cost effectiveness improving rapidly with technical innovation

Ion Exchange

Disadvantages

- High levels of suspended solids in wastewater may cause clogging of non-selective resins
- Generates a secondary waste stream in the form of a concentrated perchlorate brine and spent exchange resins
- Competitive uptake by other anions may limit the effectiveness of non-selective exchange resins
- Effectiveness of treatment is strongly influenced by water chemistry of a site (e.g., competing anions, pH)

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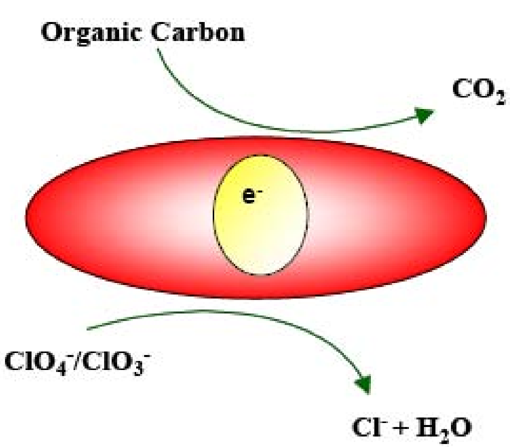
In situ Anaerobic Remediation

- Studies have shown that perchlorate can be successfully biodegraded to the chloride ion but only anaerobically
- Mechanism: naturally occurring microorganisms are used to biodegrade or consume perchlorate as a food source.
- An electron donor (i.e., carbon source) such as acetate or molasses is added to perchlorate-contaminated groundwater or soil to stimulate the microorganisms to degrade the contaminant in situ.



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In situ Anaerobic Remediation

Advantages

- Treats groundwater without pumping to the surface; should result in significant cost savings over pump-and-treat systems
- Biodegrades perchlorate relatively quickly
- Abundance of naturally occurring perchlorate-reducing microorganisms in environment
- Carbon sources demonstrated to date are relatively inexpensive
- May treat other soil or groundwater contaminants simultaneously
- Can be used to treat soil hot spots, which would prevent subsequent contamination of groundwater
- Land aboveground is usable during treatment period

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In situ Anaerobic Remediation

Disadvantages

- Drilling is required to deliver carbon source - cost?
- Less certain, non-uniform treatment results due to variability in aquifer, climate, weather and soil characteristics
- Require careful control of site-specific media characteristics (e.g., O_2 content, pH) to maintain optimal treatment conditions
- Free movement of microorganisms, electron donors, or treatment by-products in groundwater may impact downstream users of groundwater, requiring longer treatment time periods
- Downstream monitoring wells, and capture and reinjection of treated water may be required

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ENVIRONMENTAL FORENSICS

What is Environmental Forensics?

Environmental forensics includes investigating, interpreting and presenting evidence of source, fate, transport, composition, age, and extent of or responsibility for contamination of all environmental media (i.e. air, soil, water or biota).

“The application of scientific methods to identify the origin and timing of a contaminant release”

When to Use Environmental Forensics

- When contamination may not be yours (remove liability)
- When contamination is from multiple sources (share liability)

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Perchlorate Sources

Natural vs. Synthetic

Natural

- Formation in the atmosphere? Chloride + O_3?
- Chilean nitrate deposits – used to produce fertilizer

Synthetic

- Manufacture of perchlorate compounds
- Perchlorate use – NASA, DOD
- Perchlorate disposal – burned in unlined areas

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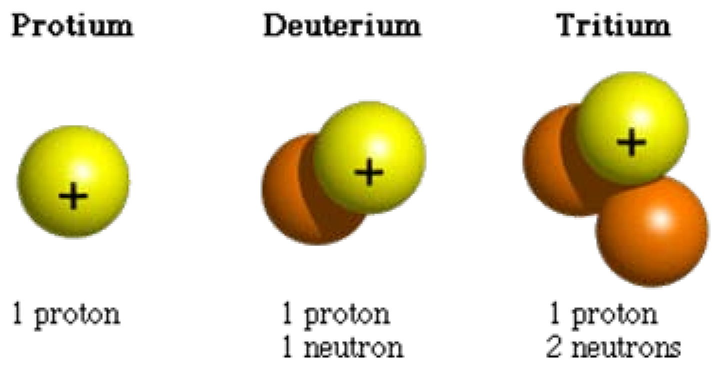
Isotope Analysis

What is an isotope?

Any of two or more forms of the same element, whose atoms all have the same number of protons but different number of neutrons.

The Nuclei of the Three Isotopes of Hydrogen



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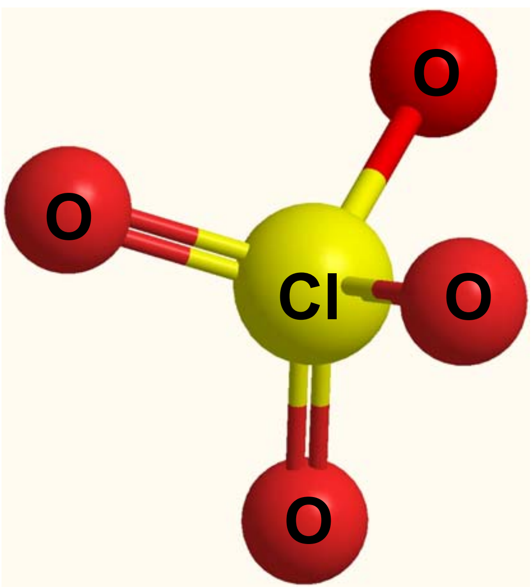
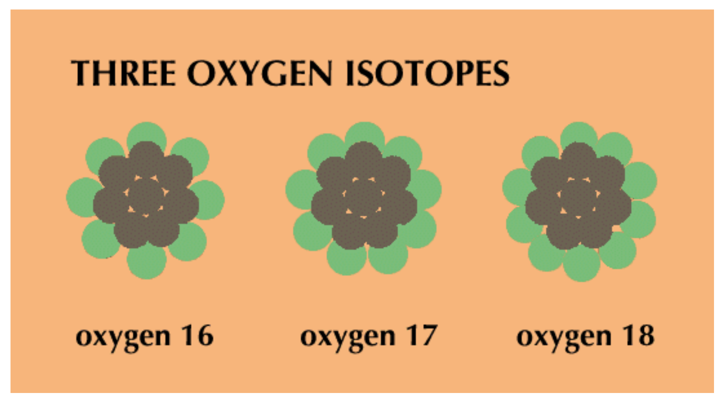
Perchlorate

ClO_4^-



^{35}Cl	^{36}Cl	^{37}Cl
34.96885 75.77%	t½=301,000 yrs	36.96590 24.23%
Stable	Cosmogenic/ anthropogenic	Stable



99.762%	0.038%	0.2%

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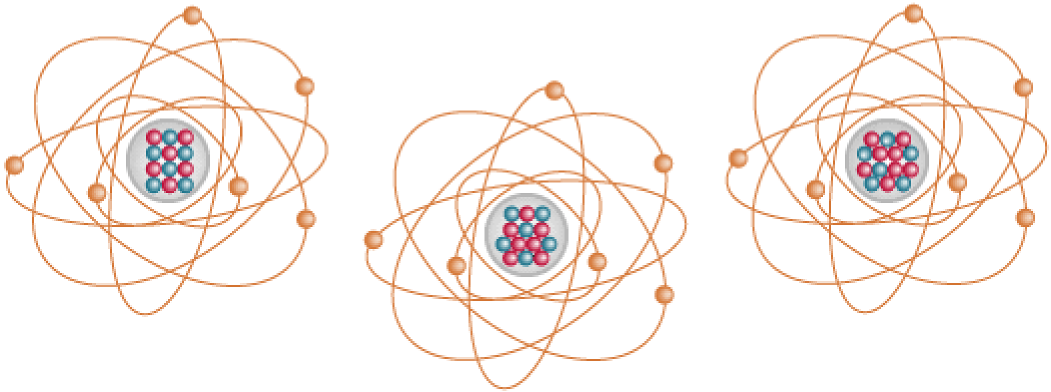
Principle of Isotope Analysis

- Can differentiate between natural and synthetic sources, or between different manufacturing sources, based on isotopic fingerprint



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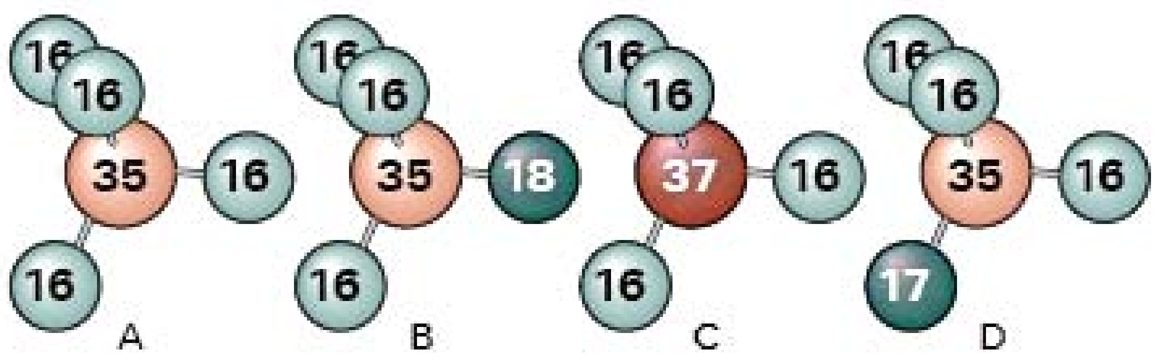
Perchlorate Isotopomers



A. Most common, incorporates the most abundant stable isotopes of chlorine and oxygen, ^{16}O and ^{35}Cl

B. Small percentage will include one or more ^{18}O isotopes

C. Some will have ^{37}Cl in place of ^{35}Cl

D. Perchlorate of atmospheric origin will occasionally incorporate the rare ^{17}O atom

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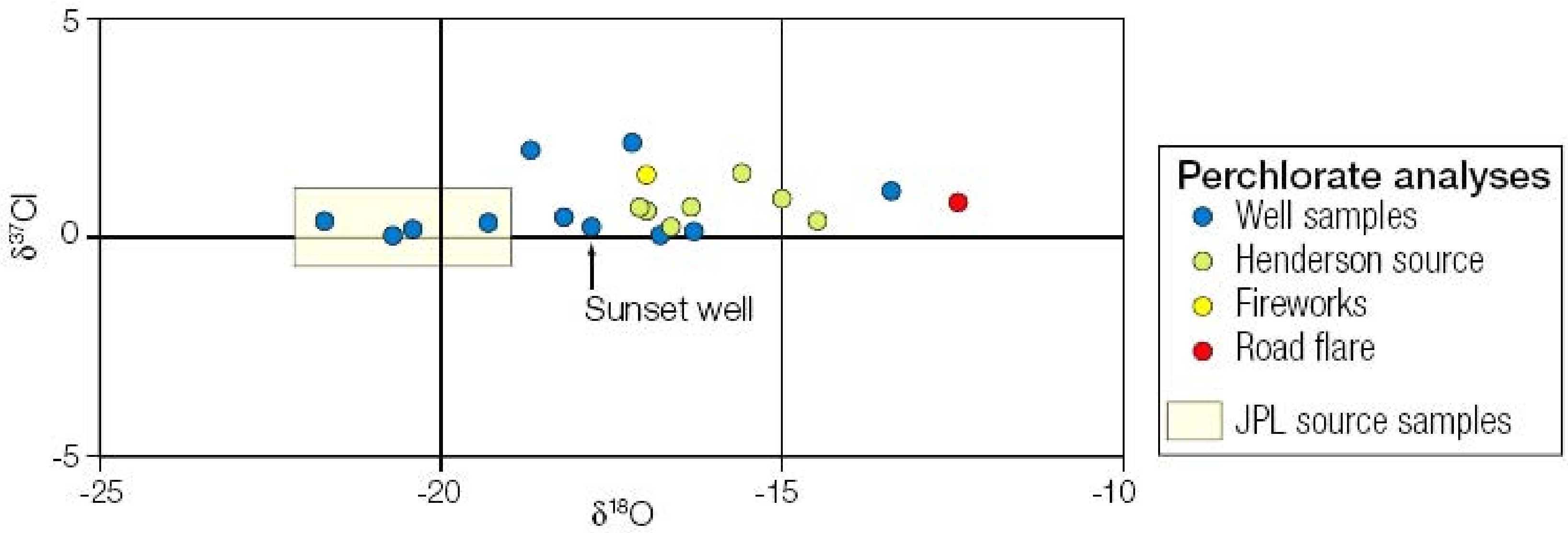

Results are interpreted by plotting isotope ratios ($^{18}O/^{16}O$ and $^{37}Cl/^{35}Cl$) against each other, and by contrasting the values obtained from different sources of perchlorate, different locations within the study area, and literature values.

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SUMMARY

- Perchlorate is an emerging contaminant that is receiving increasing publicity
- Exposures to perchlorate are in the process of being better characterized
- Treatment technologies are varied and are being funded and developed with unusual fervor

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Questions