



Perchlorate-Future Regulations and Treatment Alternatives

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Presentation Summary

- The Nature of the Beast
- Where are Perchlorates Found?
- Health Impacts: Why Should We be Concerned?
- Regulatory Response
- Treatment Strategies

The Nature of the Beast

Perchlorates??? I've Heard of Them

Common Inorganic Forms of Chlorine Compounds

Chemical Symbol	Name	No. of Oxygen Atoms	Chlorine Atom Valance
Cl ⁻	Chloride (ion)	0	-1
Cl ₂	Chlorine	0	0
OCl ⁻	Hypochlorite (ion)	1	+1
ClO ₂ ⁻	Chlorite (ion)	2	+3
ClO ₂	Chlorine dioxide	2	+4
ClO ₃ ⁻	Chlorate (ion)	3	+5
ClO ₄ ⁻	Perchlorate (ion)	4	+7 (most highly oxidized)

Common Inorganic Chlorine Compounds and Prevalence - 1



Chloride

NaCl (sodium chloride)



Chlorine

Cl₂ Elemental chlorine (gas)



Hypochlorite

NaOCl (sodium hypochlorite)

Common Inorganic Chlorine Compounds and Prevalence - 2

- Chlorite and Chlorine Dioxide
 - NaClO_2 (sodium chlorite) + Cl_2
 \longrightarrow Chlorine dioxide (disinfectant)
- Chlorate
 - NaClO_3 (sodium chlorate)
 - Dominant Decomposition Pathway of Sodium Hypochlorite
 - $3 \text{NaOCl} \rightleftharpoons \text{NaClO}_3 + 2 \text{NaCl}$



Industrial Uses of Perchlorates

- Strong Oxidizers
- Propellants
- Explosives



Properties of Perchlorate Ions

- Strong oxidant, but slow kinetics limits reactivity
- Non-volatile
- Highly soluble in water
- Non-complexing in nature
- Poor sorption properties
- Does not bio accumulate
- Persists in the environment

Where are Perchlorates Found?

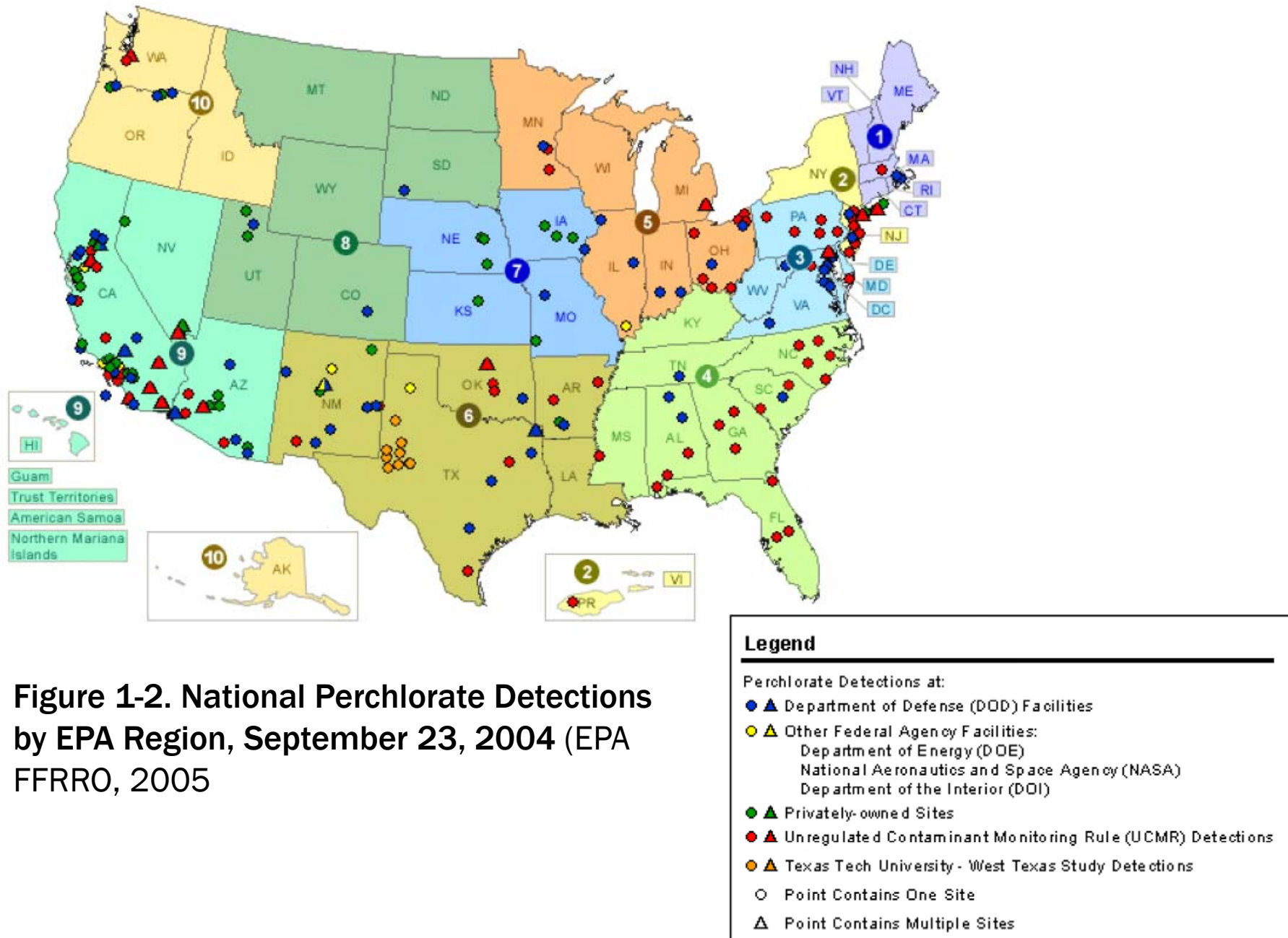


Figure 1-2. National Perchlorate Detections by EPA Region, September 23, 2004 (EPA FFRRO, 2005)

Presence of of Perchlorates

- Natural Occurrences
 - More common in arid regions
 - Phosphate minerals used for fertilizers
 - Occurs in the atmosphere and in photochemical oxidation of salts in soils (via UV, ozone, lightning)
- Other Occurrences
 - Can be found in sodium hypochlorite solutions
 - Possibly produced from ClO_3^- at elevated temperatures if heated carefully to avoid evolution of O_2
- Discovered on Surface of Mars
 - 2008 Phoenix Mission
 - UV radiation acting on chloride rich soils



Health Impacts: Why Should We be Concerned?

Numerous Health Impacts on Thyroid Function

- Interferes with iodine uptake (similar ionic radius)
- Reduces production of necessary thyroid hormones
- Resulting impacts
 - Metabolism
 - Mental functions
 - Development of fetuses and young children
- Perchlorates were used medicinally to treat hyperthyroidism
- Chronic oral reference dose is 0.0007 mg/kg body weight per day

Regulatory Response

EPA Position

- Currently not regulated
- Drivers for Regulatory Action
 - Known health effects
 - Substantial Likelihood of prevalence (detected in 4% of Public Water supplies)
 - Meaningful opportunity for health risk reduction
- Placed on Contaminant Candidate List (1998)
- Interim Health advisory of 15 µg/L (2009)
- Initial EPA proposal for public comment-Dec. 2013

Other State Regulations

- California
 - MCL for perchlorate established at 6 mg/L (2007)
 - Sampling reveals peak concentrations observed > 90 mg/L
- Massachusetts MCL established at 2 mg/L

Treatment Strategies

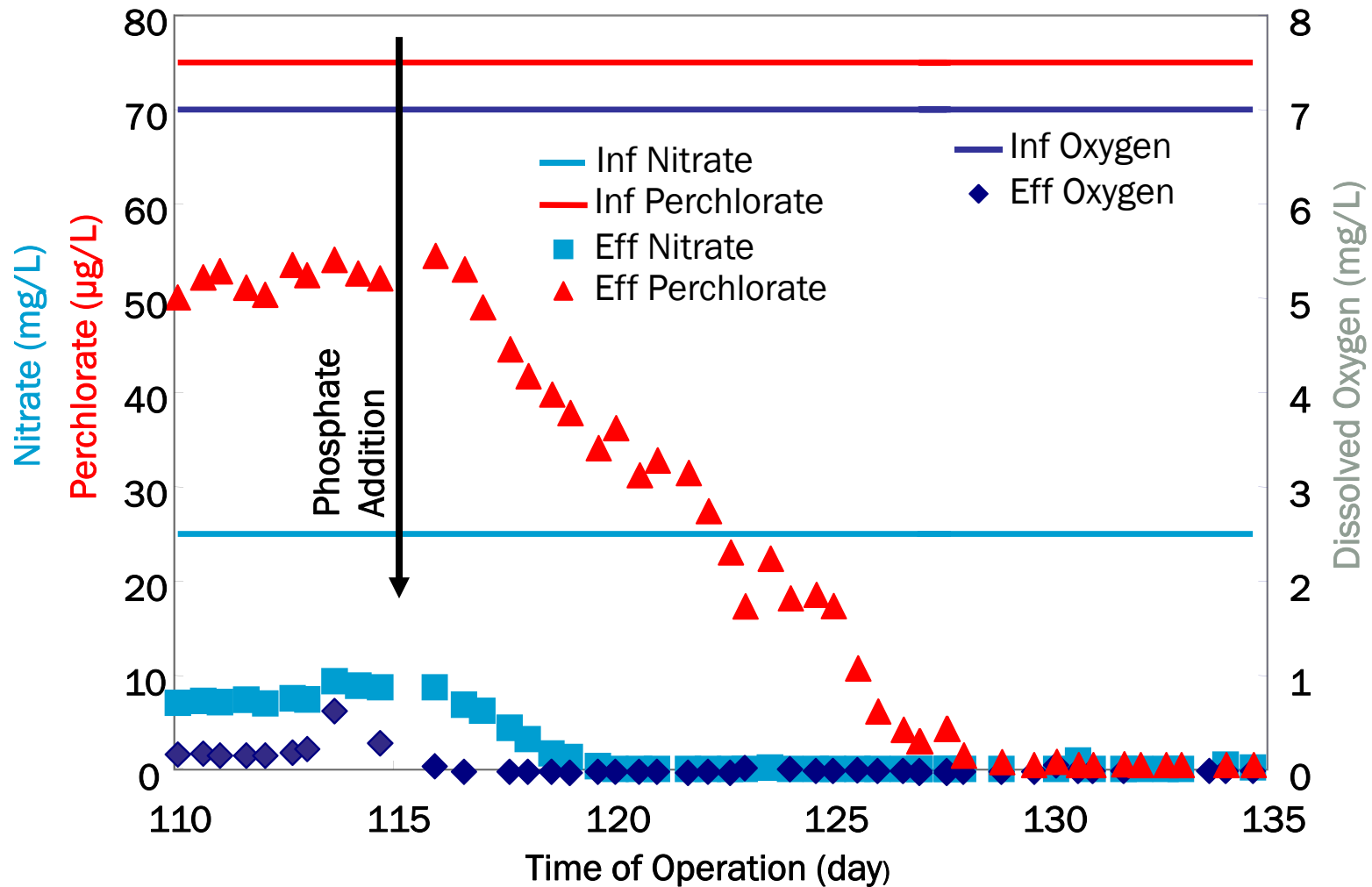
General Nature of Treatment Strategies

- *Ex Situ* Treatment (processed at a treatment plant)
- *In Situ* Treatment (typical in soil remediation)

***Ex Situ* Treatment Strategies-Established Methods**

- Selective Ion Exchange
 - Strong base, anion exchange resin
 - Regenerated with brine (7% effective) or FeCl_3/HCl (~100% effective)
 - Exchanges ClO_4^- with Cl^-
 - Most often recommended
- Biological reduction (will need electron donor, e.g. supplemental carbon source addition)
- Membrane filtration (RO or NF only)
- Granular Activated Carbon (with some media conditioning needed-quarternary amine)

Perchlorate and Nitrate Results: Bench-scale



***Ex Situ* Treatment Strategies-Novel Methods**

- Iron nanoparticles and elevated temperatures
- Hydrogen gas catalytic reactor
- Electrochemical Reduction Cell
 - Nickel or titanium cathode as reducing agent
- Capacitance Deionization
 - High surface area electrochemical cell
 - Promises to be cost effective
 - Flow through capacitor
 - In research phase
- Alum WTP Sludge Sorbent
 - Acts as a sorbent
 - Can Reduce ClO_4^- to Cl^-
 - Perhaps 65% to 75% removal with 24 hour contact time

In Situ Treatment

- Bioremediation (reduction)
- Phytoremediation
 - Vegetative treatment with French tarragon, cottonwood, willow
 - Mechanism not understood



Questions?

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