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Los Alamos National Laboratory Perchlorate Issues Update

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Executive Summary

Perchlorate Issue at Los Alamos National Laboratory

Perchlorate is utilized at the laboratory in two forms, perchlorate salts (of various forms but primarily magnesium, sodium, potassium and some ammonium) and perchloric acid ($HClO_4$). Perchlorates, because of their strong oxidizing potential, are currently the primary ingredient of explosives and propellants. Perchloric acid, because it is non-complexing and an excellent oxidant when heated, is used in actinide research.

Concern

In 1998, perchlorate was placed on the Environmental Protection Agency (EPA) Contaminant Candidate List for consideration for possible regulation. In 1999, EPA required drinking water monitoring for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). In 2001, •LANL's NPDES Permit requires perchlorate monitoring at Technical Area (TA) 50 Radioactive Liquid Waste Treatment Facility (RLLWTF) & TA-16 High Explosive Waste Treatment Facility (HEWTF). The state of New Mexico is proposing to add perchlorate to its list of toxic pollutants [groundwater and surface water] this year. The Laboratory already has a legacy problem with perchlorates in shallow, intermediate and deep groundwaters underlying the Lab. EPA's guidance range is 4-18 ppb (μg/l).

Current Operations Using Perchlorates

1. Dynamic Experimentation (DX) Division uses small amounts of perchlorate salts and perchloric acid in development of propellants. Liquid high explosive (HE) wastewater is sent to the High Explosives Waste Water Treatment Facility (HEWTF) at TA-16.
2. Actinide research using perchloric acid is conducted at TA-3, TA-48, and TA-59. Perchloric acid fuming or sample preparation is conducted only in fume hoods dedicated for this activity. Wastewater from these facilities goes to the Radioactive Liquid Waste Treatment Facility (RLWTF) at TA-50.

Past Operations Generated Legacy Waste

1. Wastewater and contaminated stormwater generated within the HE corridor (since the early 1940's) has been discharged into Pajarito Canyon, Water Canyon and Cañon de Valle, through a number of outfalls with no perchlorate treatment. Effluent samples at HEWTF show a range of perchlorate concentrations from 4 to 58 ppb.
2. Perchlorates in treated effluents, from actinide research, were discharged into Mortandad canyon for a period of approximately 40 years (ion exchange treatment added in 2002).

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Perchlorate levels ranging from 140 ppb (perched groundwater) to 400 ppb (core sample) have been detected.

3. Acid Canyon (tributary of Pueblo Canyon) received wastewater from actinide research from 1943 to 1951, and treated effluents containing residual radionuclides from 1951 to 1964. Perchlorates, at concentrations of about 2 to 4 ppb have been detected in water supply well, Otowi-1 (O-1), in Pueblo Canyon.
4. DP Canyon received effluent from actinide research (the plutonium processing facility at TA-21), from 1952 to 1986. Perchlorate concentrations, in the core samples, of 200 to 1000 ppb have been detected in wells drilled down gradient from TA-21.
5. Pajarito Canyon received wastewater from high explosives synthesis and testing operations (TA-9) from 1952 to 1997. In 2003, high explosives wastewater, from the Anchor East Site (TA-9), has been recently analyzed and revealed perchlorate concentrations of over 500 ppb.
6. Ten Site Canyon (tributary to Mortandad Canyon) received insufficiently treated wastewater from the Ten Site Wastewater Treatment Plant (TA-35) from 1951 to 1963.

Successes in Managing Perchlorate Compound Risks (including shock sensitivity and environmental releases)

1. In March of 2001, LANL completed the replacement of 720 filters contaminated with perchlorates and radionuclides, at the CMR facility. Since that time, perchloric acid fuming has been limited to one (1) dedicated fume hood, located in Wing 5. A wet scrubber is installed in this hood as a practical technique for eliminating deposition of perchlorate salts in the ductwork and air emissions.
2. Perchlorate fuming operations at TA-48 and TA-59 are now restricted to fume hoods dedicated for this activity. Remediation includes wash down of hoods and exhaust ductwork, with all wastewater sent to TA-50 for treatment. In addition, investigations are ongoing for the replacement of perchloric acid in some sample preparation procedures; one option under study is microwave digestion.
3. Installation of an ion exchange treatment system at the TA-50 RLWTF reduced perchlorate in the effluent to < 1 ppb.
4. An ion exchange was installed at the TA-16 HEWTF and became operational May 23, 2003.
5. New buildings for explosives research are being designed to eliminate waste streams Characterization of High Energetic Materials (CHEM) Laboratory Building: Case Study (LAUR-03-2317).

Immediate and Ongoing Actions

1. Continue surface water monitoring
2. Continue groundwater monitoring onsite at observation wells and offsite at LA & SF production wells.
3. Subsurface characterization of perchlorate contamination; extent, fate, and transport.
4. Analytical improvement. The EPA has approved one analytical method for the analysis of perchlorate with a detection limit of 4 ppb in natural waters. Lab and collaborator development of a low-level perchlorate analysis method by coupling liquid chromatography and tandem mass spectrometry technique (LC/MS/MS) is ongoing.
5. Identify points of treatment/control for legacy perchlorates.

6. Source reduction.
7. Replacement of effluent and sampling lines (where suspected radiological contamination exists) at the RLWTF.
8. Conduct public meeting to discuss known LANL perchlorate issues and collect public citizen concerns.

Long Term Needs

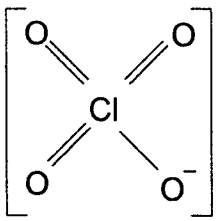
1. Establish up gradient/upstream surface and groundwater monitoring.
2. Develop an analysis for technological solutions/approaches.
3. Research and development for improved treatment options for legacy wastes.
4. Evaluation of where treatment is best applied.
5. Evaluation of perchlorate generation/formation in piping, ducts, filters, or sumps.
6. Evaluation of airborne discharges and their expected impact on subsequent surface contamination.
7. Coordination amongst perchlorate users to establish key facilities and appropriate controls.
8. Address treatment mandates that focus on contaminants on a species by species basis and anticipate future issues? Conduct additional characterization of historical perchlorate issues and the extent of contamination from releases.

Introduction

Perchlorate has become a national regulatory and public health concern due to the potential health effects of perchlorate in drinking water. In 1998, perchlorate was placed on the Environmental Protection Agency's (EPA) Contaminant Candidate List for consideration for possible regulation. In 1999, EPA required drinking water monitoring for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). EPA's guidance range is 4-18 ppb (parts per billion – ppb or μg/l). The state of New Mexico is proposing to add perchlorate to its list of toxic pollutants [groundwater and surface water] this year. Due to the extensive historical use and aqueous-and vapor-phase releases of perchlorate, or precursors to perchlorate, at Los Alamos National Laboratory (LANL) perchlorate is present in shallow, intermediate and deep ground waters underlying the Laboratory. The New Mexico Environmental Department/Oversight Bureau (NMED-OB), using an experimental LC/MS/MS method detected perchlorate at 0.5 ppb in one Technical Area 3 (TA-3) drinking water sample; this had not been confirmed by LANL sampling. In order to proactively address this problem, a team of experts from across the Laboratory has been pulled together to gather background information on perchlorate, the processes generating perchlorate waste streams, human health and environmental risks associated with perchlorate in the environment, technical options for elimination, and economic implications of any proposed plans and ideas. The team used a comprehensive approach to provide recommendations that may help eliminate future potential "problem" contaminants (e.g. other ions like perchlorate). Several internal and external organizations have already researched this issue and are providing technical solutions to the problem. Their research and recommendations are referenced at the end of this document

Perchlorate Structure and Nationwide Use

Perchlorate (ClO_4^-) is the soluble anion associated with the solid salts of ammonium, potassium, magnesium, and sodium perchlorate. Another common commercial form is perchloric acid ($HClO_4$).



Ammonium perchlorate (NH_4ClO_4) is manufactured as an oxygen-adding component in solid fuel propellant for rockets, missiles, explosives and fireworks. Solid rocket fuels typically consist of ammonium perchlorate (potassium perchlorate or sodium perchlorate may also be used), which serves as the oxidizer; aluminum, which serves as the fuel; a binder; and a plastic that serves to give the material its rigidity. Large-scale production of ammonium perchlorate began in the United States in the mid 1940's. Ammonium perchlorate has a limited shelf life, and must be periodically replaced in munitions and rockets, or in inventory. This has lead to the disposal of large volumes of the compound since the 1940's in Nevada, California, Utah, and likely other states. Examples of industrial sites contaminated with perchlorate are listed in Table 1. About 90% of perchlorate compounds produced by major U.S. manufacturers has been shipped as ammonium perchlorate for use as rocket fuel oxidizer.

Table 1. A Partial List of Characterized Perchlorate Contaminated Sites with Identified Co-Contaminants

Site	Contaminated Media	Other Identified Contaminants	Identified Perchlorate Impurities and Products
Aerojet Facility, Rancho Cordova, CA	Groundwater	Tichloroethylene (TCE), N-nitrosodimethylamine (NDMA), nitrate, sulfate	
Aerojet Facility, San Gabriel, CA	Groundwater	Nitrate, TCE	
Big Dalton Well Site, Los Angeles, CA	Groundwater	Nitrate, sulfate	
La Puente, CA	Groundwater	NDMA, 1,4-dioxane, sulfate, volatile organic compounds (VOCs)	
Confidential site	Groundwater	Nitrate	Chlorate
DoD site, WV	Groundwater	Nitrate, sulfate	
Edwards Air Force Base, CA	Groundwater	Nitrate, sulfate	
Henderson, NV	Groundwater	Sulfate, sodium, calcium, magnesium, nitrate, boron, hexavalent chromium	Chlorate, chloride
Lawrence Livermore National Laboratory, Site 300, Livermore, CA	Groundwater	VOCs, nitrate, explosive compounds	
Pueblo Chemical Depot, CO	Soil, Groundwater	HMX, RDX, nitrate	

As can be seen in Table 1, the most common co-contaminants at sites are nitrate and sulfate. Co-contaminants may be significant for treatment option considerations (interference) and also for use as tracers at contaminated sites.

Potassium perchlorate ($KClO_4$), until recently was used to treat hyperthyroidism resulting from Grave's disease, and is still used diagnostically to test thyroid hormone production in some clinical settings. In addition, potassium perchlorate is used in breathing equipment on Air National Guard aircraft and in naval emergency escape equipment. Other uses of perchlorate salts include in nuclear reactors and electronic tubes, as additives in lubricating oil, in tanning and finishing leather, as a fixer for fabrics and dyes, and in electroplating, aluminum refining, rubber manufacture, and production of paints and enamels. Potassium perchlorate is believed to be the original source for a fraction of the perchlorate contamination found in the U.S., however, most of the contamination appears to have come from the legal discharge decades ago of then unregulated waste effluents containing high levels of ammonium perchlorate.

Perchlorate originates as a contaminant in ground water and surface waters when the salts of ammonium, potassium, magnesium, or sodium dissociate in water, as shown for ammonium perchlorate in equation 1.

$$NH_4ClO_4(s) \xrightarrow{water} NH_4^+(aq) + ClO_4^-(aq) \quad (1)$$

Salts of perchlorate have different solubility in water, with potassium perchlorate being the least soluble (Table 2). In groundwater, the perchlorate ion is highly mobile, migrating faster than many other ground water contaminants. It is repelled by the predominantly negatively-charged subsurface minerals, precluding adsorption reactions that serve to retain other uncharged or positively-charged contaminants. It can persist in the environment for many decades under typical ground water and surface water conditions because of its resistance to reactions with other available constituents.

Table 2. Properties of Perchlorate Compounds

Properties	Ammonium Perchlorate (NH_4ClO_4)	Potassium Perchlorate ($KClO_4$)	Sodium Perchlorate ($NaClO_4$)	Perchloric Acid ($HClO_4$)
Chemical Abstract Service (CAS) #	7790-98-9	7778-74-7	7601-89-0	7601-90-3
Density/Specific Gravity	1.95 g/cm^3	2.53 g/cm^3	2.52 g/cm^3	1.67 g/cm^3
Solubility	200 g/L water @ 25°C	15 g/L water @ 25°C	2096 g/L water @ 25°C	Miscible in cold water
Sorption Capacity	Very low	Very low	Very low	Very low
Volatility	Nonvolatile	Nonvolatile	Nonvolatile	Volatile

Areas of natural occurrence of perchlorate are rare; however one natural source of solid perchlorate is found in potassium nitrate in Chile (Chile saltpeter), which may be used in chemical fertilizer originating from Chile. All types of nitrate products (nitric acid, etc.) were manufactured with Chilean Nitrate in years past. Today, it is mostly used for fertilizer. The United States Geological Survey (USGS) and the Air Force Research Laboratory have also found potassium perchlorate in samples of sylvite in New Mexico. Additional areas of natural occurrence of perchlorate have not been identified, but are speculated to exist, based on confirmed existence of several species of perchlorate-reducing microorganisms. In fact, perchlorate-reducers are increasingly predicted to be ubiquitous in nature, as they have been found in many locations, both contaminated and uncontaminated. The reason for their existence in uncontaminated soils is currently not known.

Releases of perchlorate to the environment have been reported in over 21 states nationwide. Many of the known releases are from sites that utilized one or more of the salts of perchlorate and include manufacturing sites, Department of Defense (DoD) sites, National Aeronautics and Space Administration (NASA) and associated sites, and industrial sites. The DoD sites associated with potential and known perchlorate releases are scattered across the United States (U.S.). These sites range from active military bases and ranges to some abandoned and

formally used sites reassigned to civilian use. NASA and some of its contractors use perchlorate in many operations. Industry also uses perchlorate compounds in the manufacture of various products and in processes to make products. Low levels of perchlorate contamination have also been found in association with certain nitrate plumes of agricultural origin. As further environmental testing for perchlorate is completed, more impacted areas may be found.

Contamination is extensive in California where perchlorate has been detected in 255 drinking water sources with 49 wells containing concentrations greater than 18 ppb. Two public water supply systems in New Mexico, Clovis and Deming, are reported to contain perchlorate concentrations greater than 4 ppb. At Clovis, a maximum perchlorate concentration of 5 ppb was reported and the Cannon Air Force Base has reported a perchlorate concentration of 24 ppb. Samples from the Deming water system were collected under the Safe Drinking Water (SDW) UCMR and perchlorate concentrations of 16 ppb were found. The sources of contamination at the Clovis and Deming sites have not been determined.

Health Issues

The toxicity of perchlorate is the subject of an active and ongoing research program. Perchlorate exerts its effect not by reacting with organs or cells, but by impeding another process. Cells in the thyroid gland (as well as the salivary and gastric glands), possess an iodide pump that brings iodide ions into the cell for subsequent generation of iodinated hormones. The pump discriminates among anions on the basis of size; consequently, perchlorate (and other large anions) interferes with this process by competing for uptake. However, unlike iodide, which is then incorporated into hormones, the perchlorate simply blocks iodide uptake. The result is lower intrathyroid-iodide and thus lower hormone output. As a result of decreased thyroid hormone production, the pituitary gland releases more thyroid-stimulating hormone (TSH), causing the thyroid to grow. The toxic effect of this perchlorate interaction is an active area of research, with most activity focusing on the above mentioned potential of perchlorate to hinder the synthesis of thyroid hormones and/or the subsequent consequences resulting from the decrease in thyroid hormones. In adults, the thyroid helps to regulate metabolism. In children, the thyroid plays a major role in proper development in addition to metabolism. Impairment of thyroid function in expectant mothers may impact the fetus and newborn and result in effects including changes in behavior, delayed development and decreased learning capability. Changes in thyroid hormone levels may also result in thyroid gland tumors.

In addition to the thyroid gland, perchlorate can also directly affect organs and tissues. The mouse mammary gland has a mechanism similar to the thyroid iodide pump that is inhibited by perchlorate; however, it is unclear whether this has any significance for human health. Much of what is known about perchlorate's effects on living organisms is derived from studies of acute toxicity over relatively short periods of time rather than chronic exposure to very low concentrations over a lifetime.

Applicable Drinking Water Regulations

Currently, no state or federal drinking water standard exists for perchlorate. EPA added perchlorate to its Contaminant Candidate List —a list of new contaminants being assessed for regulation—in 1998. In 1999, the EPA issued interim guidance for perchlorate recommending a

provisional action level in the 4-18 ppb range. During this same year the EPA also initiated a requirement for the monitoring of drinking water, for perchlorate, under the UCMR. Under the UCMR, all large public water systems and a representative sample of small public water systems are required to be monitored for perchlorate over the next two years to determine whether the public is being exposed to perchlorate in drinking water nationwide.

In March 2002, the EPA released the results of its long-awaited draft toxicity assessment for perchlorate. The draft assessment concludes that the potential human health risks of perchlorate exposure include (1) interference with iodide uptake and disruption of normal thyroid function, (2) impacts to the developing nervous system in the fetus and newborn, and (3) tumor formation. The draft assessment established a draft reference dose (RfD) for perchlorate in drinking water of 0.00003 mg/kg/day resulting in a derived Maximum Concentration Limit (MCL) of 1 ppb drinking water standard. The preliminary human health risk estimates established by the assessment are undergoing review and do not represent EPA policy at this time. In January 2003, the EPA reaffirmed their 4-18 ppb interim guidance as appropriate in the absence of a finalized risk benchmark for perchlorate. A final rule is not expected until 2004, at the earliest.

A 2002 perchlorate health effects assessment, conducted by the Oregon Health & Science University, Portland, OR, found EPA's proposed 1 ppb MCL standard to significantly understate how much perchlorate exposure is "safe". This analysis recommends a drinking water equivalent of 300 ppb as protective. Further information on this study is available at, http://ehpnet1.niehs.nih.gov/docs/2002/110p927-937greer/abstract.htm

Nationwide, many states have established action or advisory levels for perchlorate, but none has set enforceable standards. Current action/advisory levels range from 1 ppb in Maryland and Massachusetts, 4 ppb in California and Texas, 14 ppb in Arizona, to 18 ppb in Nevada. The State of New Mexico has proposed adding perchlorate to the Water Quality Control Commission Regulations as a toxic pollutant; toxic pollutants are not assigned a specific numerical limit or standard, but are risk-based contaminants (lifetime risk greater than one cancer per 100,000 exposed persons). A hearing on the adoption of perchlorate as toxic pollutant has been scheduled for June 2003 before the New Mexico Water Quality Control Commission.

Water Supply System Monitoring

Monitoring of the Los Alamos Water Supply System for perchlorate began in late 1997 following the discovery of perchlorate in California drinking water wells – two years prior to EPA guidance on testing requirements. Two rounds of sampling were conducted in 1997 and 1998 at the "entry points to the distribution system". All sample results in 1997 and 1998 were non-detect for perchlorate. All samples were analyzed using EPA Method 314 (Ion Chromatography). See Table 3.

Table 3. EPA Analytical Method 314 for Perchlorate

Analytical Method For Perchlorate		
Method	Method Detection Limit (ppb)	Reporting Limit/Practical Quantitation Limit (ppb)
Ion Chromatography (de ionized water)	1	NA
Ion Chromatography (natural water)	4	12

Beginning in 2000, many environmental water samples collected around LANL have been analyzed for perchlorate:

- All groundwater and many surface water samples collected at environmental monitoring stations;
- Samples from water supply wells operated by Los Alamos County, San Ildefonso Pueblo, and City of Santa Fe (2001); and
- Water samples from wells drilled for the Hydrogeologic Workplan.

In June 2000, a sample from water supply well Otowi-1 (O-1) was reported to contain 3.5 ppb perchlorate. In response, the Laboratory issued a press release regarding this discovery. Following the detection at O-1, the joint Laboratory-Los Alamos County Water Quality Steering Committee recommended monthly sampling of O-1. O-1 is a standby water supply well for Los Alamos County and the County is currently managing this well based on information provided by the LANL Water Quality Steering Committee.

Perchlorate was detected in 10 of the 14 samples collected from O-1 in 2000 at an average concentration of 2.48 ppb. Perchlorate was not detected in any of the other 11 water supply wells during 2000. All samples in 2000 were analyzed for perchlorate using EPA Method 314, Ion Chromatography.

Monthly monitoring and reporting to Los Alamos County for perchlorate was expanded in 2001 and 2002 to include water supply wells Pajarito Mesa–3 (PM-3) and PM-5, in addition to O-1. Also, semi-annual monitoring was instituted at the remaining nine water supply wells. During 2001 and 2002, perchlorate monitoring continued to confirm the presence of perchlorate in O-1 at concentrations between 2 ppb to 4 ppb. While estimated detections (<4 ppb) were reported at other water supply wells, none were repeatable and were attributed to deficiencies in the ion chromatography method; at concentrations between the method's reporting limit (12 ppb) and the detection limit (4 ppb) the ion chromatography method is imprecise due to interference by other ions in the sample matrix. Additional discussion on analytical methods is provided in the section, *Search for Lower Perchlorate Detection Limit.*

The Laboratory is continuing to conduct monthly monitoring at PM-3, PM-5, and O-1 and semiannual monitoring at the remaining nine water supply wells in 2003. Beginning in May

2003, water supply wells PM-1, PM-2, and PM-4 will be added to the monthly monitoring schedule.

In January 2003, the NMED-OB reported that a sample of tap water from TA-3 showed perchlorate at a concentration of 0.24 ppb. A follow-up sample showed perchlorate at a concentration of 0.5 ppb. Both samples were analyzed using a new, low-level analytical technique for perchlorate called liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS). The LC/MS/MS is an analytical method in development and has not been approved by the EPA for perchlorate analysis. It is discussed further in a later section.

Beginning in 2003, the NMED, Drinking Water Bureau, will begin monitoring the Los Alamos Water System for perchlorate under the SDW UCMR. Data collected under the UCMR provides the EPA with information on the occurrence of emerging contaminants and is used to support regulatory decision-making.

Detailed and complete water monitoring data can be found in the LANL Environmental Surveillance Reports, http://eshint.lanl.gov/publications.shtml#environmental.

Current Laboratory Perchlorate Use

Perchlorate is utilized at the laboratory in two forms, perchlorate salts (of various forms but primarily magnesium, sodium, potassium and some ammonium) and perchloric acid ($HClO_4$). Perchloric acid is used in actinide research because it is non-complexing and an excellent oxidant when heated.

Perchloric acid and actinide chemistry

The group of elements known as the actinides consists of the elements from actinium (element 89) to lawrencium (element 103), in the periodic table. All actinides are metals and all are radioactive. As a result, they dominate the study of nuclear chemistry. Fundamental understanding of actinides is needed to assess the nation's nuclear stockpile, help stem the clandestine proliferation of nuclear weapons, and to understand the implications of nuclear fuels' (such as enriched uranium) use and storage.

Stockpile stewardship, DOE's program for certifying the long-term safety and performance of the enduring stockpile without underground nuclear testing, has resulted in increased importance of assessing and predicting the long-term behavior of actinides. A major focus is on obtaining a better scientific understanding of the isotopes uranium-235 and, especially, plutonium-239; the two actinides of most interest to Los Alamos scientists.

Plutonium (Pu) is the most complex and perplexing element in the periodic table. The element's complexity stems in part from its mercurial nature. Depending on temperature, it assumes one of six different oxidation states, each with different density, volume and chemical properties. Virtually all plutonium is currently produced in a metallic state; as a consequence, initial solution preparation for research purposes involves dissolution of the metal. Because of its highly electropositive nature, plutonium metal is soluble in a number of mineral acids and plutonium ions in solution commonly exist in the (III), (IV), (V), and (VI) oxidation states, as Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_3^+, respectively. The oxidation state produced by dissolution of plutonium is

dependent on the acid employed and can be analytically determined by absorption spectrum. However, because perchloric acid tends to be non-complexing (spectra of perchloric acid solutions reflect plutonium ions containing only water molecules in the coordination sphere), and can sequentially oxidize plutonium, from oxidation state III through VI, by heating, it has been extensively used. In solutions containing more strongly complexing anions the spectra are generally different, complicating the interpretation of spectrometry results. The complexation tendencies of the more common anions were found to decrease in the order

$$F^- > NO_3^- > Cl^- > ClO_4^-$$

With perchloric acid, it is possible to prepare Pu(III), (IV), and (VI) solutions of greater than 99% purity, and Pu(V) solutions of 97 ± 3% purity.

Facilities and technical areas within the laboratory, with current perchloric acid chemical inventories include the CMR, TA-3; the Sigma Complex (Sigma building), TA-3; Radioactive Liquid Waste Treatment Facility (RLWTF), TA-50; Occupational Health, TA-59; Radiochemistry, TA-48; the Anchor East Site, TA-9; Health Research Lab, TA-43; and TA-46. See Table 4.

Table 4. LANL Technical Areas with Perchloric Acid Chemical Inventories

Technical Area	Building	Division	Group
TA-3	CMR	Chemistry	Actinide Analytical Chemistry (C-AAC)
TA-3	Sigma building	Materials Science and Technology	Materials Technology Metallurgy (MST-6) Structure/Property Relations (MST-8)
TA-9	0029	Dynamic Experimentation	Materials Dynamics (DX-2)
TA-43	0001	Bioscience	Langham Resource (B-2)
TA-46	217	Bioscience	Michelson Resource (B-4)
TA-48	0001	Chemistry	Isotope and Nuclear Chemistry (C-INC)
TA-48	0045	Chemistry	C-INC
TA-50	0001	Facilities and Waste Operations	Waste Facilities Management (FWO-WFM)
TA-59	0001	Chemistry	Actinide, Catalysis, and Separations Chemistry (C-ACS)

Ammonium perchlorate and explosives research

The Dynamic Experimentation (DX) Division is the Laboratory's primary experimental resource for high explosives research for maintaining a safe and reliable nuclear weapons stockpile in the absence of nuclear testing. DX Division personnel perform research, engineering, and experimentation on high explosives and dynamic processes essential to the success of the nation's Science-Based Stockpile Stewardship program. The division's stockpile management

responsibilities include the manufacture of production detonators for the stockpile and surveillance of stockpile detonators and energetic materials. The division operates and maintains a suite of explosives firing sites—both locally and at the Nevada Test Site—with state-of-the-art diagnostics that include world-class radiographic machines.

DX Division encompasses the following principal programs and facilities:

- AGEX I—hydrodynamic testing
- AGEX II—explosively driven pulsed-power physics and high-energy-density physics
- Detonator production
- High-explosives (HE) science
- Department of Defense Programs - advanced conventional munitions development
- PHERMEX—Pulsed High-Energy Radiographic Machine Emitting X-Rays
- DARHT—Dual-Axis Radiographic Hydrotest facility (under construction)
- U1a—Nevada Test Site facility for the underground testing of special nuclear materials

DX Division uses small amounts of perchlorate salts and perchloric acid to develop propellants. DX-2 is a group within the DX division at LANL concerned with all aspects of high explosives (HE) from cradle to grave. These aspects include chemistry, engineering, materials properties, and physics related to the synthesis, formulation, performance, and safety of explosives; monitoring and surveillance of explosives in the enduring nuclear stockpile; unique applications of explosives; and environmentally-conscious destruction/disposal of explosives and explosive devices. The two areas where perchlorate is used (in small amounts) are organic synthesis and propellants. The synthesis of new explosive compounds is the most chemical-intensive operation, involving an an almost unlimited number of small amounts of inorganic and organic chemicals. Most syntheses produce milligram quantities of new compounds. However, following testing, large quantities may be synthesized for use in pilot scale experiments. Larger quantities of chemicals and glassware are often needed for the preparation of precursors and intermediates in the synthesis process. Large fume hoods are required for this process.

Wastewater generated by DX is sent to the Engineering Sciences and Applications (ESA) High Explosives Waste Water Treatment Facility (HEWTF). An ion exchange installed at the TA-16 HEWTF (installed and operational as of May 23, 2003) provides treatment of liquid wastewater, contaminated with both HE and perchlorate, prior to discharge.

Technical areas within the laboratory, with current perchlorate (various) chemical inventories include the TA-3, 9, 35, 43, 46, 48, 50, 53, and 55. See Table 5.

Table 5. LANL Technical Areas with Current Perchlorate Salt (Various) Chemical Inventories

Technical Area	Building	Division	Group
TA-3	CMR	Chemistry	Actinide Analytical Chemistry (C-AAC)
TA-3	Sigma building	Materials Science and Technology	Materials Technology Metallurgy (MST-6) Electronic and Electrochemical

			Materials and Devices (MST-11)
TA-9	0021	Dynamic Experimentation	Materials Dynamics (DX-2)
TA-9	0029	Dynamic Experimentation	DX-2
TA-35	0085E	Bioscience	Szilard Resource (B-3)
TA-35	0085W	Chemistry	Applied Chemical Technologies (C-ACT)
TA-43	0001	Bioscience	Langham Resource (B-2)
TA-43	0001	Bioscience	McClintock Resource (B-1)
TA-43	0001	Materials Science and Technology	Superconductivity Technology Center
TA-46	0031, 0154, 0158	Chemistry	Physical Chemistry and Applied Spectroscopy (C-PCS)
TA-46	0041, 0154	Chemistry	Advanced Chemical Diagnostics and Instrumentation (C-ADI)
TA-46	0076	Chemistry	Actinide, Catalysis, and Separations Chemistry (C-ACS)
TA-46	0158	Bioscience	Michelson Resource (B-4)
TA-46	0250	Materials Science and Technology	Materials Integration Science Laboratory
TA-46	0250	Chemistry	C-ACT
TA-48	0001	Chemistry	Isotope and Nuclear Chemistry (C-INC)
TA-48	0001	Nuclear Materials Technology	Actinide Process Chemistry (NMT-2)
TA-48	0001	Chemistry	C-ACS
TA-48	0001	Chemistry	Division Office (C-DO)
TA-50	0001	Facilities and Waste Operations	Waste Facilities Management (FWO-WFM)
TA-53	0001	Physics	Neutron Science and Technology (P-23)
TA-53	0622	Los Alamos Neutron Science Center (LANSCE)	LANSCE-12
TA-55	0001	Nuclear Materials Technology	Actinide & Fuels Cycle Technologies (NMT-11)

Waste profile forms have identified perchlorate waste at the laboratory, which is packaged and transported to TA-54 for storage at Area L. For the fiscal years 2000 through 2002, the following table details the volume (in kilograms) of perchlorate containing waste disposed, by group. See Table 6.

Table 6. Perchlorate Waste Disposal

Group	FY 2000	FY 2001	FY 2002
B-DO			0.95
C-AAC			0.67
C-ACS		5.5	1.89
C-ACT		0.2	0.11
C-FM*		5499.5	35.8
C-SIC			0.91
DX-2	2.01	0.11	
E-ET	1.4	2.04	
ESH-5 (now HSR)		0.07	
FWO-SWO		2.04	
P-24		1.4	
MST-6	5.5	3.8	2.4
MST-7	5.9	0.6	0.2
MST-8	3.3		
MST-11	6.5	1.06	0.7
NMT-1	0.9		
NMT-7		0.57	5.8
Total	**25.51**	**5516.89**	**49.43**

*The FY 2001 and 2002 perchlorate waste generated by the Chemistry Division Facility Management Group (C-FM) was almost entirely contaminated ductwork, decon water, and duct wash down sludge from the perchlorate cleanup up at TA-48, building RC-1.

Successes in Managing Perchlorate Compound Risks (including shock sensitivity and environmental releases)

Replacement of HEPA Filters at CMR: Risk Reduced by Comprehensive Waste Characterization (LAUR-02-0339): The laboratory Chemistry and Metallurgy Research Facility (CMR) has been operating since 1952, providing actinide and analytical chemistry and materials characterization in support of stockpile surveillance, pit manufacturing, stockpile lifetime extension, and nuclear weapons certification. During this time, perchloric acid has been fumed as part of performing actinide chemistry at the CMR facility. This has resulted in the deposition of perchlorate in the ductwork of the facility's ventilation systems. Both the exhaust from glove boxes and fume hoods are discharged to a common duct that is filtered to remove airborne toxic and radioactive particulates before discharge. In March of 2001, LANL completed the replacement of 720 filters contaminated with perchlorate and radionuclides, at the CMR facility. Since that time, perchloric acid fuming has been limited to one (1) dedicated fume hood, located in Wing 5. A wet scrubber is installed in this hood as a practical technique for eliminating deposition of perchlorate salts in the ductwork and air emissions.

Perchlorate Fuming Operations at TA-48 and TA-59: Two buildings at TA-48 are used for actinide research, Radiochemistry 1 (RC-1) and RC-45. As was the case at the CMR facility, the RC-1 building also underwent perchlorate contamination cleanup of the ductwork beginning in 2001. Since that time a new Hazard Control Plan (HCP-CFM-010.2) was implemented for perchlorate work. Perchloric acid use is currently limited to approved, labeled hoods that exhaust to ductwork equipped with wash down systems. Wash down systems prevent the build up of perchlorate in the ductwork, but does not prevent the exhaust of perchlorate in the air stream. Hoods that are approved for perchloric fuming have labels stating "Perchloric acid fuming permitted. No organics permitted." Two types of wash downs are performed: hood wash downs and ductwork wash downs. The user performs the hood wash down following the fuming of perchloric acid in the hood. The Facility Coordinator performs the ductwork wash down following user hood wash downs (on the same day as perchloric acid fuming), and at least weekly (regardless of perchloric acid fuming) while the laboratories are in operational mode. Each hood and ductwork wash down is for a minimum of 10 minutes.

The facilities at RC-45 are currently rewriting HCP's and will specifically address perchlorate fuming in the new revisions. Currently, perchlorate fuming is handled under HCP-C-INC-004, and requires hood wash downs following use and routine wash downs of the facility exhaust ductwork, by the facility coordinator (note, at the time of this draft the schedule of the routine wash downs, by the facility coordinator, had not been specified). This facility processes approximately 1500 samples a year, and each sample requires 0.25 – 0.50 ml of perchloric acid.

Perchloric acid fuming has also been a required activity for sample preparation at TA-59. Historically, approximately 1 to 2 liters of perchloric acid were fumed a year. Two groups at TA-59 have conducted perchloric acid fuming for sample preparation in the past, Radiochemistry and Inorganic Analysis. Perchloric fuming of samples within the Inorganic Analysis team has been replaced by microwave digestion. The Radiochemistry team is currently evaluating alternative sample preparation methods also. One alternative method is high temperature muffling, to rid the samples of organics, and it would eliminate the use of perchlorate. Any perchlorate operations that currently occur are conducted in a dedicated fume hood with wash down procedures.

Wastewater from all of these facilities goes to the RLWTF at TA-50.

Testing Perchloric Acid Fume Scrubber at TA-59: The Isotope and Nuclear Chemistry Group (C-INC) are testing the performance of a perchloric acid fume scrubber. The use of fuming perchloric acid in chemistry operations is severely limited because of safety concerns about the buildup of potentially explosive perchlorate salts in fume hoods and ducts. Perchloric acid fuming operations are restricted to only a few approved hoods with wash down capability. Researchers from C-INC are testing an acid fume scrubber that removes the perchloric acid fumes before they enter the fume hoods and ductwork. The perchloric acid fumes pass through a water spray that captures the perchloric acid. The wastewater can then be disposed of normally or, if necessary, treated prior to disposal. The scrubber unit uses much less water than is presently required to wash down the fume hoods and ducts. The scrubber is portable and can be moved to wherever it is needed. Testing will take place at TA-59 and, if successful, the unit will be deployed at TA-48.

Perchlorate Reduction at TA-50 RLWTF (LAUR-01-6519): During the Spring of 2000, it came to the attention of the RLWTF management that the presence of perchlorate in the RLWTF effluent needed to be addressed. Typically, perchlorate concentrations in the RLWTF effluent were in the range of several hundred ppb. As a result, a perchlorate waste stream survey was performed to identify generators of perchlorate waste at LANL. Additionally, a best available treatment survey for perchlorate was performed. It was concluded from this survey that ion exchange would be the best option for the RLWTF waste stream. Pilot scale ion exchange tests were begun in September 2000 and continued until June 2001 to quantify the effectiveness of ion exchange removal of perchlorate and to identify the most effective ion exchange resin. Design and installation of the full-scale treatment system for the RLWTF effluent stream was completed in March 2002. Since March of 2002 the perchlorate in the effluent from the RLWTF has been less than 1 ppb.

Waste Minimization or Elimination Through Sustainable Building Design
The Characterization of High Energetic Materials (CHEM) Laboratory Building:
An NNSA Waste Stream Elimination Case Study (LAUR-03-2317): Los Alamos National Laboratory management (Associate Director for Operations) has requested an evaluation of the impact of eliminating waste streams on Laboratory operations. A case study has been developed using the CHEM Laboratory Building, which is being proposed as part of the DX Strategic Facility Plan. This case study was undertaken to ascertain if sustainable building design could significantly reduce or eliminate waste streams. In particular, perchlorate or HE found in DX-2's wastewater. The CHEM Laboratory building is projected to cost approximately $20 million and typical operations would be expected to produce about 14,000 gallons of HE wastewater a year. At present this wastewater is treated at the HEWTF when it meets their Waste Acceptance Criteria (WAC). However, cumulative experience shows that operations are subject to shifting boundary conditions that make wastewater treatment uncertain: operations change with missions, and new or more stringent regulatory requirements have been applied. This leaves Lab national security research and development programs at risk, and can result in the suspension or reduction of operations until a suitable alternative can be identified and implemented. The results of this study indicate that DX's ability to manage HE wastewater begins in the earliest stages of building design and that adding operational flexibility into the building design provides significant future benefits. For example, having exposed drain lines located in a partial basement and readily accessible allows for the easy hook up of appropriate treatment processes where the water can be reused and/or evaporated. It is expected that with such a flexible building design, the HE wastewater could be significantly reduced if not eliminated entirely. It is expected that the discounted lifecycle savings (50 year life expectancy) would be about $2.2 million by the elimination or reduction of this waste through flexible design. This savings has a payback time of approximately nine years. Lifecycle savings would come from cost avoidance (e.g. the digging up of contaminated or leaking pipes), waste management cost, the isolation of particular wastewater that may need special treatment (no disposal path), and assure compliance with increasingly stringent environmental regulations.

Permeable Reactive Barrier Feasibility – Mortandad Canyon
A field-scale permeable reactive barrier (PRB) was installed in Mortandad Canyon in the winter of 2002 at a site downstream from the discharge point of the RLWTF, a National Pollutant

Discharge Elimination System (NPDES) -permitted outfall. Alluvial groundwater in Mortandad Canyon is being treated using a Multi-Barrier technology that consists of four different cells of materials (scoria basalt, hydroxyapatite, cotton seed meal and pecan shells, and limestone) arranged as a PRB. Among the targeted contaminants are perchlorate, nitrate, and strontium-90. The perchlorate removal mechanism in the Multi-Barrier is through microbial reduction to harmless chloride ion. The Multi-Barrier uses one cell that provides biological activity sufficient to reduce perchlorate to chloride. This cell is made of inexpensive waste materials including cottonseed meal and pecan shells. Both cotton seed meal and pecan shells are capable of supporting the growth of a microbial biofilm that is highly effective at reducing both nitrate and perchlorate to non-detectable levels as the groundwater flows through the barrier. Strontium-90 is removed from groundwater through adsorption processes involving hydroxyapatite. This project is a field-scale demonstration of the Multi-Barrier system that has multiple sampling points at strategic locations in each cell, and at sampling stations upstream and downstream from the PRB.

This summer, data from the PRB will be collected, and a report of the findings will be available in the fall of 2003.

Potential Perchlorate Sites and Sources

In September 1999, the NMED, Hazardous and Radioactive Materials Bureau, asked the Laboratory to conduct a survey to identify potential perchlorate-related sites. The survey findings, submitted to the NMED in December 1999, identified two areas at the Laboratory that contain potential perchlorate-related sites: the HE Corridor, and Mortandad Canyon.

High-Explosives Corridor

Wastewater generated within the HE corridor (since the early 1940's) has been discharged into Pajarito Canyon, Water Canyon, and Cañon de Valle, prior to the installation of the HEWTF. As a result, perchlorate has been sampled at Fishladder seep (in Fishladder Drainage) and the Fishladder 'waterfall' at the confluence of the Fishladder Drainage and Cañon de Valle – have detected perchlorate concentrations of 17 ppb and 7 ppb respectively. Cañon de Valle ultimately drains into Water Canyon.

In addition, soils from firing and rocket sites have become contaminated from past experiments and burning within the HE corridor. Stormwater contacting this contaminated soil may be another source and major transport mechanism.

Mortandad Canyon

Perchlorate was present in alluvial groundwater in Mortandad Canyon at values up to 280 ppb in 2000. The alluvial groundwater is separated from the regional aquifer by about 900 ft. Cores from four wells in Mortandad Canyon show that pore water perchlorate concentrations in the vadose zone beneath the canyon floor average 300 to 400 ppb down to at least 400 ft. This indicates a considerable inventory of perchlorate beneath the canyon floor as a result of 40 years of effluent discharge. At monitoring well, MCOBT-4.4 groundwater was observed between depths of 492 and 532 ft. The perched groundwater was encountered in the Puye Formation and Cerro del Rio basalt. Perchlorate was detected in this perched groundwater between

concentrations of 140 and 180 ppb. These are the highest concentrations of perchlorate observed in perched groundwater at the laboratory.

Three nearby regional aquifer monitoring wells have not shown perchlorate contamination, though analysis of several samples has produced analytical results that are near or below the detection limit of 4 ppb. None of the five surrounding Los Alamos County water supply wells (O-4, PM-1, -3, -4, -5) have detectable perchlorate contamination.

The LANL Integrated Groundwater Protection Strategy Team is conducting extensive evaluation and study of Mortandad canyon. This team is calculating the drinking-water ingestion risk (in terms of probability of exceeding 1 ppb perchlorate) associated with perchlorate moving from the TA-50 discharge point (since 1963) and the TA-35 discharge point (since approximately 1954), through the canyon alluvium, vadose zone, regional water-supply aquifer, and into the capture-zone of water-supply wells. The results will be then interpreted via traditional quantitative decision analysis methods to identify and rank (according to relative risk reduction per dollar spent) alternative actions to reduce the impact of perchlorate. The Mortandad Canyon risk-based decision analysis will be complete in early June. The other major sources (below) will be similarly addressed throughout the summer and fall.

Other Perchlorate Site

Rio Grande Springs

The NMED-OB has reported discovery of perchlorate in samples from some springs along the Rio Grande. Numerous follow up samples have not confirmed these findings, which remain mired in questions over analytical accuracy near the method detection limit. Samples analyzed by one of our analytical laboratories prior to April 25, 2001 showed many false positives due to lack of all the anion removal steps required in the EPA analytical method. Removal of other anions present in water prevents matrix interference in the analysis. Thus many of the apparent detections indicated in LANL data are not bona fide perchlorate detections.

Specific information on potential sources of perchlorate at the Laboratory is presented below.

Active Effluent Sources

The Laboratory has two active outfalls in the current National Pollutant Discharge Elimination System (NPDES) permit. NPDES Outfall 051 (RLWTF) and outfall 05A055 (HEWTF).

***Radioactive Liquid Waste Treatment Facility (RLWTF) at TA-50* (Mortandad Canyon).**

In 2000 and 2001, the annual average concentration of perchlorate in the RLWTF's effluent was 254 ppb and 169 ppb, respectively. In March 2002, the RLWTF began operating an ion exchange treatment system to remove perchlorate from the facility's effluent. Routine monitoring of RLWTF effluent since treatment began shows no detectable concentrations of perchlorate. In response to perchlorate reduction in the RLWTF effluent, by November 2002, the concentration nearest the outfall had dropped to near the detection limit of 4 ppb and concentrations at other stations were decreasing slowly.

***High Explosives Wastewater Treatment Facility (HEWTF)* at TA-16** (Cañon de Valle). Elimination of 19 NPDES-permitted HE outfalls was completed in 1997. All water from HE operations is now collected and treated at the HEWTF, which discharges into Fish Ladder Drainage and ultimately Cañon de Valle. Analysis of holding tank and effluent samples at the HEWTF shows a range of perchlorate concentrations from 4 to 58 ppb. The primary perchlorate source has been tracked to a single contributing facility at TA-9, Anchor East Site. An ion exchange system was installed on May 23, 2003 and is currently operational.

Perchloric Acid Fuming, TA-48 and TA-59
The majority of perchlorate release is associated with operations requiring fuming of perchloric acid. It has been estimated that 70% of the perchloric acid used is discharged as gaseous effluent in fume hoods. These fume hoods have wash downs and the exhaust ducts are also washed down regularly. The remaining 30% is released as liquid effluent via the radioactive liquid waste drains, which are treated at the RLWTF. There is however, considerable uncertainty in the relative percentages of gaseous release versus liquid effluent release.

Programs that utilized these operations, in order of perchloric acid use, are the Weapons Test Program, Environmental Sample Analyses Programs, Miscellaneous Programs (generally short term programs), Iridium Anomalies Study, Rover Program, and Natural Analogs Program.

Potential Uncharacterized Source
Commercial perchlorate is prepared electrochemically, from treatment of aqueous chlorides with sufficient voltage to prepare adequate concentrations (typically several tens of percent by weight) of perchlorate (either as acid or salts). However it is possible to prepare perchlorate chemically and by other means, which may lead to the low concentrations of perchlorate being observed in systems where it has not been added. In general, any chlorine-containing species (e.g., hydrochloric acid, hypochlorites, chlorites, chlorates, and perhaps even some organic chlorides) may react with strong acids, oxidizing agents such as peroxides, ozone (whether naturally or artificially produced), ultraviolet light/air, etc. to produce small amounts of perchlorate on the order that can be detected by more sensitive chemical analysis. It must be noted that while perchlorate has been in use since the early 1800s, the technology to detect it at ppb levels has only existed in the last decade.

Since perchlorate is an environmentally (and chemically) stable species, it is important to understand its adventitious production to discriminate between so-called 'natural' or unintentional sources and that arising from perchlorate-contaminated waste. However, this has been difficult to determine, as the wastewater contamination is intermittent and sporadic, even sampling the same piping and sumps.

Inactive Effluent Sources - probable discharges of perchlorate

***TA-1, TA-45* (Acid Canyon and Pueblo Canyon).**
Acid Canyon, a small tributary of Pueblo Canyon, was the original disposal site for liquid wastes generated by research on nuclear materials for the World War II Manhattan Engineer District atomic bomb project at TA-1 (Los Alamos townsite). Acid Canyon received untreated radioactive industrial effluent from 1943 to 1951. The TA-45 treatment plant was completed in 1951, and from 1951 to 1964 the plant discharged treated effluents that contained residual

radionuclides into nearby Acid Canyon. Based on similarity of processes to TA-50 (including nuclear chemistry research), the effluents probably contained similar amounts of perchlorate.

As indicated previously, perchlorate is present in water supply well O-1 (Pueblo Canyon) at concentrations of about 2 to 4 ppb. Though these values are below the ion chromatography detection limit, results of numerous analyses are consistent enough to support the conclusion that perchlorate is present. Los Alamos County only uses this well as a stand-by supply.

***TA-21* (DP Canyon).**
An industrial liquid waste treatment plant that served the old plutonium processing facility at TA-21 discharged effluent containing radionuclides into DP Canyon, a tributary to Los Alamos Canyon, from 1952 to 1986. Based on similarity of processes to TA-50 (including nuclear chemistry research), the effluents probably contained similar amounts of perchlorate.

Recent evaluation of core from well # LADP-4, drilled down gradient of the former radioactive liquid effluent outfall at TA-21, revealed perchlorate concentrations of 200 to 1000 ppb. Rock core samples from this well were sampled to a depth of 800 ft. with the deepest perchlorate concentration observed at a depth of 280 ft. The regional aquifer in this area is at a depth of 1000 ft. These perchlorate concentrations indicate a residual foot print in the rock above the saturated zone, which warrants more evaluation. These concentrations are similar to those in the vadose zone beneath Mortandad Canyon.

There may be several buildings at TA-21, including those still standing, that had outfalls other than the sanitary sewage treatment plant. Further evaluation of the complete TA-21 situation is warranted.

***TA-9* (Pajarito Canyon).**
Since 1950, operations at Anchor East Site have discharged wastewater from high explosives synthesis and testing operations. The Anchor East Site, TA-9, was identified as a significant perchlorate contributor. A recent analysis of wastewater, from this facility, showed it contained over 500 ppb of perchlorate, which is used as an oxidizer in high explosives. While outfalls from these buildings were shut down by 1997, and wastewater is now hauled to the HEWTF, discharge from these outfalls entered upper Pajarito Canyon for the previous 45 years. This area warrants further evaluation.

TA-46, TA-48, TA-59 outfalls (Mortandad Canyon)
Nuclear (actinide) chemistry research has been ongoing at these faculties. Prior to the installation of the RLWTF, untreated radioactive industrial effluent was most likely discharged into the nearby Mortandad Canyon.

TA-35, and Ten Site Wastewater Treatment Plant (Mortandad Canyon and Ten Site Canyon)
Numerous accidental waste spills and intentional releases of waste materials occurred at TA-35. Experimentation with several radionuclides, especially plutonium and tritium, were conducted at TA-35 in the 1950s and 1960s. Waste liquids, generated by washing of hot cells used in TA-35-2, were stored in four 50,000 gallon concrete tanks (TA-35-10) to allow decay of the short-lived radionuclides. The wastewater was then discharged into Mortandad Canyon. The discovery that

other radionuclides with longer half-lives were also stored in the tanks, and were being concentrated in these wastes, necessitated construction of a wastewater treatment plant. From 1951 to 1963 this facility treated radioactive wastes produced by various reactor and hot cell experiments at TA-35. The wastewater treatment plant was constantly beset by problems, and inadvertent spills of insufficiently-treated wastewater into Ten Site Canyon (tributary to Mortandad Canyon) occurred frequently. The potential for perchlorate releases exist due to chemistry's, similar to actinide research, which may have been used.

Search for Lower Perchlorate Detection Limit

With potential State and/or Federal regulations setting discharge limits in the range of 1-18 ppb perchlorate, the accuracy and sensitivity of perchlorate detection methods is extremely important. The EPA has approved one analytical method for the analysis of perchlorate, Method 314 using Ion Chromatography. This method has a detection limit of 4 ppb in natural waters, with a practical quantitation limit (the lowest concentration that can be reliably determined) of 12 ppb. These detection limit values are based on several verification studies using natural groundwater. However, careful screening or cleanup steps are required with the current IC analytical method to lessen the occurrence of interference from other ions. Frequently these steps have not been used by all analytical laboratories, resulting in interference from other ions (inherent in real, environmental matrices), particularly sulfate, chloride, nitrate and carbonate, which produce random and highly-variable noise in the baseline at the known perchlorate retention time on the chromatogram. This can result in a significant background signal above zero and "false positives" in the range of 1 to 4 ppb. In addition, as mentioned previously, the potential for a drinking water standard below 4 ppb creates a need for an analytical method with a lower detection limit.

The Department of Energy's (DOE) National Nuclear Security Administration (NNSA) Albuquerque Operations Office Analytical Management Program (NNSA-AL AMP) is collaborating with LANL in evaluating a low-level perchlorate analysis method by coupling liquid chromatography (LC) and a tandem mass spectrometry (MS) technique (LC/MS/MS). The two MS steps serve as a confirmation for the presence and level of perchlorate. The first MS detects ClO_4^- and in the process strips one oxygen from the ion, the second MS then detects ClO_3^-, and the two concentrations must balance. In addition, because the chlorine atom exists in two forms, of different masses (75% as Cl^{35} and 25% as Cl^{37}), corroboration of the number and type of chlorine atoms detected by each MS ensures specificity for perchlorate analysis. EPA's Office of Water is also interested in the method. See Table 7.

Table 7. New Analytical Method for Perchlorate (Proposed)

Analytical Method For Perchlorate (Proposed)		
Method	Method Detection Limit (ppb) (proposed)	Reporting Limit/Practical Quantitation Limit (ppb) (proposed)
Liquid Chromatography/ Mass Spectrometry/Mass Spectrometry	0.05	0.15

The method works well across a range of natural water chemistry, but has suffered from problems with the internal standard. These problems have previously resulted in erroneously high analytical results and have plagued the perchlorate LC/MS/MS method from the beginning. General Engineering Laboratories (GEL) completed work on their internal standard in early April of 2003. Work on the analytical method was also completed by GEL and they were ready to receive samples by early April of 2003. GEL plans on submitting this updated analytical method to the EPA Office of Water (no date available).

A consensus was also reached at the January 9th meeting that NMED-OB, DOE, NNSA and LANL would jointly perform a performance evaluation of the LC/MS/MS method prior to the Laboratory employing it for low-level perchlorate analysis. Los Alamos area environmental water samples will be part of the evaluation. Design of the performance evaluation, with input from the NMED-OB, Los Alamos Department of Public Utilities, and the DOE has occurred. Also, 116 water samples have been collected (May 12 – 15, 2003) and submitted to GEL (May 29, 2003) with results are expected back to the LANL Environmental Surveillance Team, Risk Reduction and Environmental Stewardship (RRES) Division Water Quality & Hydrology (WQH) Group, by June 30, 2003. Following data validation and approvals from all of the entities involved, the data will be available for review.

Treatment

Treatment of perchlorate contamination in water is complicated because the perchlorate anion does not respond to typical water treatment technologies due to its fundamental physical and chemical nature. The perchlorate tetrahedron itself is structured such that the four oxygen atoms surround the central chlorine atom, effectively blocking reductants from directly attacking the chlorine. The perchlorate anion is soluble and very mobile in aqueous systems. It can persist in the environment for many decades under typical groundwater and surface water conditions because of its resistance to react with other available constituents. While perchlorate is thermodynamically a strong oxidizing agent, with the chlorine in the +7 oxidation state, the kinetics of reduction are generally very slow. Common reducing agents do not reduce perchlorate, and common cations do not coordinate with or precipitate it. Consequently, standard practices of water treatment will neither remove it physically nor destroy it chemically.

Perchlorate treatment technologies may be generally classified into categories of removal or reduction technologies. Physical removal processes include anion exchange, membrane filtration (including reverse osmosis and nanofiltration), and electrodialysis, which all require subsequent disposal of removed perchlorate. Reduction processes include biological reduction, chemical reduction, and electrochemical reduction. It must be noted that because of the newly emerging nature of perchlorate contamination and the associated cleanup concerns, that nearly all treatment techniques remain to be demonstrated for effectiveness. Further, little or no cost or performance data is available.

The optimum treatment technology for a given perchlorate occurrence may depend on several factors, including perchlorate concentration, the presence and concentration of co-contaminants, other water quality parameters (pH, alkalinity, natural organic matter (NOM), total dissolved

solids, metals, etc.), and geochemical parameters (nitrate, sulfate, chloride, dissolved oxygen, redox potential, etc.).

Physical Removal Processes, Treatment options identified

1. *Ion Exchange* – Ion exchange is a technology for the treatment of groundwater, surface water, and leachate. It works on perchlorate by capturing perchlorate anions on a positively charged resin and releasing a harmless chloride ion in its place. The exchange resin can be made from natural or synthetic organic, inorganic, or polymeric material that contain functional ionic groups.

   Ion exchange is energy-intensive due to the "pump and treat" nature of its operation. It requires frequent changing or regeneration of exchange resins and generates a problematic residual waste in the form of brine or contaminated resins that still contain the perchlorate. The secondary wastes generated during treatment would require additional treatment or disposal. It is possible that a treatment train using ion exchange and *ex situ* biological treatment of the secondary waste could be used to treat low levels of perchlorate contamination in surface waters and wetlands

   Private sector organizations have been successfully applying ion exchange for many years for different applications. This success has extended to continuous ion exchange units that have effectively demonstrated the ability to reduce perchlorate to below 4 ppb in remediation and drinking water applications.

   The DoD has been investigating the use of ion exchange to treat perchlorate-contaminated groundwater at Edwards Air Force Base, California. Edwards Air Force Base (AFB) will soon begin field-testing a new class of anion exchange resins in a conventional fixed-bed ion exchange system. Pilot-scale tests of the system were completed in June 2001 and were proven successful at treating contaminated groundwater.

   Capital and operational cost of ion exchange systems vary depending on a number of factors, such as discharge requirements, the volume of water to be treated, contaminant concentration, the presence of other contaminants, resin and regenerant utilization, brine disposal, and site-specific hydrological and geochemical conditions.

2. *Membrane Filtration* – Membrane filtration, reverse osmosis and nanofiltration, are established treatment technologies used for the removal of contaminants such as salts, disinfection by-product precursors, nitrates, and selected pesticides. While it is anticipated that these processes may be effective for the removal of perchlorate, there is little to no peer-reviewed data that demonstrates their applicability to perchlorate contamination at concentrations of 1000 ppb and lower. Influent perchlorate concentrations would have to be below 400 ppb to have permeate concentrations below 18 ppb. Two examples offered from Azita Yazdani, (President) & Fred Reinhard (VP/Senior Engineer) of Exergy Technologies Corporation are:

   - *Membrane Electrolysis (ME)* - large variety of recovery and maintenance applications of chemical process solutions, but also equipped with patented pending design, latest proprietary ion exchange membranes and electrodes.

- *Advance Reverse Osmosis (ARO)* - utilizes selected reverse osmosis membranes to allow process water/chemical recovery at elevated total dissolved solids concentrations and an expanded pH range from 0.5 to 13.

Also, treatment of the perchlorate-concentrated secondary stream will need to be addressed.

3. *Electrodialysis* – Electrodialysis systems separate ionic species from aqueous solutions using an applied direct current potential across ion-permeable and selective membranes. No known demonstration projects were found.

4. *Exergy Technologies Corporation*- This Company has technologies to address perchlorate as well as other organic issues. An example of a technology that is used to eliminate perchlorates in the wastewater is the Continuous Electrodeionization. This technology combines ion exchange/membrane/electrolysis technologies and utilizes unique proprietary ion exchange membranes and electrodes to replace conventional ion exchange systems in industrial recovery applications.

5. *Ultraviolet and Ozone Peroxide System* - This approach has the dual advantage of eliminating perchlorates and other organics from waste wastewater while conserving water usage. Hydrothermal and other wet oxidation technologies were evaluated for their efficacy in destroying these contaminants. Wet oxidation converts the organic materials present to carbon dioxide and water and the inorganic contaminants to their common salts (nitrates, chlorides, sulfates, etc.). After destruction is completed, the salts can be removed with standard deionization resins and recycled. Literature indicates that mixtures of ozone and hydrogen peroxide coupled with ultraviolet light offers the most effective treatment. A pilot project conducted at C-Division to test the efficacy of using an UV/Ozone/Peroxide treatment process indicated that it would destroy 95% of the contamination within a single pass.

Chemical/Biological Removal Processes, Treatment options identified

1. *Anaerobic Bioremediation* – Studies have shown that perchlorate can be successfully biodegraded to the chloride ion, but only under anaerobic conditions. The *in situ* (in place) anaerobic bioremediation of perchlorate is a promising technology in which naturally occurring microorganisms are used to reduce perchlorate to innocuous chloride upon addition of a carbon source. For *in situ* bioremediation to occur, an electron donor (i.e. carbon-source) is added to perchlorate-contaminated groundwater or soil. A variety of electron donors have been used to stimulate perchlorate reduction, including alcohols, organic acids, edible oils and some sugars. The carbon source stimulates aerobic microorganisms to remove oxygen and nitrate, resulting in redox conditions amenable to reduction of perchlorate *in situ*. However, *in situ* bioremediation requires careful consideration of environmental conditions, hydraulic flow, and residence time of the contaminated water in the underground reactive zone. Because perchlorate reduction only occurs in the absence of oxygen and nitrate, initial research into the use of *in situ* bioremediation as a means of treating perchlorate-contaminated groundwater has focused on developing and optimizing anaerobic bioremediation techniques.

More than 30 different strains of perchlorate-reducing microbes have been isolated from diverse environments. In this reductive process, bacteria utilize the perchlorate ion as a terminal electron acceptor. A carbon or hydrogen electron donor (e.g., acetate) is normally necessary to drive the reaction sequence for optimal remediation rate. It is now generally accepted that microbial reduction of perchlorate proceeds according to the following:

$$\underset{\text{(Perchlorate)}}{ClO_4^-} \rightarrow \underset{\text{(Chlorate)}}{ClO_3^-} \rightarrow \underset{\text{(Chlorite)}}{ClO_2^-} \rightarrow \underset{\text{(Hypochlorite)}}{ClO^-} \rightarrow \underset{\text{(Chloride)}}{Cl^-} + O_2$$

As can be seen, perchlorate is ultimately completely converted into chloride and oxygen through the anaerobic reduction process. The perchlorate-to-chlorate step is thought to be the rate-limiting step, being considerably slower than the other steps. Buildup of toxic intermediates, specifically chlorite, does not occur because the chlorite-to-chloride step proceeds at a rate on the order of 1000 times that of the accepted rate-limiting step.

Current approaches for the remediation of perchlorate-contaminated groundwater typically involve long-term pump-and-treat solutions. Comparison of cost estimates for *in situ* versus *ex situ* treatment for perchlorate plumes at several DoD field cases suggests that *in situ* bioremediation cost between 50 to 75 percent of *ex situ* treatment costs. The ability to jointly treat perchlorate and common co-contaminants such as nitrate and chlorinated solvents via *in situ* bioremediation will also increase cost savings.

Laboratory-, and pilot-scale studies of *in situ* anaerobic bioremediation for treating perchlorate-contaminated groundwater are ongoing. A summary of projects is shown in Table 8.

Table 8. Summary of *In Situ* Bioremediation Projects

Project Name	Location/Funding Source	Scale/Media	Status of Project
Bioreduction and Removal of Ammonium Perchlorate	Carbondale, IL / SERDP[1]	Lab/W	In-Progress
Bioremediation of Perchlorate	Lawrenceville, NJ / SERDP[1]	Lab/GW	Complete FY01
Bioremediation of Perchlorate-Impacted GW	Six SERDP[1] test sites; 1) Edwards Air Force Base, CA 2) DOD site, West Virginia 3) Rocket Manf., CA 4) Aerojet Superfund Site, CA 5) U.S. Navy, CA 6) Industrial Site, Nevada	Lab/Pilot GW	Complete FY01
Treatability Studies on GW from Henderson, NV	Panama City, FL / Kerr-McGee Chemical LLC	Lab/GW	Complete (2000)
Insoluble Organic Substrates (Edible Oils) for Degradation of	Edwards AFB, CA / AFCEE[2]	Pilot/GW	In Progress

Perchlorate			

[1] Strategic Environmental Research and Development Program (SERDP) – DoD's corporate environmental R&D program.
[2] Air Force Center for Environmental Excellence.

2. *Permeable Reactive Barriers* – The Permeable Reactive Barrier (PRB) is a groundwater cleanup technology that consists of a wall of reactive material installed in the path of a flowing contaminated groundwater plume to treat pollutants as they penetrate through the wall. The PRB contains materials that target specific contaminants and chemically and/or biologically treats them. As with any biological treatment system, PRBs require careful control of environmental conditions within the reactive zone to maintain the anaerobic conditions that encourage the bacteria to biodegrade the perchlorate. The regular addition of nutrients and electron donors may be necessary depending on the efficiency of the PRB system and the reactive material used.

   PRBs are increasingly being used to treat a variety of groundwater contaminants and are recognized as a cost-effective, passive remediation method.

   The DoD has successfully used PRBs to treat perchlorate at the Naval Weapons Industrial Reserve Plant in McGregor, Texas. The system is believed to represent the first full-scale *in situ* bioremediation of perchlorate. Pilot- and full-scale studies of PRBs for treating perchlorate-contaminated groundwater are ongoing. A summary of projects is shown in Table 9.

Table 9. Summary of Permeable Reactive Barrier Projects

Project Name	Location/Funding Source	Scale/Media	Status of Project
Insoluble Organic Substrates (Edible Oils) for Degradation of Perchlorate	Edwards AFB, CA / AFCEE[2]	Pilot/GW	In Progress
Permeable Reactive Barrier Feasibility	Los Alamos, NM / U.S. DOE, LANL	Pilot/GW	In Progress
In situ GW Remediation	McGregor, TX / U.S. Navy	Full Scale/GW	In Progress

3. *Phytoremediation* – Phytoremediation is a treatment technology that uses natural plant processes and microorganisms associated with the root system to remove, contain, or degrade environmental contaminants in soil, sediment, and water. There are several processes associated with phytoremediation. Depending on the contaminant to be treated and site-specific conditions, these processes may work together, with the entire plant acting as a single system to remove the contaminant, or they may work individually with certain processes having a greater influence on contaminant removal.

   Several recent studies have shown that plants are capable of taking up, and at least partially reducing perchlorate. Research funded by the Air Force Aeronautic Systems Center and the

US Army Operations and Support Command have confirmed the ability of phytoremediation to remove perchlorate from contaminated water and soils. The two most important phytoremediation processes for perchlorate involve the uptake and subsequent phytodegradation of the chemical in branches and leaves, and rhizodegradation. Phytodegradation uses naturally occurring plant enzymes to degrade contaminants within the plant tissues. Rhizodegradation, on the other hand, occurs in the soil surrounding plant roots. Natural substances released by the plant roots serve as substrates for the microorganisms present in the rhizoshpere and speed up contaminant degradation.

Pilot- studies of phytoremediation for treating perchlorate-contaminated groundwater are ongoing. Defensible data on cost and performance need to be developed. See Table 10.

Table 10. Summary of Phytoremediation Projects

Project Name	Location/Funding Source	Scale/ Media	Status of Project
Longhorn Army Ammunition Plant Phytoremediation – Greenhouse Testing	Karnack, TX / US Army Operations, US Air Force	Pilot/GW	In Progress
Phytoremediation By Native Salt cedar	Athens, GA / US Air Force, Wright Patterson AFB	Lab/GW, soil	Complete FY 2000
	Las Vegas, NV / U.S. EPA	Field /GW	Complete FY 2000

4. *Bioreactors* – Bioreactors are an *ex situ* form of biological treatment in which contaminated process wastewater or extracted groundwater is pumped into an above ground reactor vessel (bioreactor), and placed into direct contact with microorganisms. These microorganisms remove perchlorate by reducing it in the presence of a food source. Careful control of environmental conditions (pH, temperature, oxygen content, nutrient sources, etc.), hydraulic flow, and residence time of the contaminated water supply in the bioreactor is necessary to support the growth of microorganisms and ensure complete reduction of the perchlorate. Common system designs include fluidized bed reactors (FBR), continuous-stirred tank or suspended growth reactors, and fixed film or packed bed reactors.

   Despite widespread use of bioreactors in the treatment of municipal and industrial wastewater, only in the past decade have studies been performed to evaluate the effectiveness of bioreactors in treating contaminated groundwater. In addition, because it has been determined that perchlorate can be successfully reduced to the harmless chloride ion under anaerobic conditions; initial research into using bioreactors to treat perchlorate-contaminated water has focused on the development and optimization of anaerobic bioreactors.

   The Air Force Research Laboratory (AFRL) Materials and Manufacturing Directorate (Tyndall Air Force Base, Florida) has led the way in developing bioreactor systems to treat process wastewater containing very high levels of perchlorate. Since 1997, a bioreactor based on the AFRL design has been treating wastewater from rocket motor production and demilitarization operations at a defense contractor facility near Brigham City, Utah.

A large, full-scale FBR system has also been operating at a site in Rancho Cordova, CA, since 1998. This system was integrated into the sites overall groundwater extraction and treatment plant to remediate perchlorate contaminated groundwater.

The first DoD facility to install a functional bioreactor for treating perchlorate-contaminated groundwater was the former Longhorn Army Ammunition Plant (LHAAP) in Karnack, Texas. Past activities at this site led to the construction of a groundwater pump-and-treat system, in 1997, for the site's production and disposal areas. However, the groundwater treatment plant was designed to extract and treat metals and volatile organic compounds, not perchlorate. After assessing the cost and technical feasibility of alternative technologies, LHAAP opted for a bioreactor, specifically an FBR, as an add-on device to the existing groundwater treatment system.

Aerojet, a significant user of ammonium perchlorate, is developing a proprietary *ex situ* bioremediation system to remediate perchlorate-contaminated groundwater. Pilot-scale testing of the biological process is taking place at the San Gabriel Valley Superfund Site. The purpose of the test is to determine whether the bioreactor, if followed by filtration and other post-bioreactor treatment, could produce potable water. The test was completed in December 2000, and in April 2002 the California Department of Health Services accepted the technology for use in the production of drinking water (Phase 2 Treatability Study Report *Aerojet GET E/F Treatment Facility, Sacramento, CA, September 2001*). Additional information on this technology, including a report describing the pilot-scale test results, is available from EPA Region 9. Four full-scale bioreactors, in operation since 1998 at Aerojet's northern California facility, have consistently reduced perchlorate levels from about 2,500 ppb to non-detectable levels (< 4.0 ppb).

Interim Conclusions

1. As soon as the issue of perchlorate health effects was raised, LANL began monitoring and reporting sources and concentrations.
2. Since 2001, NPDES monitoring & reporting to EPA, DOE, & NMED for TA-50 RLWTF & TA-16 HEWTF
3. Active sources of perchlorate contamination have been identified, mediated and virtually eliminated.
4. Perchlorate reduction activities completed or underway at LANL include:
    a. Replacement of HEPA Filters at the CMR Facility.
    b. Ductwork replacement and cleanup at TA-48.
    c. Perchlorate fume hood and ductwork wash down procedures implemented at TA 48 and TA-59.
    d. Ion exchange installed at TA-50 RLWTF to remove perchlorate. Successfully decreased perchlorate in its effluent to <1 ppb.
    e. Ion exchange at TA-16 HEWTF to remove perchlorate completed May 23, 2003.
    f. Field-scale (feasibility study) installation of permeable reactive barrier in Mortandad Canyon.
5. Integration of activities related to measuring, monitoring and treatment is occurring.
6. Technical options for long-term mitigation of contamination are being identified and evaluated.

7. Improvement of the resolution of detection methods is in progress.

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Acronyms

AFB - Air Force Base
AFRL - Air Force Research Laboratory Materials and Manufacturing Directorate
AGEX I - Hydrodynamic testing
AGEX II - Explosively driven pulsed-power physics and high-energy-density physics
ARO - Advance Reverse Osmosis
B-1 - Bioscience Division McClintock Resource Group
B-2 - Bioscience Division Langham Resource Group
B-3 - Bioscience Division Szilard Resource Group
B-4 - Bioscience Division Michelson Resource Group
CAS - Chemical Abstract Service
C-DO - Chemistry Division
C-AAC - Chemistry Division Actinide Analytical Chemistry Group
C-ACS - Chemistry Division Actinide, Catalysis, and Separations Chemistry Group
C-ACT- Chemistry Division Applied Chemical Technologies
C-ADI - Chemistry Division Advanced Chemical Diagnostics and Instrumentation
C-INC - Chemistry Division Isotope and Nuclear Chemistry Group
C-PCS - Chemistry Division Physical Chemistry and Applied Spectroscopy
CHEM - Characterization High Energetic Materials Laboratory
CMR - Chemistry and Metallurgy Research Facility
DARHT - Dual-Axis Radiographic Hydrotest Facility
DOE-NNSA - Department of Energy National Nuclear Security Administration
DoD - Department of Defense
DoD-SERDP - Department of Defense Strategic Environmental Research and Development Program
DX-DO - Dynamic Experimentation Division
DX-2 - Dynamic Experimentation Division Materials Dynamics Group
EMRTC - Energetic Materials Research and Testing Center
EPA - Environmental Protection Agency
ESA - Engineering Sciences and Applications
FBR-Fluidized bed reactors
FWO-WFM - Facilities and Waste Operations Division Waste Facilities Management Group
GEL - General Engineering Laboratories
HCP - Hazardous Control Plan
HE - High Explosives
HEWTF - High Explosives Waste Water Treatment Facility
HSR - Health, Safety, and Radiation Protection (HSR) formerly ESH
Kg - Kilograms
LANSCE-12 - Los Alamos Neutron Science Center
LANL - Los Alamos National Laboratory
LAUR - Los Alamos unlimited releases
LC/MS/MS - Liquid chromatography and tandem mass spectrometry technique
LHAAP - Longhorn Army Ammunition Plant
MCL - Maximum Concentration Limit
ME - Membrane Electrolysis
MST-6 - Materials Science and Technology Division Materials Technology Metallurgy Group
MST-7 – Materials Science and Technology Division The Polymers and Coatings Group
MST-8 - Materials Science and Technology Division Structure/Property Relations Group
MST-11 - Materials Science and Technology Division Electronic and Electrochemical Materials and Devices
NASA - National Aeronautics and Space Administration
NDMA - N-Nitrosodimethylamine

NMED-OB - New Mexico Environmental Department/Oversight Bureau
NMT-2 – Nuclear Materials Technology Division Actinide Process Chemistry
NMT-7 – Nuclear Materials Technology Division Waste Management / Environmental Compliance
NMT-11- Nuclear Materials Technology Division Actinide & Fuels Cycle Technologies
NNSA-AL AMP - Department of Energy National Nuclear Security Administration Albuquerque Operations Office Analytical Management Program
NPDES - National Pollutant Discharge Elimination System
O - Otowi
P-23 - Physics Division Neutron Science and Technology Group
P-24 - Plasma Physics Group
PHERMEX - Pulsed High-Energy Radiographic Machine Emitting X-Rays
PM- Pajarito Mesa
ppb - Part per billion
PRB - Permeable Reactive Barrier
Pu - plutonium
RC - Radiochemistry
R&D - Research and Development
RfD - Draft reference dose
RLWTF - Radioactive Liquid Waste Treatment Facility
RRES-WQH - Risk Reduction and Environmental Stewardship Division Water Quality & Hydrology Group
SDW - Safe Drinking Water
TA - Technical Area
TCE - Trichloroethylene
Ula - Nevada Test Site facility for the underground testing of special nuclear materials
UCMR - Unregulated Contaminant Monitoring Rule
USGS - U.S. Geological Survey
VOCs - Volatile organic compounds
WAC - Waste Acceptance Criteria
TSH - Thyroid-stimulating hormone

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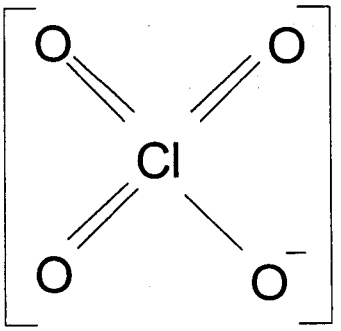
Los Alamos National Laboratory Perchlorate Issues



A Summary of Laboratory Information as of August 2003

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Los Alamos National Laboratory Perchlorate Issues

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Executive Summary

Perchlorate Issue at Los Alamos National Laboratory

Perchlorate is utilized at the laboratory in two forms, perchlorate salts (of various forms but primarily magnesium, sodium, potassium and some ammonium) and perchloric acid ($HClO_4$). Perchlorates, because of their strong oxidizing potential, are currently the primary ingredient of explosives and propellants. Perchloric acid, because it is non-complexing and an excellent oxidant when heated, is used in actinide research.

Concern

In 1998, perchlorate was placed on the Environmental Protection Agency (EPA) Contaminant Candidate List for consideration for possible regulation. In 1999, EPA required drinking water monitoring for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). In 2001, the Los Alamos National Laboratory (LANL) National Pollutant Discharge Elimination System (NPDES) permit began requiring perchlorate monitoring at Technical Area (TA) 50 Radioactive Liquid Waste Treatment Facility (RLWTF) and TA-16 High Explosive Waste Treatment Facility (HEWTF). In 2002, EPA released a draft toxicity assessment on perchlorate which proposes a 1 ppb (μg/l) drinking water standard.[10] In the absence of a finalized oral health risk benchmark for perchlorate, but in light of ongoing assessment activities by EPA, states and other interested parties, the EPA, in January of 2003, reaffirmed the 1999 interim guidance range of 4-18 ppb.[22] As of July 2003, the EPA declined to set regulatory limits for perchlorate and instead has decided to leave it up to each state to set safety standards. The state of New Mexico is proposing to add perchlorate to its list of toxic pollutants [groundwater and surface water] this year. The Laboratory already has a legacy problem with perchlorates in shallow, intermediate and deep groundwaters underlying the Lab.

Current Operations Using Perchlorates

1. Dynamic Experimentation (DX) Division uses small amounts of perchlorate salts and perchloric acid in research and development of explosives and propellants. Liquid high explosive (HE) wastewater is sent to the HEWTF at TA-16.
2. Actinide research using perchloric acid is conducted at TA-3, TA-48, and TA-59. Perchloric acid fuming or sample preparation is conducted only in fume hoods dedicated for this activity. Wastewater from these facilities goes to the RLWTF at TA-50.

Past Operations Generated Legacy Waste

1. Wastewater and contaminated stormwater generated within the HE corridor (since the early 1940's) has been discharged into Pajarito Canyon, Water Canyon and Cañon de Valle, through a number of outfalls with no perchlorate treatment. Effluent samples at HEWTF show a range of perchlorate concentrations from 4 to 58 ppb.
2. Perchlorates in treated effluents, from actinide research, were discharged into Mortandad canyon for a period of approximately 40 years (ion exchange treatment added in 2002). Perchlorate levels ranging from 140 ppb (perched groundwater) to 400 ppb (core sample) have been detected.
3. Acid Canyon (tributary of Pueblo Canyon) received wastewater from actinide research from 1943 to 1951, and treated effluents containing residual radionuclides from 1951 to 1964. Perchlorates, at concentrations of about 2 to 4 ppb have been detected in water supply well, Otowi-1 (O-1), in Pueblo Canyon.
4. DP Canyon received effluent from actinide research (the plutonium processing facility at TA-21), from 1952 to 1986. Perchlorate concentrations, in the core samples, of 200 to 1000 ppb have been detected in wells drilled down gradient from TA-21.
5. Pajarito Canyon received wastewater from high explosives synthesis and testing operations (TA-9) from 1952 to 1997. High explosives wastewater, from the Anchor East Site (TA-9), has been recently analyzed and revealed perchlorate concentrations of over 500 ppb.
6. Ten Site Canyon (tributary to Mortandad Canyon) received insufficiently treated wastewater from the Ten Site Wastewater Treatment Plant (TA-35) from 1951 to 1963.

Successes in Managing Perchlorate Compound Risks (including shock sensitivity and environmental releases)

1. In March of 2001, LANL completed the replacement of 720 filters contaminated with perchlorates and radionuclides, at the CMR facility. Since that time, perchloric acid fuming has been limited to one (1) dedicated fume hood, located in Wing 5. A wet scrubber is installed in this hood as a practical technique for eliminating deposition of perchlorate salts in the ductwork and air emissions.
2. Perchlorate fuming operations at TA-48 and TA-59 are now restricted to fume hoods dedicated for this activity. Remediation includes wash down of hoods and exhaust ductwork, with all wastewater sent to TA-50 for treatment. In addition, investigations are ongoing for the replacement of perchloric acid in some sample preparation procedures; one option under study is microwave digestion.
3. Installation of an ion exchange treatment system at the TA-50 RLWTF reduced perchlorate in the effluent to < 1 ppb.
4. In 1997, the elimination of 19 permitted HE outfalls was completed. All water from HE operations is now collected and treated at the TA-16 HEWTF.
5. An ion exchange was installed at the TA-16 HEWTF and became operational May 23, 2003.
6. New buildings for explosives research are being designed to eliminate waste streams Characterization of High Energetic Materials (CHEM) Laboratory Building: Case Study (LAUR-03-2317).

Immediate and Ongoing Actions

1. Continue surface water monitoring
2. Continue groundwater monitoring onsite at observation wells and offsite at Los Alamos and Santa Fe production wells.
3. Subsurface characterization of perchlorate contamination; extent, fate, and transport.
4. Analytical improvement. The EPA has approved one analytical method for the analysis of perchlorate with a detection limit of 4 ppb in natural waters. Lab and collaborator development of a low-level perchlorate analysis method by coupling liquid chromatography and tandem mass spectrometry technique (LC/MS/MS) is ongoing.
5. Identify points of treatment/control for legacy perchlorates.
6. Source reduction.
7. Replacement of effluent and sampling lines (where suspected radiological contamination exists) at the RLWTF.
8. Conduct public meeting to discuss known LANL perchlorate issues and collect public citizen concerns.

Long Term Needs

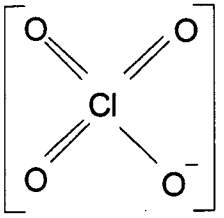
1. Establish upgradient/upstream surface and groundwater monitoring.
2. Develop an analysis for technological solutions/approaches.
3. Research and development for improved treatment options for legacy wastes.
4. Evaluation of where treatment is best applied.
5. Evaluation of perchlorate generation/formation in piping, ducts, filters, or sumps.
6. Evaluation of airborne discharges and their expected impact on subsequent surface contamination.
7. Coordination amongst perchlorate users to establish key facilities and appropriate controls.
8. Address treatment mandates that focus on contaminants on a species by species basis and anticipate future issues? Conduct additional characterization of historical perchlorate issues and the extent of contamination from releases.

Introduction

Perchlorate has become a national regulatory and public health concern due to the potential health effects of perchlorate in drinking water. In 1998, perchlorate was placed on the Environmental Protection Agency's (EPA) Contaminant Candidate List for consideration for possible regulation. In 1999, EPA required drinking water monitoring for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). EPA's guidance range is 4-18 ppb (parts per billion – ppb or μg/l). In 2002, EPA released its draft toxicity assessment, "Perchlorate Environmental Contamination Toxicological Review and Risk Characterization" and proposed a 1 ppb (μg/l) drinking water standard. In the absence of a finalized oral health risk benchmark for perchlorate, but in light of ongoing assessment activities by EPA, states and other interested parties, the EPA, in January of 2003, reaffirmed the 1999 interim guidance range of 4-18 ppb. As of July 2003, the EPA declined to set regulatory limits for perchlorate and instead has decided to leave it up to each state to set safety standards. The state of New Mexico is proposing to add perchlorate to its list of toxic pollutants [groundwater and surface water] this year. Due to the extensive historical use and aqueous-and vapor-phase releases of perchlorate, or precursors to perchlorate, at Los Alamos National Laboratory (LANL) perchlorate is present in shallow, intermediate and deep ground waters underlying the Laboratory. The New Mexico Environmental Department/Oversight Bureau (NMED-OB), using an experimental LC/MS/MS method detected perchlorate at 0.5 ppb in one Technical Area 3 (TA-3) drinking water sample; this had not been confirmed by LANL sampling. In order to proactively address this problem, a team of experts from across the Laboratory has been pulled together to gather background information on perchlorate, the processes generating perchlorate waste streams, human health and environmental risks associated with perchlorate in the environment, technical options for elimination, and economic implications of any proposed plans and ideas. The team used a comprehensive approach to provide recommendations that may help eliminate future potential "problem" contaminants (e.g. other ions like perchlorate). Several internal and external organizations have already researched this issue and are providing technical solutions to the problem. Their research and recommendations are referenced at the end of this document

Perchlorate Structure and Nationwide Use

Perchlorate (ClO_4^-) is the soluble anion associated with the solid salts of ammonium, potassium, magnesium, and sodium perchlorate. Another common commercial form is perchloric acid ($HClO_4$).



Ammonium perchlorate (NH_4ClO_4) is manufactured as an oxygen-adding component in solid fuel propellant for rockets, missiles, explosives and fireworks. Solid rocket fuels typically consist of ammonium perchlorate (potassium perchlorate or sodium perchlorate may also be used), which serves as the oxidizer; aluminum, which serves as the fuel; a binder; and a plastic that serves to give the material its rigidity. Large-scale production of ammonium perchlorate began in the United States in the mid 1940's. Ammonium perchlorate has a limited shelf life, and must be

periodically replaced in munitions and rockets, or in inventory. This has lead to the disposal of large volumes of the compound since the 1940's in Nevada, California, Utah, and likely other states. Examples of industrial sites contaminated with perchlorate are listed in Table 1. About 90% of perchlorate compounds produced by major U.S. manufacturers has been shipped as ammonium perchlorate for use as rocket fuel oxidizer.

Table 1. A Partial List of Characterized Perchlorate Contaminated Sites with Identified Co-Contaminants [11]

Site	Contaminated Media	Other Identified Contaminates	Identified Perchlorate Degradation Products
Aerojet Facility, Rancho Cordova, CA	Groundwater	Tichloroethylene (TCE), N-nitrosodimethylamine (NDMA), nitrate, sulfate	
Aerojet Facility, San Gabriel, CA	Groundwater	Nitrate, TCE	
Big Dalton Well Site, Los Angeles, CA	Groundwater	Nitrate, sulfate	
La Puente, CA	Groundwater	NDMA, 1,4-dioxane, sulfate, volatile organic compounds (VOCs)	
Confidential site	Groundwater	Nitrate	Chlorate
DoD site, WV	Groundwater	Nitrate, sulfate	
Edwards Air Force Base, CA	Groundwater	Nitrate, sulfate	
Henderson, NV	Groundwater	Sulfate, sodium, calcium, magnesium, nitrate, boron, hexavalent chromium	Chlorate, chloride
Lawrence Livermore National Laboratory, Site 300, Livermore, CA	Groundwater	VOCs, nitrate, explosive compounds	
Pueblo Chemical Depot, CO	Soil, Groundwater	HMX, RDX, nitrate	

As can be seen in Table 1, the most common co-contaminants at sites are nitrate and sulfate. Co-contaminants may be significant for treatment option considerations (interference) and also for use as tracers at contaminated sites.

Potassium perchlorate ($KClO_4$), until recently was used to treat hyperthyroidism resulting from Grave's disease, and is still used diagnostically to test thyroid hormone production in some clinical settings. In addition, potassium perchlorate is used in breathing equipment on Air National Guard aircraft and in naval emergency escape equipment. Other uses of perchlorate salts include in nuclear reactors and electronic tubes, as additives in lubricating oil, in tanning and finishing leather, as a fixer for fabrics and dyes, and in electroplating, aluminum refining, rubber manufacture, and production of paints and enamels. Potassium perchlorate is believed to be the original source for a fraction of the perchlorate contamination found in the U.S., however,

most of the contamination appears to have come from the legal discharge decades ago of then unregulated waste effluents containing high levels of ammonium perchlorate.

Perchlorate originates as a contaminant in ground water and surface waters when the salts of ammonium, potassium, magnesium, or sodium dissociate in water, as shown for ammonium perchlorate in equation 1.

$$NH_4ClO_4(s) \xrightarrow{water} NH_4^+(aq) + ClO_4^-(aq) \quad (1)$$

Salts of perchlorate have different solubility in water, with potassium perchlorate being the least soluble (Table 2). In groundwater, the perchlorate ion is highly mobile, migrating faster than many other ground water contaminants. It is repelled by the predominantly negatively-charged subsurface minerals, precluding adsorption reactions that serve to retain other uncharged or positively-charged contaminants. It can persist in the environment for many decades under typical ground water and surface water conditions because of its resistance to reactions with other available constituents.

Table 2. Properties of Perchlorate Compounds [11]

Properties	Ammonium Perchlorate (NH_4ClO_4)	Potassium Perchlorate ($KClO_4$)	Sodium Perchlorate ($NaClO_4$)	Perchloric Acid ($ClHO_4$)
Chemical Abstract Service (CAS) #	7790-98-9	7778-74-7	7601-89-0	7601-90-3
Density/Specific Gravity	1.95 g/cm^3	2.53 g/cm^3	2.52 g/cm^3	1.67 g/cm^3
Solubility	200 g/L water @ 25°C	15 g/L water @ 25°C	2096 g/L water @ 25°C	Miscible in cold water
Sorption Capacity	Very low	Very low	Very low	Very low
Volatility	Nonvolatile	Nonvolatile	Nonvolatile	Volatile

Areas of natural occurrence of perchlorate are rare; however one natural source of solid perchlorate is found in potassium nitrate in Chile (Chile saltpeter), which may be used in chemical fertilizer originating from Chile. All types of nitrate products (nitric acid, etc.) were manufactured with Chilean Nitrate in years past. Today, it is mostly used for fertilizer. The United States Geological Survey (USGS) and the Air Force Research Laboratory have also found potassium perchlorate in samples of sylvite in New Mexico. Additional areas of natural occurrence of perchlorate have not been identified, but are speculated to exist, based on confirmed existence of several species of perchlorate-reducing microorganisms. In fact, perchlorate-reducers are increasingly predicted to be ubiquitous in nature, as they have been found in many locations, both contaminated and uncontaminated. The reason for their existence in uncontaminated soils is currently not known.

Releases of perchlorate to the environment have been reported in over 21 states nationwide. Many of the known releases are from sites that utilized one or more of the salts of perchlorate and include manufacturing sites, Department of Defense (DoD) sites, National Aeronautics and Space Administration (NASA) and associated sites, and industrial sites. The DoD sites associated with potential and known perchlorate releases are scattered across the United States (U.S.). These sites range from active military bases and ranges to some abandoned and formally

used sites reassigned to civilian use. NASA and some of its contractors use perchlorate in many operations. Industry also uses perchlorate compounds in the manufacture of various products and in processes to make products. Low levels of perchlorate contamination have also been found in association with certain nitrate plumes of agricultural origin. As further environmental testing for perchlorate is completed, more impacted areas may be found.

Contamination is extensive in California where perchlorate has been detected in 255 drinking water sources with 49 wells containing concentrations greater than 18 ppb. Two public water supply systems in New Mexico, Clovis and Deming, are reported to contain perchlorate concentrations greater than 4 ppb. At Clovis, a maximum perchlorate concentration of 5 ppb was reported and the Cannon Air Force Base has reported a perchlorate concentration of 24 ppb. Samples from the Deming water system were collected under the Safe Drinking Water (SDW) UCMR and perchlorate concentrations of 16 ppb were found. The sources of contamination at the Clovis and Deming sites have not been determined.

Health Issues

Analytical technology advancements in the mid 1990's enabled the detection of perchlorate in water systems at levels as low as 4 ppb, through the use of an ion chromatographic method. It was this increase in detection capabilities that led to discovery of perchlorate in water supplies and concerns over what the presence meant for human health. The toxicity and human health risks continue to be the subject of active and ongoing research programs. In the EPA 2002 draft perchlorate toxicity assessment, oral uptake was noted as the major route of exposure, because perchlorate is readily absorbed from the intestinal tract, whereas exposure through skin contact (perchlorate does not pass readily through skin) and inhalation (vapor pressure of perchlorate salts and acids is low at room temperature) is expected to be negligible. Further, droplet size during showering likely would preclude inhalation of perchlorate-contaminated water as an aerosol.

Perchlorate exerts its effect not by reacting with organs or cells, but by impeding another process. Cells in the thyroid gland (as well as the salivary and gastric glands), possess an iodide pump that brings iodide ions into the cell for subsequent generation of iodinated hormones. The pump discriminates among anions on the basis of size; consequently, perchlorate (and other large anions) interferes with this process by competing for uptake. However, unlike iodide, which is then incorporated into hormones, the perchlorate simply blocks iodide uptake. The result is lower intrathyroid-iodide and thus lower hormone output. As a result of decreased thyroid hormone production, the pituitary gland releases more thyroid-stimulating hormone (TSH), causing the thyroid to grow. The toxic effect of this perchlorate interaction is an active area of research, with most activity focusing on the above mentioned potential of perchlorate to hinder the synthesis of thyroid hormones and/or the subsequent consequences resulting from the decrease in thyroid hormones. In adults, the thyroid helps to regulate metabolism. In children, the thyroid plays a major role in proper development in addition to metabolism. Impairment of thyroid function in expectant mothers may impact the fetus and newborn and result in effects including changes in behavior, delayed development and decreased learning capability. Changes in thyroid hormone levels may also result in thyroid gland tumors.

In addition to the thyroid gland, perchlorate can also directly affect organs and tissues. The mouse mammary gland has a mechanism similar to the thyroid iodide pump that is inhibited by

perchlorate; however, it is unclear whether this has any significance for human health. Much of what is known about perchlorate's effects on living organisms is derived from studies of acute toxicity over relatively short periods of time rather than chronic exposure to very low concentrations over a lifetime.

Applicable Drinking Water Regulations

Currently, no state or federal drinking water standard exists for perchlorate. EPA added perchlorate to its Contaminant Candidate List —a list of new contaminants being assessed for regulation—in 1998. In 1999, the EPA issued interim guidance for perchlorate recommending a provisional action level in the 4-18 ppb range. During this same year the EPA also initiated a requirement for the monitoring of drinking water, for perchlorate, under the UCMR. Under the UCMR, all large public water systems and a representative sample of small public water systems are required to be monitored for perchlorate over the next two years to determine whether the public is being exposed to perchlorate in drinking water nationwide.

In March 2002, the EPA released the results of its long-awaited draft toxicity assessment for perchlorate. The draft assessment concludes that the potential human health risks of perchlorate exposure include (1) interference with iodide uptake and disruption of normal thyroid function, (2) impacts to the developing nervous system in the fetus and newborn, and (3) tumor formation. The draft assessment established a draft reference dose (RfD) for perchlorate in drinking water of 0.00003 mg/kg/day resulting in a derived Maximum Concentration Limit (MCL) of 1 ppb drinking water standard. A 2002 perchlorate health effects assessment, conducted by the Oregon Health & Science University, Portland, OR, found EPA's proposed 1 ppb MCL standard to significantly understate how much perchlorate exposure is "safe". This analysis recommends a drinking water equivalent of 300 ppb as protective (full report available at, http://ehpnet1.niehs.nih.gov/docs/2002/110p927-937greer/abstract.htm). Human oral health risk assessments are ongoing, including an EPA request to the National Academy of Sciences to study the perchlorate issue. In the absence of a finalized risk benchmark for perchlorate, the EPA, in January 2003, reaffirmed their 4-18 ppb interim guidance range. Shortly thereafter, in July 2003, the EPA issued a statement declining to set perchlorate regulatory limits for the foreseeable future. Instead the EPA decided to leave it up to each state to set safety standards.

Nationwide, many states have established action or advisory levels for perchlorate, but none has set enforceable standards. Current action/advisory levels range from 1 ppb in Maryland and Massachusetts, 4 ppb in California and Texas, 14 ppb in Arizona, to 18 ppb in Nevada. The State of New Mexico has proposed adding perchlorate to the Water Quality Control Commission Regulations as a toxic pollutant; toxic pollutants are not assigned a specific numerical limit or standard, but are risk-based contaminants (lifetime risk greater than one cancer per 100,000 exposed persons). A hearing on the adoption of perchlorate as toxic pollutant has been scheduled for September 2003 before the New Mexico Water Quality Control Commission.

Water Supply System Monitoring

Monitoring of the Los Alamos Water Supply System for perchlorate began in late 1997 following the discovery of perchlorate in California drinking water wells – two years prior to EPA guidance on testing requirements. Two rounds of sampling were conducted in 1997 and 1998 at the "entry points to the distribution system". All sample results in 1997 and 1998 were

non-detect for perchlorate. All samples were analyzed using EPA Method 314 (Ion Chromatography). See Table 3.

Table 3. EPA Analytical Method 314 for Perchlorate

Analytical Method For Perchlorate		
Method	Method Detection Limit (ppb)	Reporting Limit/Practical Quantitation Limit (ppb)
Ion Chromatography (de ionized water)	1	NA
Ion Chromatography (natural water)	4	12

Beginning in 2000, many environmental water samples collected around LANL have been analyzed for perchlorate:

- All groundwater and many surface water samples collected at environmental monitoring stations;
- Samples from water supply wells operated by Los Alamos County, San Ildefonso Pueblo, and City of Santa Fe (2001); and
- Water samples from wells drilled for the Hydrogeologic Workplan.

In June 2000, a sample from water supply well Otowi-1 (O-1) was reported to contain 3.5 ppb perchlorate. In response, the Laboratory issued a press release regarding this discovery. Following the detection at O-1, the joint Laboratory-Los Alamos County Water Quality Steering Committee recommended monthly sampling of O-1. O-1 is a standby water supply well for Los Alamos County and the County is currently managing this well based on information provided by the LANL Water Quality Steering Committee.

Perchlorate was detected in 10 of the 14 samples collected from O-1 in 2000 at an average concentration of 2.48 ppb. Perchlorate was not detected in any of the other 11 water supply wells during 2000. All samples in 2000 were analyzed for perchlorate using EPA Method 314, Ion Chromatography.

Monthly monitoring and reporting to Los Alamos County for perchlorate was expanded in 2001 and 2002 to include water supply wells Pajarito Mesa–3 (PM-3) and PM-5, in addition to O-1. Also, semi-annual monitoring was instituted at the remaining nine water supply wells. During 2001 and 2002, perchlorate monitoring continued to confirm the presence of perchlorate in O-1 at concentrations between 2 ppb to 4 ppb. While estimated detections (<4 ppb) were reported at other water supply wells, none were repeatable and were attributed to deficiencies in the ion chromatography method; at concentrations between the method's reporting limit (12 ppb) and the detection limit (4 ppb) the ion chromatography method is imprecise due to interference by other ions in the sample matrix. Additional discussion on analytical methods is provided in the section, *Search for Lower Perchlorate Detection Limit.*

The Laboratory is continuing to conduct monthly monitoring at PM-3, PM-5, and O-1 and semiannual monitoring at the remaining nine water supply wells in 2003. Beginning in May 2003, water supply wells PM-1, PM-2, and PM-4 will be added to the monthly monitoring schedule.

In January 2003, the NMED-OB reported that a sample of tap water from TA-3 showed perchlorate at a concentration of 0.24 ppb. A follow-up sample showed perchlorate at a concentration of 0.5 ppb. Both samples were analyzed using a new, low-level analytical technique for perchlorate called liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS). The LC/MS/MS is an analytical method in development and has not been approved by the EPA for perchlorate analysis. It is discussed further in a later section.

Beginning in 2003, the NMED, Drinking Water Bureau, will begin monitoring the Los Alamos Water System for perchlorate under the SDW UCMR. Data collected under the UCMR provides the EPA with information on the occurrence of emerging contaminants and is used to support regulatory decision-making.

Detailed and complete water monitoring data can be found in the LANL Environmental Surveillance Reports, http://eshint.lanl.gov/publications.shtml#environmental.

Current Laboratory Perchlorate Use

Perchlorate is utilized at the laboratory in two forms, perchlorate salts (of various forms but primarily magnesium, sodium, potassium and some ammonium) and perchloric acid ($HClO_4$). Perchloric acid is used in actinide research because it is non-complexing and an excellent oxidant when heated.

Perchloric acid and actinide chemistry

The group of elements known as the actinides consists of the elements from actinium (element 89) to lawrencium (element 103), in the periodic table. All actinides are metals and all are radioactive. As a result, they dominate the study of nuclear chemistry. Fundamental understanding of actinides is needed to assess the nation's nuclear stockpile, help stem the clandestine proliferation of nuclear weapons, and to understand the implications of nuclear fuels' (such as enriched uranium) use and storage.

Stockpile stewardship, DOE's program for certifying the long-term safety and performance of the enduring stockpile without underground nuclear testing, has resulted in increased importance of assessing and predicting the long-term behavior of actinides. A major focus is on obtaining a better scientific understanding of the isotopes uranium-235 and, especially, plutonium-239; the two actinides of most interest to Los Alamos scientists.

Plutonium (Pu) is the most complex and perplexing element in the periodic table. The element's complexity stems in part from its mercurial nature. Depending on temperature, it assumes one of six different oxidation states (plutonium ions in solution exist in four different oxidation states), each with different density, volume and chemical properties. Virtually all plutonium is currently used in a metallic state; as a consequence, initial solution preparation for research purposes involves dissolution of the metal. Because of its highly electropositive nature, plutonium metal

is soluble in a number of mineral acids and plutonium ions in solution commonly exist in the (III), (IV), (V), and (VI) oxidation states, as Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_3^+, respectively. The oxidation state produced by dissolution of plutonium is dependent on the acid employed and can be analytically determined by absorption spectrum. However, because perchloric acid tends to be non-complexing (spectra of perchloric acid solutions reflect plutonium ions containing only water molecules in the coordination sphere), and can sequentially oxidize plutonium, from oxidation state III through VI, by heating, it has been extensively used. In solutions containing more strongly complexing anions the spectra are generally different, complicating the interpretation of spectrometry results. The complexation tendencies of the more common anions were found to decrease in the order

$$F^- > NO_3^- > Cl^- > ClO_4^-$$

With perchloric acid, it is possible to prepare Pu(III), (IV), and (VI) solutions of greater than 99% purity, and Pu(V) solutions of 97 ± 3% purity.

Facilities and technical areas within the laboratory, with current perchloric acid chemical inventories include the CMR, TA-3; the Sigma Complex (Sigma building), TA-3; Radioactive Liquid Waste Treatment Facility (RLWTF), TA-50; Occupational Health, TA-59; Radiochemistry, TA-48; the Anchor East Site, TA-9; Health Research Lab, TA-43; and TA-46. See Table 4.

Table 4. LANL Technical Areas with Perchloric Acid Chemical Inventories

Technical Area	Building	Division	Group
TA-3	CMR	Chemistry	Actinide Analytical Chemistry (C-AAC)
TA-3	Sigma building	Materials Science and Technology	Materials Technology Metallurgy (MST-6) Structure/Property Relations (MST-8)
TA-9	0029	Dynamic Experimentation	Materials Dynamics (DX-2)
TA-43	0001	Bioscience	Langham Resource (B-2)
TA-46	217	Bioscience	Michelson Resource (B-4)
TA-48	0001	Chemistry	Isotope and Nuclear Chemistry (C-INC)
TA-48	0045	Chemistry	C-INC
TA-50	0001	Facilities and Waste Operations	Waste Facilities Management (FWO-WFM)
TA-59	0001	Chemistry	Analytical Chemistry Sciences (C-ACS)

Ammonium perchlorate and explosives research

The Dynamic Experimentation (DX) Division is the Laboratory's primary experimental resource for high explosives research for maintaining a safe and reliable nuclear weapons stockpile in the absence of nuclear testing. DX Division personnel perform research, engineering, and

experimentation on high explosives and dynamic processes essential to the success of the nation's Science-Based Stockpile Stewardship program. The division's stockpile management responsibilities include the manufacture of production detonators for the stockpile and surveillance of stockpile detonators and energetic materials. The division operates and maintains a suite of explosives firing sites—both locally and at the Nevada Test Site—with state-of-the-art diagnostics that include world-class radiographic machines.

DX Division encompasses the following principal programs and facilities:

- AGEX I—hydrodynamic testing
- AGEX II—explosively driven pulsed-power physics and high-energy-density physics
- Detonator production
- High-explosives (HE) science
- Department of Defense Programs - advanced conventional munitions development
- PHERMEX—Pulsed High-Energy Radiographic Machine Emitting X-Rays
- DARHT—Dual-Axis Radiographic Hydrotest facility (completion anticipated August 2003)
- U1a—Nevada Test Site facility for the underground testing of special nuclear materials

DX Division uses small amounts of perchlorate salts and perchloric acid for research and development of explosives and propellants. DX-2 is a group within the DX division at LANL concerned with all aspects of high explosives (HE) from cradle to grave. These aspects include chemistry, engineering, materials properties, and physics related to the synthesis, formulation, performance, and safety of explosives; monitoring and surveillance of explosives in the enduring nuclear stockpile; unique applications of explosives; and environmentally-conscious destruction/disposal of explosives and explosive devices. The two areas where perchlorate is used (in small amounts) are organic synthesis and propellants. The synthesis of new explosive compounds is the most chemical-intensive operation, involving an an almost unlimited number of small amounts of inorganic and organic chemicals. Most syntheses produce milligram quantities of new compounds. However, following testing, large quantities may be synthesized for use in pilot scale experiments. Larger quantities of chemicals and glassware are often needed for the preparation of precursors and intermediates in the synthesis process. Large fume hoods are required for this process.

Wastewater generated by DX is sent to the Engineering Sciences and Applications (ESA) High Explosives Waste Water Treatment Facility (HEWTF). An ion exchange installed at the TA-16 HEWTF (installed and operational as of May 23, 2003) provides treatment of liquid wastewater, contaminated with both HE and perchlorate, prior to discharge.

Technical areas within the laboratory, with current perchlorate (various) chemical inventories include the TA-3, 9, 35, 43, 46, 48, 50, 53, and 55. See Table 5.

Table 5. LANL Technical Areas with Current Perchlorate Salt (Various) Chemical Inventories

Technical Area	Building	Division	Group
TA-3	CMR	Chemistry	Actinide Analytical Chemistry (C-AAC)
TA-3	Sigma bldg	Materials Science and Technology	Materials Technology Metallurgy (MST-6) Electronic and Electrochemical Materials and Devices (MST-11)
TA-9	0021	Dynamic Experimentation	Materials Dynamics (DX-2)
TA-9	0029	Dynamic Experimentation	DX-2
TA-35	0085E	Bioscience	Szilard Resource (B-3)
TA-35	0085W	Chemistry	Applied Chemical Technologies (C-ACT)
TA-43	0001	Bioscience	Langham Resource (B-2)
TA-43	0001	Bioscience	McClintock Resource (B-1)
TA-43	0001	Materials Science and Technology	Superconductivity Technology Center
TA-46	0031, 0154, 0158	Chemistry	Physical Chemistry and Applied Spectroscopy (C-PCS)
TA-46	0041, 0154	Chemistry	Advanced Chemical Diagnostics and Instrumentation (C-ADI)
TA-46	0076	Chemistry	Actinide, Catalysis, and Separations Chemistry (C-ACS)
TA-46	0158	Bioscience	Michelson Resource (B-4)
TA-46	0250	Materials Science and Technology	Materials Integration Science Laboratory
TA-46	0250	Chemistry	C-ACT
TA-48	0001	Chemistry	Isotope and Nuclear Chemistry (C-INC)
TA-48	0001	Nuclear Materials Technology	Actinide Process Chemistry (NMT-2)
TA-48	0001	Chemistry	C-ACS
TA-48	0001	Chemistry	Division Office (C-DO)
TA-50	0001	Facilities and Waste Operations	Waste Facilities Management (FWO-WFM)
TA-53	0001	Physics	Neutron Science and Technology (P-23)

TA-53	0622	Los Alamos Neutron Science Center	LANSCE-12
TA-55	0001	Nuclear Materials Technology	Actinide & Fuels Cycle Technologies (NMT-11)

Waste profile forms have identified perchlorate waste at the laboratory, which is packaged and transported to TA-54 for storage at Area L. For the fiscal years 2000 through 2002, the following table details the mass (in kilograms) of perchlorate containing waste disposed, by group. See Table 6.

Table 6. Perchlorate Waste Disposal

Group	FY 2000	FY 2001	FY 2002
B-DO			0.95
C-AAC			0.67
C-ACS		5.5	1.89
C-ACT		0.2	0.11
C-FM*		5499.5	35.8
C-SIC			0.91
DX-2	2.01	0.11	
E-ET	1.4	2.04	
ESH-5 (now HSR)		0.07	
FWO-SWO		2.04	
P-24		1.4	
MST-6	5.5	3.8	2.4
MST-7	5.9	0.6	0.2
MST-8	3.3		
MST-11	6.5	1.06	0.7
NMT-1	0.9		
NMT-7		0.57	5.8
Total	**25.51**	**5516.89**	**49.43**

Kg

*The FY 2001 and 2002 perchlorate waste generated by the Chemistry Division Facility Management Group (C-FM) was almost entirely contaminated ductwork, decon water, and duct wash down sludge from the perchlorate cleanup up at TA-48, building RC-0001.

Successes in Managing Perchlorate Compound Risks (including shock sensitivity and environmental releases)

Replacement of HEPA Filters at CMR: Risk Reduced by Comprehensive Waste Characterization (LAUR-02-0339): The laboratory Chemistry and Metallurgy Research

Facility (CMR) has been operating since 1952, providing actinide and analytical chemistry and materials characterization in support of stockpile surveillance, pit manufacturing, stockpile lifetime extension, and nuclear weapons certification. During this time, perchloric acid has been fumed as part of performing actinide chemistry at the CMR facility. This has resulted in the deposition of perchlorate in the ductwork of the facility's ventilation systems. Both the exhaust from glove boxes and fume hoods are discharged to a common duct that is filtered to remove airborne toxic and radioactive particulates before discharge. In March of 2001, LANL completed the replacement of 720 filters contaminated with perchlorate and radionuclides, at the CMR facility. Since that time, perchloric acid fuming has been limited to one (1) dedicated fume hood, located in Wing 5. A wet scrubber is installed in this hood as a practical technique for eliminating deposition of perchlorate salts in the ductwork and air emissions.

Perchlorate Fuming Operations at TA-48 and TA-59: Two buildings at TA-48 are used for actinide research, Radiochemistry 1 (RC-0001) and RC-0045. As was the case at the CMR facility, the RC-0001 building also underwent perchlorate contamination cleanup of the ductwork beginning in 2001. Since that time a new Hazard Control Plan (HCP-CFM-010.2) was implemented for perchlorate work. Perchloric acid use is currently limited to approved, labeled hoods that exhaust to ductwork equipped with wash down systems. Wash down systems prevent the build up of perchlorate in the ductwork, but does not prevent the exhaust of perchlorate in the air stream. Hoods that are approved for perchloric fuming have labels stating "Perchloric acid fuming permitted. No organics permitted." Two types of wash downs are performed: hood wash downs and ductwork wash downs. The user performs the hood wash down following the fuming of perchloric acid in the hood. The Facility Coordinator performs the ductwork wash down following user hood wash downs (on the same day as perchloric acid fuming), and at least weekly (regardless of perchloric acid fuming) while the laboratories are in operational mode. Each hood and ductwork wash down is for a minimum of 10 minutes.

The facilities at RC-0045 are currently rewriting HCP's and will specifically address perchlorate fuming in the new revisions. Currently, perchlorate fuming is handled under HCP-C-INC-004, and requires hood wash downs following use and routine wash downs of the facility exhaust ductwork, by the facility coordinator (note, at the time of this draft the schedule of the routine wash downs, by the facility coordinator, had not been specified). This facility processes approximately 1500 samples a year, and each sample requires 0.25 – 0.50 ml of perchloric acid.

Perchloric acid fuming has also been a required activity for sample preparation at TA-59. Historically, approximately 1 to 2 liters of perchloric acid were fumed a year. Two groups at TA-59 have conducted perchloric acid fuming for sample preparation in the past, Radiochemistry and Inorganic Analysis. Perchloric fuming of samples within the Inorganic Analysis team has been replaced by microwave digestion. The Radiochemistry team is currently evaluating alternative sample preparation methods also. One alternative method is high temperature muffling, to rid the samples of organics, and it would eliminate the use of perchlorate. Any perchlorate operations that currently occur are conducted in a dedicated fume hood with wash down procedures.

Wastewater from all of these facilities goes to the RLWTF at TA-50.

Testing Perchloric Acid Fume Scrubber at TA-59: The Isotope and Nuclear Chemistry Group (C-INC) are testing the performance of a perchloric acid fume scrubber. The use of fuming perchloric acid in chemistry operations is severely limited because of safety concerns about the buildup of potentially explosive perchlorate salts in fume hoods and ducts. Perchloric acid fuming operations are restricted to only a few approved hoods with wash down capability. Researchers from C-INC are testing an acid fume scrubber that removes the perchloric acid fumes before they enter the fume hoods and ductwork. The perchloric acid fumes pass through a water spray that captures the perchloric acid. The wastewater can then be disposed of normally or, if necessary, treated prior to disposal. The scrubber unit uses much less water than is presently required to wash down the fume hoods and ducts. The scrubber is portable and can be moved to wherever it is needed. Testing will take place at TA-59 and, if successful, the unit will be deployed at TA-48.

Perchlorate Reduction by Engineering Sciences & Applications (ESA) Division: In support of RRES Division's effort to reduce the use of perchlorate at LANL, ESA identified a rocket testing program that uses ammonium perchlorate-based rocket fuel. ESA voluntarily agreed to cease any testing of perchlorate-based fuels and either find another off-site user for the fuel or dispose of it. In keeping with RRES's goal, if an off-site user cannot be found, ESA will not use any of the on-site permitted facilities to open burn/detonate this waste. Instead, they will seek funding to send it to an off-site incinerator.

Perchlorate Reduction at TA-50 RLWTF (LAUR-01-6519): During the Spring of 2000, it came to the attention of the RLWTF management that the presence of perchlorate in the RLWTF effluent needed to be addressed. Typically, perchlorate concentrations in the RLWTF effluent were in the range of several hundred ppb. As a result, a perchlorate waste stream survey was performed to identify generators of perchlorate waste at LANL. Additionally, a best available treatment survey for perchlorate was performed. It was concluded from this survey that ion exchange would be the best option for the RLWTF waste stream. Pilot scale ion exchange tests were begun in September 2000 and continued until June 2001 to quantify the effectiveness of ion exchange removal of perchlorate and to identify the most effective ion exchange resin. Design and installation of the full-scale treatment system for the RLWTF effluent stream was completed in March 2002. Since March of 2002 the perchlorate in the effluent from the RLWTF has been less than 1 ppb.

Waste Minimization or Elimination Through Sustainable Building Design
The Characterization of High Energetic Materials (CHEM) Laboratory Building:
An NNSA Waste Stream Elimination Case Study (LAUR-03-2317): Los Alamos National Laboratory management (Associate Director for Operations) has requested an evaluation of the impact of eliminating waste streams on Laboratory operations. A case study has been developed using the CHEM Laboratory Building, which is being proposed as part of the DX Strategic Facility Plan. This case study was undertaken to ascertain if sustainable building design could significantly reduce or eliminate waste streams. In particular, perchlorate or HE found in DX-2's wastewater. The CHEM Laboratory building is projected to cost approximately $20 million and typical operations would be expected to produce about 14,000 gallons of HE wastewater a year. At present this wastewater is treated at the HEWTF when it meets their Waste Acceptance Criteria (WAC). However, cumulative experience shows that operations are subject to shifting

boundary conditions that make wastewater treatment uncertain: operations change with missions, and new or more stringent regulatory requirements have been applied. This leaves Lab national security research and development programs at risk, and can result in the suspension or reduction of operations until a suitable alternative can be identified and implemented. The results of this study indicate that DX's ability to manage HE wastewater begins in the earliest stages of building design and that adding operational flexibility into the building design provides significant future benefits. For example, having exposed drain lines located in a partial basement and readily accessible allows for the easy hook up of appropriate treatment processes where the water can be reused and/or evaporated. It is expected that with such a flexible building design, the HE wastewater could be significantly reduced if not eliminated entirely. It is expected that the discounted lifecycle savings (50 year life expectancy) would be about $2.2 million by the elimination or reduction of this waste through flexible design. This savings has a payback time of approximately nine years. Lifecycle savings would come from cost avoidance (e.g. the digging up of contaminated or leaking pipes), waste management cost, the isolation of particular wastewater that may need special treatment (no disposal path), and assure compliance with increasingly stringent environmental regulations.

Permeable Reactive Barrier Feasibility – Mortandad Canyon

A field-scale permeable reactive barrier (PRB) was installed in Mortandad Canyon in the winter of 2002 at a site downstream from the discharge point of the RLWTF, a National Pollutant Discharge Elimination System (NPDES) -permitted outfall. Alluvial groundwater in Mortandad Canyon is being treated using a Multi-Barrier technology that consists of four different cells of materials (scoria basalt, hydroxyapatite, cotton seed meal and pecan shells, and limestone) arranged as a PRB. Among the targeted contaminants are perchlorate, nitrate, and strontium-90. The perchlorate removal mechanism in the Multi-Barrier is through microbial reduction to harmless chloride ion. The Multi-Barrier uses one cell that provides biological activity sufficient to reduce perchlorate to chloride. This cell is made of inexpensive waste materials including cottonseed meal and pecan shells. Both cotton seed meal and pecan shells are capable of supporting the growth of a microbial biofilm that is highly effective at reducing both nitrate and perchlorate to non-detectable levels as the groundwater flows through the barrier. Strontium-90 is removed from groundwater through adsorption processes involving hydroxyapatite. This project is a field-scale demonstration of the Multi-Barrier system that has multiple sampling points at strategic locations in each cell, and at sampling stations upstream and downstream from the PRB.

This summer, data from the PRB will be collected, and a report of the findings will be available in the fall of 2003.

Potential Perchlorate Sites and Sources

In September 1999, the NMED, Hazardous and Radioactive Materials Bureau, asked the Laboratory to conduct a survey to identify potential perchlorate-related sites. The survey findings, submitted to the NMED in December 1999, identified two areas at the Laboratory that contain potential perchlorate-related sites: the HE Corridor, and Mortandad Canyon.

High-Explosives Corridor

Wastewater generated within the HE corridor (since the early 1940's) has been discharged into Pajarito Canyon, Water Canyon, and Cañon de Valle, prior to the installation of the HEWTF. As a result, perchlorate has been sampled at Fishladder seep (in Fishladder Drainage) and the Fishladder 'waterfall' at the confluence of the Fishladder Drainage and Cañon de Valle – have detected perchlorate concentrations of 17 ppb and 7 ppb respectively. Cañon de Valle ultimately drains into Water Canyon.

In addition, soils from firing and rocket sites have become contaminated from past experiments and burning within the HE corridor. Stormwater contacting this contaminated soil may be another source and major transport mechanism.

Mortandad Canyon

Perchlorate was present in alluvial groundwater in Mortandad Canyon at values up to 280 ppb in 2000. The alluvial groundwater is separated from the regional aquifer by about 900 ft. Cores from four wells in Mortandad Canyon show that pore water perchlorate concentrations in the vadose zone beneath the canyon floor average 300 to 400 ppb down to at least 400 ft. This indicates a considerable inventory of perchlorate beneath the canyon floor as a result of 40 years of effluent discharge. At monitoring well, MCOBT-4.4 groundwater was observed between depths of 492 and 532 ft. The perched groundwater was encountered in the Puye Formation and Cerro del Rio basalt. Perchlorate was detected in this perched groundwater between concentrations of 140 and 180 ppb. These are the highest concentrations of perchlorate observed in perched groundwater at the laboratory.

Three nearby regional aquifer monitoring wells have not shown perchlorate contamination, though analysis of several samples has produced analytical results that are near or below the detection limit of 4 ppb. None of the five surrounding Los Alamos County water supply wells (O-4, PM-1, -3, -4, -5) have detectable perchlorate contamination.

The LANL Integrated Groundwater Protection Strategy Team is conducting extensive evaluation and study of Mortandad canyon. This team is calculating the drinking-water ingestion risk (in terms of probability of exceeding 1 ppb perchlorate) associated with perchlorate moving from the TA-50 discharge point (since 1963) and the TA-35 discharge point (since approximately 1954), through the canyon alluvium, vadose zone, regional water-supply aquifer, and into the capture-zone of water-supply wells. The results will be then interpreted via traditional quantitative decision analysis methods to identify and rank (according to relative risk reduction per dollar spent) alternative actions to reduce the impact of perchlorate. The Mortandad Canyon risk-based decision analysis will be complete in early June. The other major sources (below) will be similarly addressed throughout the summer and fall.

Other Perchlorate Site

Rio Grande Springs

The NMED-OB has reported discovery of perchlorate in samples from some springs along the Rio Grande. Numerous follow up samples have not confirmed these findings, which remain mired in questions over analytical accuracy near the method detection limit. Samples analyzed by one of our analytical laboratories prior to April 25, 2001 showed many false positives due to

lack of all the anion removal steps required in the EPA analytical method. Removal of other anions present in water prevents matrix interference in the analysis. Thus many of the apparent detections indicated in LANL data are not bona fide perchlorate detections.

Specific information on potential sources of perchlorate at the Laboratory is presented below.

Active Effluent Sources

The Laboratory has two active outfalls in the current National Pollutant Discharge Elimination System (NPDES) permit. NPDES Outfall 051 (RLWTF) and outfall 05A055 (HEWTF).

***Radioactive Liquid Waste Treatment Facility (RLWTF) at TA-50* (Mortandad Canyon).**
In 2000 and 2001, the annual average concentration of perchlorate in the RLWTF's effluent was 254 ppb and 169 ppb, respectively. In March 2002, the RLWTF began operating an ion exchange treatment system to remove perchlorate from the facility's effluent. Routine monitoring of RLWTF effluent since treatment began shows no detectable concentrations of perchlorate. In response to perchlorate reduction in the RLWTF effluent, by November 2002, the concentration nearest the outfall had dropped to near the detection limit of 4 ppb and concentrations at other stations were decreasing slowly.

***High Explosives Wastewater Treatment Facility (HEWTF)* at TA-16** (Cañon de Valle).
Elimination of 19 NPDES-permitted HE outfalls was completed in 1997. All water from HE operations is now collected and treated at the HEWTF, which discharges into Fish Ladder Drainage and ultimately Cañon de Valle. Analysis of holding tank and effluent samples at the HEWTF shows a range of perchlorate concentrations from 4 to 58 ppb. The primary perchlorate source has been tracked to a single contributing facility at TA-9, Anchor East Site. An ion exchange system was installed on May 23, 2003 and is currently operational.

Perchloric Acid Fuming, TA-48 and TA-59
The majority of perchlorate release is associated with operations requiring fuming of perchloric acid. It has been estimated that 70% of the perchloric acid used is discharged as gaseous effluent in fume hoods. These fume hoods have wash downs and the exhaust ducts are also washed down regularly. The remaining 30% is released as liquid effluent via the radioactive liquid waste drains, which are treated at the RLWTF. There is however, considerable uncertainty in the relative percentages of gaseous release versus liquid effluent release.

Programs that utilized these operations, in order of perchloric acid use, are the Weapons Test Program, Environmental Sample Analyses Programs, Miscellaneous Programs (generally short term programs), Iridium Anomalies Study, Rover Program, and Natural Analogs Program.

Potential Uncharacterized Source
Commercial perchlorate is prepared electrochemically, from treatment of aqueous chlorides with sufficient voltage to prepare adequate concentrations (typically several tens of percent by weight) of perchlorate (either as acid or salts). However it is possible to prepare perchlorate chemically and by other means, which may lead to the low concentrations of perchlorate being observed in systems where it has not been added. In general, any chlorine-containing species (e.g., hydrochloric acid, hypochlorites, chlorites, chlorates, and perhaps even some organic chlorides)

may react with strong acids, oxidizing agents such as peroxides, ozone (whether naturally or artificially produced), ultraviolet light/air, etc. to produce small amounts of perchlorate on the order that can be detected by more sensitive chemical analysis. It must be noted that while perchlorate has been in use since the early 1800s, the technology to detect it at ppb levels has only existed in the last decade.

Since perchlorate is an environmentally (and chemically) stable species, it is important to understand its adventitious production to discriminate between so-called 'natural' or unintentional sources and that arising from perchlorate-contaminated waste. However, this has been difficult to determine, as the wastewater contamination is intermittent and sporadic, even sampling the same piping and sumps.

Inactive Effluent Sources - probable discharges of perchlorate

***TA-1, TA-45* (Acid Canyon and Pueblo Canyon).**

Acid Canyon, a small tributary of Pueblo Canyon, was the original disposal site for liquid wastes generated by research on nuclear materials for the World War II Manhattan Engineer District atomic bomb project at TA-1 (Los Alamos townsite). Acid Canyon received untreated radioactive industrial effluent from 1943 to 1951. The TA-45 treatment plant was completed in 1951, and from 1951 to 1964 the plant discharged treated effluents that contained residual radionuclides into nearby Acid Canyon. Based on similarity of processes to TA-50 (including nuclear chemistry research), the effluents probably contained similar amounts of perchlorate.

As indicated previously, perchlorate is present in water supply well O-1 (Pueblo Canyon) at concentrations of about 2 to 4 ppb. Though these values are below the ion chromatography detection limit, results of numerous analyses are consistent enough to support the conclusion that perchlorate is present. Los Alamos County only uses this well as a stand-by supply.

***TA-21* (DP Canyon).**

An industrial liquid waste treatment plant that served the old plutonium processing facility at TA-21 discharged effluent containing radionuclides into DP Canyon, a tributary to Los Alamos Canyon, from 1952 to 1986. Based on similarity of processes to TA-50 (including nuclear chemistry research), the effluents probably contained similar amounts of perchlorate.

Recent evaluation of core from well # LADP-4, drilled down gradient of the former radioactive liquid effluent outfall at TA-21, revealed perchlorate concentrations of 200 to 1000 ppb. Rock core samples from this well were sampled to a depth of 800 ft. with the deepest perchlorate concentration observed at a depth of 280 ft. The regional aquifer in this area is at a depth of 1000 ft. These perchlorate concentrations indicate a residual foot print in the rock above the saturated zone, which warrants more evaluation. These concentrations are similar to those in the vadose zone beneath Mortandad Canyon.

There may be several buildings at TA-21, including those still standing, that had outfalls other than the sanitary sewage treatment plant. Further evaluation of the complete TA-21 situation is warranted.

***TA-9* (Pajarito Canyon).**
Since 1950, operations at Anchor East Site have discharged wastewater from high explosives synthesis and testing operations. The Anchor East Site, TA-9, was identified as a significant perchlorate contributor. A recent analysis of wastewater, from this facility, showed it contained over 500 ppb of perchlorate, which is used as an oxidizer in high explosives. While outfalls from these buildings were shut down by 1997, and wastewater is now hauled to the HEWTF, discharge from these outfalls entered upper Pajarito Canyon for the previous 45 years. This area warrants further evaluation.

TA-46, TA-48, TA-59 outfalls (Mortandad Canyon)
Nuclear (actinide) chemistry research has been ongoing at these faculties. Prior to the installation of the RLWTF, untreated radioactive industrial effluent was most likely discharged into the nearby Mortandad Canyon.

TA-35, and Ten Site Wastewater Treatment Plant (Mortandad Canyon and Ten Site Canyon)
Numerous accidental waste spills and intentional releases of waste materials occurred at TA-35. Experimentation with several radionuclides, especially plutonium and tritium, were conducted at TA-35 in the 1950s and 1960s. Waste liquids, generated by washing of hot cells used in TA-35-2, were stored in four 50,000 gallon concrete tanks (TA-35-10) to allow decay of the short-lived radionuclides. The wastewater was then discharged into Mortandad Canyon. The discovery that other radionuclides with longer half-lives were also stored in the tanks, and were being concentrated in these wastes, necessitated construction of a wastewater treatment plant. From 1951 to 1963 this facility treated radioactive wastes produced by various reactor and hot cell experiments at TA-35. The wastewater treatment plant was constantly beset by problems, and inadvertent spills of insufficiently-treated wastewater into Ten Site Canyon (tributary to Mortandad Canyon) occurred frequently. The potential for perchlorate releases exist due to chemistry's, similar to actinide research, which may have been used.

Search for Lower Perchlorate Detection Limit
With potential State and/or Federal regulations setting discharge limits in the range of 1-18 ppb perchlorate, the accuracy and sensitivity of perchlorate detection methods is extremely important. The EPA has approved one analytical method for the analysis of perchlorate, Method 314 using Ion Chromatography. This method has a detection limit of 4 ppb in natural waters, with a practical quantitation limit (the lowest concentration that can be reliably determined) of 12 ppb. These detection limit values are based on several verification studies using natural groundwater. However, careful screening or cleanup steps are required with the current ion chromatography analytical method to lessen the occurrence of interference from other ions. Frequently these steps have not been used by all analytical laboratories, resulting in interference from other ions (inherent in real, environmental matrices), particularly sulfate, chloride, nitrate and carbonate, which produce random and highly-variable noise in the baseline at the known perchlorate retention time on the chromatogram. This can result in a significant background signal above zero and "false positives" in the range of 1 to 4 ppb. In addition, as mentioned previously, the potential for a drinking water standard below 4 ppb creates a need for an analytical method with a lower detection limit.

The Department of Energy's (DOE) National Nuclear Security Administration (NNSA)

Albuquerque Operations Office Analytical Management Program (NNSA-AL AMP) is collaborating with LANL in evaluating a low-level perchlorate analysis method by coupling liquid chromatography (LC) and a tandem mass spectrometry (MS) technique (LC/MS/MS). The detection of perchlorate by dual mass spectrometry is achieved by the passing of perchlorate (ClO_4^-) in the first stage and the daughter ion chlorate (ClO_3^-) in the second stage. A detector following the dual mass spectrometers measures the ClO_3^- ion signal. Perchlorate is quantified by monitoring the ClO_3^- ion signal. In addition, because chlorine has two naturally occurring isotopes (75% as Cl^{35} and 25% as Cl^{37}), the specificity of perchlorate detection can be further assured by the observation of same abundance by the tandem mass spectrometers. The DOE NNSA Service Center - Environmental Programs Department stated in a January 31, 2003, e-mail to complexes associated with the DOE Albuquerque Operations Office that the EPA Office of Water was interested in the LC/MS/MS method and has been in contact with General Engineering Laboratories (GEL), Charleston, South Carolina. See Table 7.

Table 7. New Analytical Method for Perchlorate (Proposed)

Analytical Method For Perchlorate (Proposed)		
Method	Method Detection Limit (ppb) (proposed)	Reporting Limit/Practical Quantitation Limit (ppb) (proposed)
Liquid Chromatography/ Mass Spectrometry/Mass Spectrometry	0.05	0.20

The method works well across a range of natural water chemistry, but has suffered from problems with the internal standard. These problems have previously resulted in erroneously high analytical results and have plagued the perchlorate LC/MS/MS method from the beginning. GEL, completed work on their internal standard in early April of 2003. Work on the analytical method was also completed by GEL and they were ready to receive samples by early April of 2003. GEL plans on submitting this updated analytical method to the EPA Office of Water (no date available).

A consensus was also reached at the January 9th, 2003, meeting that NMED-OB, DOE, NNSA and LANL would jointly perform a performance evaluation of the LC/MS/MS method prior to the Laboratory employing it for low-level perchlorate analysis. Los Alamos area environmental water samples will be part of the evaluation. Design of the performance evaluation, with input from the NMED-OB, Los Alamos Department of Public Utilities, and the DOE has occurred. Also, 116 water samples, resulting from a round of sampling during the week of May 12, 2003, were submitted to GEL (May 29, 2003) for the performance evaluation study. Results were expected back to the LANL Environmental Surveillance Team, Risk Reduction and Environmental Stewardship (RRES) Division Water Quality & Hydrology (WQH) Group, by June 30, 2003. Following data validation and approvals from all of the entities involved, the data will be available for review.

Treatment

Treatment of perchlorate contamination in water is complicated because the perchlorate anion does not respond to typical water treatment technologies due to its fundamental physical and chemical nature. The perchlorate tetrahedron itself is structured such that the four oxygen atoms surround the central chlorine atom, effectively blocking reductants from directly attacking the chlorine. The perchlorate anion is soluble and very mobile in aqueous systems. It can persist in the environment for many decades under typical groundwater and surface water conditions because of its resistance to react with other available constituents. While perchlorate is thermodynamically a strong oxidizing agent, with the chlorine in the +7 oxidation state, the kinetics of reduction are generally very slow. Common reducing agents do not reduce perchlorate, and common cations do not coordinate with or precipitate it. Consequently, standard practices of water treatment will neither remove it physically nor destroy it chemically.

Perchlorate treatment technologies may be generally classified into categories of removal or reduction technologies. Physical removal processes include anion exchange, membrane filtration (including reverse osmosis and nanofiltration), and electrodialysis, which all require subsequent disposal of removed perchlorate. Reduction processes include biological reduction, chemical reduction, and electrochemical reduction. It must be noted that because of the newly emerging nature of perchlorate contamination and the associated cleanup concerns, that nearly all treatment techniques remain to be demonstrated for effectiveness. Further, little or no cost or performance data is available.

The optimum treatment technology for a given perchlorate occurrence may depend on several factors, including perchlorate concentration, the presence and concentration of co-contaminants, other water quality parameters (pH, alkalinity, natural organic matter (NOM), total dissolved solids, metals, etc.), and geochemical parameters (nitrate, sulfate, chloride, dissolved oxygen, redox potential, etc.).

Physical Removal Processes, Treatment options identified

1. *Ion Exchange* – Ion exchange is a technology for the treatment of groundwater, surface water, and leachate. It works on perchlorate by capturing perchlorate anions on a positively charged resin and releasing a harmless chloride ion in its place. The exchange resin can be made from natural or synthetic organic, inorganic, or polymeric material that contain functional ionic groups.

   Ion exchange is energy-intensive due to the "pump and treat" nature of its operation. It requires frequent changing or regeneration of exchange resins and generates a problematic residual waste in the form of brine or contaminated resins that still contain the perchlorate. The secondary wastes generated during treatment would require additional treatment or disposal. It is possible that a treatment train using ion exchange and *ex situ* biological treatment of the secondary waste could be used to treat low levels of perchlorate contamination in surface waters and wetlands

   Private sector organizations have been successfully applying ion exchange for many years for different applications. This success has extended to continuous ion exchange units that have effectively demonstrated the ability to reduce perchlorate to below 4 ppb in remediation and drinking water applications.

The DoD has been investigating the use of ion exchange to treat perchlorate-contaminated groundwater at Edwards Air Force Base, California. Edwards Air Force Base (AFB) will soon begin field-testing a new class of anion exchange resins in a conventional fixed-bed ion exchange system. Pilot-scale tests of the system were completed in June 2001 and were proven successful at treating contaminated groundwater.

Capital and operational cost of ion exchange systems vary depending on a number of factors, such as discharge requirements, the volume of water to be treated, contaminant concentration, the presence of other contaminants, resin and regenerant utilization, brine disposal, and site-specific hydrological and geochemical conditions.

2. *Membrane Filtration* – Membrane filtration, reverse osmosis and nanofiltration, are established treatment technologies used for the removal of contaminants such as salts, disinfection by-product precursors, nitrates, and selected pesticides. While it is anticipated that these processes may be effective for the removal of perchlorate, there is little to no peer-reviewed data that demonstrates their applicability to perchlorate contamination at concentrations of 1000 ppb and lower. Influent perchlorate concentrations would have to be below 400 ppb to have permeate concentrations below 18 ppb. Two examples offered from Azita Yazdani, (President) & Fred Reinhard (VP/Senior Engineer) of Exergy Technologies Corporation are:
   - *Membrane Electrolysis (ME)* - large variety of recovery and maintenance applications of chemical process solutions, but also equipped with patented pending design, latest proprietary ion exchange membranes and electrodes.
   - *Advance Reverse Osmosis (ARO)* - utilizes selected reverse osmosis membranes to allow process water/chemical recovery at elevated total dissolved solids concentrations and an expanded pH range from 0.5 to 13.

   Also, treatment of the perchlorate-concentrated secondary stream will need to be addressed.

3. *Electrodialysis* – Electrodialysis systems separate ionic species from aqueous solutions using an applied direct current potential across ion-permeable and selective membranes. No known demonstration projects were found.

4. *Exergy Technologies Corporation*- This Company has technologies to address perchlorate as well as other organic issues. An example of a technology that is used to eliminate perchlorates in the wastewater is the Continuous Electrodeionization. This technology combines ion exchange/membrane/electrolysis technologies and utilizes unique proprietary ion exchange membranes and electrodes to replace conventional ion exchange systems in industrial recovery applications.

5. *Ultraviolet and Ozone Peroxide System* - This approach has the dual advantage of eliminating perchlorates and other organics from waste wastewater while conserving water usage. Hydrothermal and other wet oxidation technologies were evaluated for their efficacy in destroying these contaminants. Wet oxidation converts the organic materials present to

carbon dioxide and water and the inorganic contaminants to their common salts (nitrates, chlorides, sulfates, etc.). After destruction is completed, the salts can be removed with standard deionization resins and recycled. Literature indicates that mixtures of ozone and hydrogen peroxide coupled with ultraviolet light offers the most effective treatment. A pilot project conducted at C-Division to test the efficacy of using an UV/Ozone/Peroxide treatment process indicated that it would destroy 95% of the contamination within a single pass.

Chemical/Biological Removal Processes, Treatment options identified

1. *Anaerobic Bioremediation* – Studies have shown that perchlorate can be successfully biodegraded to the chloride ion, but only under anaerobic conditions. The *in situ* (in place) anaerobic bioremediation of perchlorate is a promising technology in which naturally occurring microorganisms are used to reduce perchlorate to innocuous chloride upon addition of a carbon source. For *in situ* bioremediation to occur, an electron donor (i.e. carbon-source) is added to perchlorate-contaminated groundwater or soil. A variety of electron donors have been used to stimulate perchlorate reduction, including alcohols, organic acids, edible oils and some sugars. The carbon source stimulates aerobic microorganisms to remove oxygen and nitrate, resulting in redox conditions amenable to reduction of perchlorate *in situ*. However, *in situ* bioremediation requires careful consideration of environmental conditions, hydraulic flow, and residence time of the contaminated water in the underground reactive zone. Because perchlorate reduction only occurs in the absence of oxygen and nitrate, initial research into the use of *in situ* bioremediation as a means of treating perchlorate-contaminated groundwater has focused on developing and optimizing anaerobic bioremediation techniques.

   More than 30 different strains of perchlorate-reducing microbes have been isolated from diverse environments. In this reductive process, bacteria utilize the perchlorate ion as a terminal electron acceptor. A carbon or hydrogen electron donor (e.g., acetate) is normally necessary to drive the reaction sequence for optimal remediation rate. It is now generally accepted that microbial reduction of perchlorate proceeds according to the following:

$$\underset{\text{(Perchlorate)}}{ClO_4^-} \rightarrow \underset{\text{(Chlorate)}}{ClO_3^-} \rightarrow \underset{\text{(Chlorite)}}{ClO_2^-} \rightarrow \underset{\text{(Hypochlorite)}}{ClO^-} \rightarrow \underset{\text{(Chloride)}}{Cl^-} + O_2$$

   As can be seen, perchlorate is ultimately completely converted into chloride and oxygen through the anaerobic reduction process. The perchlorate-to-chlorate step is thought to be the rate-limiting step, being considerably slower than the other steps. Buildup of toxic intermediates, specifically chlorite, does not occur because the chlorite-to-chloride step proceeds at a rate on the order of 1000 times that of the accepted rate-limiting step.

   Current approaches for the remediation of perchlorate-contaminated groundwater typically involve long-term pump-and-treat solutions. Comparison of cost estimates for *in situ* versus *ex situ* treatment for perchlorate plumes at several DoD field cases suggests that *in situ* bioremediation cost between 50 to 75 percent of *ex situ* treatment costs. The ability to jointly treat perchlorate and common co-contaminants such as nitrate and chlorinated solvents via *in situ* bioremediation will also increase cost savings.

Laboratory-, and pilot-scale studies of *in situ* anaerobic bioremediation for treating perchlorate-contaminated groundwater are ongoing. A summary of projects is shown in Table 8.

Table 8. Summary of *In Situ* Bioremediation Projects [11]

Project Name	Location/Funding Source	Scale/Media	Status of Project
Bioreduction and Removal of Ammonium Perchlorate	Carbondale, IL / SERDP[1]	Lab/W	In-Progress
Bioremediation of Perchlorate	Lawrenceville, NJ / SERDP[1]	Lab/GW	Complete FY01
Bioremediation of Perchlorate-Impacted GW	Six SERDP[1] test sites; 1) Edwards Air Force Base, CA 2) DOD site, West Virginia 3) Rocket Manf., CA 4) Aerojet Superfund Site, CA 5) U.S. Navy, CA 6) Industrial Site, Nevada	Lab/Pilot GW	Complete FY01
Treatability Studies on GW from Henderson, NV	Panama City, FL / Kerr-McGee Chemical LLC	Lab/GW	Complete (2000)
Insoluble Organic Substrates (Edible Oils) for Degradation of Perchlorate	Edwards AFB, CA / AFCEE[2]	Pilot/GW	In Progress

[1] Strategic Environmental Research and Development Program (SERDP) – DoD's corporate environmental R&D program.
[2] Air Force Center for Environmental Excellence.

2. *Permeable Reactive Barriers* – The Permeable Reactive Barrier (PRB) is a groundwater cleanup technology that consists of a wall of reactive material installed in the path of a flowing contaminated groundwater plume to treat pollutants as they penetrate through the wall. The PRB contains materials that target specific contaminants and chemically and/or biologically treats them. As with any biological treatment system, PRBs require careful control of environmental conditions within the reactive zone to maintain the anaerobic conditions that encourage the bacteria to biodegrade the perchlorate. The regular addition of nutrients and electron donors may be necessary depending on the efficiency of the PRB system and the reactive material used.

PRBs are increasingly being used to treat a variety of groundwater contaminants and are recognized as a cost-effective, passive remediation method.

The DoD has successfully used PRBs to treat perchlorate at the Naval Weapons Industrial Reserve Plant in McGregor, Texas. The system is believed to represent the first full-scale *in situ* bioremediation of perchlorate. Pilot- and full-scale studies of PRBs for treating

perchlorate-contaminated groundwater are ongoing. A summary of projects is shown in Table 9.

Table 9. Summary of Permeable Reactive Barrier Projects [11]

Project Name	Location/Funding Source	Scale/ Media	Status of Project
Insoluble Organic Substrates (Edible Oils) for Degradation of Perchlorate	Edwards AFB, CA / AFCEE[2]	Pilot/GW	In Progress
Permeable Reactive Barrier Feasibility	Los Alamos, NM / U.S. DOE, LANL	Pilot/GW	In Progress
In situ GW Remediation	McGregor, TX / U.S. Navy	Full Scale/GW	In Progress

3. *Phytoremediation* – Phytoremediation is a treatment technology that uses natural plant processes and microorganisms associated with the root system to remove, contain, or degrade environmental contaminants in soil, sediment, and water. There are several processes associated with phytoremediation. Depending on the contaminant to be treated and site-specific conditions, these processes may work together, with the entire plant acting as a single system to remove the contaminant, or they may work individually with certain processes having a greater influence on contaminant removal.

Several recent studies have shown that plants are capable of taking up, and at least partially reducing perchlorate. Research funded by the Air Force Aeronautic Systems Center and the US Army Operations and Support Command have confirmed the ability of phytoremediation to remove perchlorate from contaminated water and soils. The two most important phytoremediation processes for perchlorate involve the uptake and subsequent phytodegradation of the chemical in branches and leaves, and rhizodegradation. Phytodegradation uses naturally occurring plant enzymes to degrade contaminants within the plant tissues. Rhizodegradation, on the other hand, occurs in the soil surrounding plant roots. Natural substances released by the plant roots serve as substrates for the microorganisms present in the rhizoshpere and speed up contaminant degradation.

Pilot- studies of phytoremediation for treating perchlorate-contaminated groundwater are ongoing. Defensible data on cost and performance need to be developed. See Table 10.

Table 10. Summary of Phytoremediation Projects [11]

Project Name	Location/Funding Source	Scale/ Media	Status of Project
Longhorn Army Ammunition Plant	Karnack, TX / US Army Operations, US Air Force	Pilot/GW	In Progress
Phytoremediation – Greenhouse Testing	Athens, GA / US Air Force, Wright Patterson AFB	Lab/GW, soil	Complete FY 2000
Phytoremediation By Native Salt cedar	Las Vegas, NV / U.S. EPA	Field /GW	Complete FY 2000

4. *Bioreactors* – Bioreactors are an *ex situ* form of biological treatment in which contaminated process wastewater or extracted groundwater is pumped into an above ground reactor vessel (bioreactor), and placed into direct contact with microorganisms. These microorganisms remove perchlorate by reducing it in the presence of a food source. Careful control of environmental conditions (pH, temperature, oxygen content, nutrient sources, etc.), hydraulic flow, and residence time of the contaminated water supply in the bioreactor is necessary to support the growth of microorganisms and ensure complete reduction of the perchlorate. Common system designs include fluidized bed reactors (FBR), continuous-stirred tank or suspended growth reactors, and fixed film or packed bed reactors.

   Despite widespread use of bioreactors in the treatment of municipal and industrial wastewater, only in the past decade have studies been performed to evaluate the effectiveness of bioreactors in treating contaminated groundwater. In addition, because it has been determined that perchlorate can be successfully reduced to the harmless chloride ion under anaerobic conditions; initial research into using bioreactors to treat perchlorate-contaminated water has focused on the development and optimization of anaerobic bioreactors.

   The Air Force Research Laboratory (AFRL) Materials and Manufacturing Directorate (Tyndall Air Force Base, Florida) has led the way in developing bioreactor systems to treat process wastewater containing very high levels of perchlorate. Since 1997, a bioreactor based on the AFRL design has been treating wastewater from rocket motor production and demilitarization operations at a defense contractor facility near Brigham City, Utah.

   A large, full-scale FBR system has also been operating at a site in Rancho Cordova, CA, since 1998. This system was integrated into the sites overall groundwater extraction and treatment plant to remediate perchlorate contaminated groundwater.

   The first DoD facility to install a functional bioreactor for treating perchlorate-contaminated groundwater was the former Longhorn Army Ammunition Plant (LHAAP) in Karnack, Texas. Past activities at this site led to the construction of a groundwater pump-and-treat system, in 1997, for the site's production and disposal areas. However, the groundwater treatment plant was designed to extract and treat metals and volatile organic compounds, not perchlorate. After assessing the cost and technical feasibility of alternative technologies, LHAAP opted for a bioreactor, specifically an FBR, as an add-on device to the existing groundwater treatment system.

   Aerojet, a significant user of ammonium perchlorate, is developing a proprietary *ex situ* bioremediation system to remediate perchlorate-contaminated groundwater. Pilot-scale testing of the biological process is taking place at the San Gabriel Valley Superfund Site. The purpose of the test is to determine whether the bioreactor, if followed by filtration and other post-bioreactor treatment, could produce potable water. The test was completed in December 2000, and in April 2002 the California Department of Health Services accepted the technology for use in the production of drinking water (Phase 2 Treatability Study Report *Aerojet GET E/F Treatment Facility, Sacramento, CA, September 2001*). Additional information on this technology, including a report describing the pilot-scale test results, is available from EPA Region 9. Four full-scale bioreactors, in operation since 1998 at

Aerojet's northern California facility, have consistently reduced perchlorate levels from about 2,500 ppb to non-detectable levels (< 4.0 ppb).

Soil Biotreatment – Soil biotreatment uses bacteria to degrade soil contaminants. Treatment alternatives can be either *ex situ* (i.e. above ground) or *in situ* (i.e. in ground), and include biotreatment cells, soil piles, and prepared treatment beds. Soil biotreatment is typically based on the principles of soil composting (controlled decomposition of matter by bacteria and fungi into a humus-like product). In ex situ processes, contaminated soils are excavated, mixed with additional soil and/or bacteria to enhance the rate of contamination degradation, and placed in above ground enclosures or treatment cells. In situ processes use a carbon source such as chicken, horse, or cow manure. In situ can be active or passive depending upon whether the carbon source is applied directly to the undisturbed soil surface (i.e. passive) or physically mixed into the soil surface layer (i.e. active). The effectiveness of both alternatives is dependent upon careful monitoring and control of environmental factors such as moisture, temperature, oxygen, and pH, and the availability of a food source for bacteria to consume.

Activities of Other Agencies

DoD Perchlorate Activities

1. DoD is the most active government agency on all fronts regarding perchlorate. The department has clearly taken the leadership role in supporting a science based risk assessment from the EPA and establishing criteria for a policy to guide any required cleanup efforts. The DoD is also pursuing an aggressive program to develop and deploy effective remediation technologies for use both within the Department and outside. Earlier this year, the EPA released its revised draft toxicity assessment, "Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization." While still undergoing review and deliberations both by the external scientific community and within EPA, when finalized, this assessment will be an important update of EPA's health assessment that reflects the state of the science regarding the health effects of the chemical perchlorate. Based on this draft assessment, the EPA has issued a guidance range for cleanup of 4-18 ppb. The DoD is providing the external review body, the National Academy of Science, with additional studies and material collected or derived from DoD Labs to support a science based conclusion.
2. The DoD has established the Air Force Center for Environmental Excellence in San Antonio, Texas as the DoD lead for the development/evaluation of remediation technologies. The Department has invested over $25 million to develop treatment technologies capable of cleaning up perchlorate-contaminated surface and groundwater. Those technologies are maturing quickly and appear to be capable of reducing perchlorate to at or below 4 ppb. A brief synopsis of these technologies was presented in the *Treatment* section above, and DoD research, demonstrations, and/or implementation projects are highlighted below:
    i. *In Situ Anaerobic Bioremediation.* The Strategic Environmental Research and Development Program (SERDP) is the DoD's corporate environmental R&D program, planned and executed in full partnership with the DOE and EPA. SERDP has directed significant efforts towards developing cost-effective *in situ* bioremediation technologies for perchlorate. Under SERDP, Southern Illinois University is developing a library of microorganisms capable of degrading perchlorate. Two private

sector companies are also conducting SERDP-funded research and testing of *in situ* anaerobic bioremediation of perchlorate.

ii. *Bioreactors*. The Air Force Research Laboratory (AFRL) Materials and Manufacturing Directorate (Tyndall Air Force Base, Florida) led the way in developing bioreactor systems to treat process wastewater containing very high levels of perchlorate. Since 1997, a bioreactor based on the AFRL design has been treating wastewater from rocket motor production and demilitarization operations at a defense contractor facility near Brigham City, Utah. The first DoD facility to install a functional bioreactor (January 2001) for treating perchlorate-contaminated groundwater was the former Longhorn Army Ammunition Plant (LHAAP) in Karnack, Texas. The LHAAP functional bioreactor uses acetic acid as an electron donor and nutrient for the microbes, which then reduce the perchlorate to harmless chloride ions. Operation of the FBR is completely automated, and all chemical feed rates, inflow, and outflow rates, pH, and control valves are viewable and adjustable from the computer console that controls the groundwater treatment plant. The reactor vessel itself is 5 ft in diameter, and 21 ft tall, and has a 8 ft x 20 ft total footprint.

iii. *Ion Exchange*. Private sector organizations have been successfully applying ion exchange for many years for different applications. The DoD has been investigating the use of ion exchange to treat perchlorate-contaminated groundwater at Edwards Air Force Base (AFB), California. Edwards AFB will soon begin field-testing a new class of anion exchange resins in a conventional fixed-bed ion exchange system. The resins were originally developed by scientists at the Oak Ridge National Laboratory to treat groundwater contaminated by an anion that is chemically similar to perchlorate. Pilot-scale tests of the system were successfully completed in June 2001 and a full-scale system was installed in 2002.

iv. *Permeable Reactive Barriers*. PRBs can be installed in one of two ways: trench systems or funnel-and-gate systems. PRBs are increasingly being used to treat a variety of groundwater contaminants and are recognized as a cost-effective, passive remediation method. The DoD has successfully used PRBs to treat perchlorate at the Naval Weapons Industrial Reserve Plant McGregor 20 miles southwest of Waco, Texas. The McGregor PRB system consists of three individual trenches, with a combined length of approximately one mile, dug to a depth of up to 25 feet below ground surface. Each trench is backfilled with highly permeable, reactive material consisting of gravel (for drainage), organic material, and electron donor.

v. *Phytoremediation*. Research funded by the Air Force Aeronautic Systems Center (ASC) Engineering Directorate and conducted by the University of Georgia, and funded by the US Army Operations Support Command and conducted by the University of Iowa, confirm the ability of phytoremediation to remove perchlorate from contaminated soils and water. To date these efforts have been laboratory and bench scale experiments.

vi. *Soil Biotreatment*. The DoD is conducting field studies using in-situ and ex-situ soil biotreatment technologies to treat soils at the Naval Weapons Industrial Reserve Plant facility in McGregor, Texas and at the Longhorn Army Ammunition Plant in Karnack, Texas. Private industry is also demonstrating *in situ* soil biotreatment technologies in field tests at a site in California.

3. The DoD is also working toward a DoD-wide policy that will include standardized data elements for all installations to be included in any perchlorate survey.
4. There are currently three cross-functional perchlorate groups spearheaded by the DoD; 1) The Perchlorate Study Group; 2) The DoD Perchlorate Working Group; and, 3) The Interagency Perchlorate Steering Committee.
5.
6. DoD's Environmental Security Technology Certification Program (ESTCP) is also funding three projects to evaluate perchlorate treatment technologies.

NASA Perchlorate Activities

1. NASA has undertaken a very modest perchlorate treatment program focused on their singular site at the Jet Propulsion Lab in California. Their program is just gearing up and will include in-situ bioremediation developed by the Navy. They are also working with Calgon on a water polishing technology subsequent to the biotreatment.

Lawrence Livermore National Lab Perchlorate Activities

1. Lawrence Livermore's perchlorate program is focused on their Site 300 where perchlorate is commingled with other contaminants. As a result, the treatment program involves adding the perchlorate treatment to the treatments in use for other contaminants such as TCE. The treatment program selected for Lawrence Livermore includes bioreactors and bioremediation (phytoremdiation). In one location, they have installed an open tank bioreactor where the water is gravity fed. They employ a traditional bioreactor in another location. Both employ an SR-7 resin manufactured by Sybron Co. They are also using a form of phytoremediation by flowing contaminated water through containers with plants. The Lab has been successful in obtaining an interim Record of Decision (ROD) from EPA's Region IX.

Interim Conclusions

1. As soon as the issue of perchlorate health effects was raised, LANL began monitoring and reporting sources and concentrations.
2. Since 2001, NPDES monitoring and reporting to EPA, DOE, and NMED for TA-50 RLWTF and TA-16 HEWTF effluents.
3. Active sources of perchlorate contamination have been identified, mediated and virtually eliminated.
4. Perchlorate reduction activities completed or underway at LANL include:
    a. Replacement of HEPA Filters at the CMR Facility.
    b. Ductwork replacement and cleanup at TA-48.
    c. Perchlorate fume hood and ductwork wash down procedures implemented at TA 48 and TA-59.

d. Ion exchange installed at TA-50 RLWTF to remove perchlorate. Successfully decreased perchlorate in its effluent to <1 ppb.
e. Ion exchange at TA-16 HEWTF to remove perchlorate completed May 23, 2003.
f. Field-scale (feasibility study) installation of permeable reactive barrier in Mortandad Canyon.

5. Integration of activities related to measuring, monitoring and treatment is occurring.
6. Technical options for long-term mitigation of contamination are being identified and evaluated.
7. Developed a working relationship with DoD perchlorate action groups.
8. Improvement of the resolution of detection methods is in progress.

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Acronyms

AFB - Air Force Base
AFRL - Air Force Research Laboratory Materials and Manufacturing Directorate
AGEX I - Hydrodynamic testing
AGEX II - Explosively driven pulsed-power physics and high-energy-density physics
ARO - Advance Reverse Osmosis
B-1 - Bioscience Division McClintock Resource Group
B-2 - Bioscience Division Langham Resource Group
B-3 - Bioscience Division Szilard Resource Group
B-4 - Bioscience Division Michelson Resource Group
CAS - Chemical Abstract Service
C-DO - Chemistry Division
C-AAC - Chemistry Division Actinide Analytical Chemistry Group
C-ACS - Chemistry Division Actinide, Catalysis, and Separations Chemistry Group
C-ACT- Chemistry Division Applied Chemical Technologies
C-ADI - Chemistry Division Advanced Chemical Diagnostics and Instrumentation
C-INC - Chemistry Division Isotope and Nuclear Chemistry Group
C-PCS - Chemistry Division Physical Chemistry and Applied Spectroscopy
CHEM - Characterization High Energetic Materials Laboratory
CMR - Chemistry and Metallurgy Research Facility
DARHT - Dual-Axis Radiographic Hydrotest Facility
DOE-NNSA - Department of Energy National Nuclear Security Administration
DoD - Department of Defense
DoD-PWG – Department of Defense Perchlorate Working Group
DoD-SERDP - Department of Defense Strategic Environmental Research and Development Program
DX-DO - Dynamic Experimentation Division
DX-2 - Dynamic Experimentation Division Materials Dynamics Group
EMRTC - Energetic Materials Research and Testing Center
EPA - Environmental Protection Agency
ESA - Engineering Sciences and Applications
FBR-Fluidized bed reactors
FWO-WFM - Facilities and Waste Operations Division Waste Facilities Management Group
GEL - General Engineering Laboratories
HCP - Hazardous Control Plan
HE - High Explosives
HEWTF - High Explosives Waste Water Treatment Facility
HSR - Health, Safety, and Radiation Protection (HSR) formerly ESH
IPSC – Interagency Perchlorate Steering Committee
JPL – Jet Propulsion Lab
Kg - Kilograms
LANSCE-12 - Los Alamos Neutron Science Center
LANL - Los Alamos National Laboratory
LAUR - Los Alamos unlimited releases
LC/MS/MS - Liquid chromatography and tandem mass spectrometry technique
LHAAP - Longhorn Army Ammunition Plant
MCL - Maximum Concentration Limit
ME - Membrane Electrolysis
MST-6 - Materials Science and Technology Division Materials Technology Metallurgy Group
MST-7 – Materials Science and Technology Division The Polymers and Coatings Group
MST-8 - Materials Science and Technology Division Structure/Property Relations Group

MST-11 - Materials Science and Technology Division Electronic and Electrochemical Materials and Devices
NASA - National Aeronautics and Space Administration
NDMA - N-Nitrosodimethylamine
NMED-OB - New Mexico Environmental Department/Oversight Bureau
NMT-2 – Nuclear Materials Technology Division Actinide Process Chemistry
NMT-7 – Nuclear Materials Technology Division Waste Management / Environmental Compliance
NMT-11- Nuclear Materials Technology Division Actinide & Fuels Cycle Technologies
NNSA-AL AMP - Department of Energy National Nuclear Security Administration Albuquerque Operations Office Analytical Management Program
NPDES - National Pollutant Discharge Elimination System
O - Otowi
P-23 - Physics Division Neutron Science and Technology Group
P-24 - Plasma Physics Group
PHERMEX - Pulsed High-Energy Radiographic Machine Emitting X-Rays
PM- Pajarito Mesa
ppb - Part per billion
PRB - Permeable Reactive Barrier
Pu - plutonium
RC - Radiochemistry
R&D - Research and Development
RfD - Draft reference dose
RLWTF - Radioactive Liquid Waste Treatment Facility
RRES-WQH - Risk Reduction and Environmental Stewardship Division Water Quality & Hydrology Group
SDW - Safe Drinking Water
TA - Technical Area
TCE - Trichloroethylene
Ula - Nevada Test Site facility for the underground testing of special nuclear materials
UCMR - Unregulated Contaminant Monitoring Rule
USGS - U.S. Geological Survey
VOCs - Volatile organic compounds
WAC - Waste Acceptance Criteria
TSH - Thyroid-stimulating hormone

Los Alamos National Laboratory Perchlorate Issues Update

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Executive Summary

Perchlorate Issue at Los Alamos National Laboratory

Perchlorate is utilized at the laboratory in two forms, perchlorate salts (of various forms but primarily magnesium, sodium, potassium and some ammonium) and perchloric acid ($HClO_4$). Perchlorates, because of their strong oxidizing potential, are currently the primary ingredient of explosives and propellants. Perchloric acid, because it is non-complexing and an excellent oxidant when heated, is used in actinide research.

Concern

In 1998, perchlorate was placed on the Environmental Protection Agency (EPA) Contaminant Candidate List for consideration for possible regulation. In 1999, EPA required drinking water monitoring for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). In 2001, •LANL's NPDES Permit requires perchlorate monitoring at Technical Area (TA) 50 Radioactive Liquid Waste Treatment Facility (RLLWTF) & TA-16 High Explosive Waste Treatment Facility (HEWTF). The state of New Mexico is proposing to add perchlorate to its list of toxic pollutants [groundwater and surface water] this year. The Laboratory already has a legacy problem with perchlorates in shallow, intermediate and deep groundwaters underlying the Lab. EPA's guidance range is 4-18 ppb (μg/l).

Current Operations Using Perchlorates

1. Dynamic Experimentation (DX) Division uses small amounts of perchlorate salts and perchloric acid in development of propellants. Liquid high explosive (HE) wastewater is sent to the High Explosives Waste Water Treatment Facility (HEWTF) at TA-16.
2. Actinide research using perchloric acid is conducted at TA-3, TA-48, and TA-59. Perchloric acid fuming or sample preparation is conducted only in fume hoods dedicated for this activity. Wastewater from these facilities goes to the Radioactive Liquid Waste Treatment Facility (RLWTF) at TA-50.

Past Operations Generated Legacy Waste

1. Wastewater and contaminated stormwater generated within the HE corridor (since the early 1940's) has been discharged into Pajarito Canyon, Water Canyon and Cañon de Valle, through a number of outfalls with no perchlorate treatment. Effluent samples at HEWTF show a range of perchlorate concentrations from 4 to 58 ppb.
2. Perchlorates in treated effluents, from actinide research, were discharged into Mortandad canyon for a period of approximately 40 years (ion exchange treatment added in 2002).

Perchlorate levels ranging from 140 ppb (perched groundwater) to 400 ppb (core sample) have been detected.

3. Acid Canyon (tributary of Pueblo Canyon) received wastewater from actinide research from 1943 to 1951, and treated effluents containing residual radionuclides from 1951 to 1964. Perchlorates, at concentrations of about 2 to 4 ppb have been detected in water supply well, Otowi-1 (O-1), in Pueblo Canyon.
4. DP Canyon received effluent from actinide research (the plutonium processing facility at TA-21), from 1952 to 1986. Perchlorate concentrations, in the core samples, of 200 to 1000 ppb have been detected in wells drilled down gradient from TA-21.
5. Pajarito Canyon received wastewater from high explosives synthesis and testing operations (TA-9) from 1952 to 1997. In 2003, high explosives wastewater, from the Anchor East Site (TA-9), has been recently analyzed and revealed perchlorate concentrations of over 500 ppb.
6. Ten Site Canyon (tributary to Mortandad Canyon) received insufficiently treated wastewater from the Ten Site Wastewater Treatment Plant (TA-35) from 1951 to 1963.

Successes in Managing Perchlorate Compound Risks (including shock sensitivity and environmental releases)

1. In March of 2001, LANL completed the replacement of 720 filters contaminated with perchlorates and radionuclides, at the CMR facility. Since that time, perchloric acid fuming has been limited to one (1) dedicated fume hood, located in Wing 5. A wet scrubber is installed in this hood as a practical technique for eliminating deposition of perchlorate salts in the ductwork and air emissions.
2. Perchlorate fuming operations at TA-48 and TA-59 are now restricted to fume hoods dedicated for this activity. Remediation includes wash down of hoods and exhaust ductwork, with all wastewater sent to TA-50 for treatment. In addition, investigations are ongoing for the replacement of perchloric acid in some sample preparation procedures; one option under study is microwave digestion.
3. Installation of an ion exchange treatment system at the TA-50 RLWTF reduced perchlorate in the effluent to < 1 ppb.
4. An ion exchange was installed at the TA-16 HEWTF and became operational May 23, 2003.
5. New buildings for explosives research are being designed to eliminate waste streams Characterization of High Energetic Materials (CHEM) Laboratory Building: Case Study (LAUR-03-2317).

Immediate and Ongoing Actions

1. Continue surface water monitoring
2. Continue groundwater monitoring onsite at observation wells and offsite at LA & SF production wells.
3. Subsurface characterization of perchlorate contamination; extent, fate, and transport.
4. Analytical improvement. The EPA has approved one analytical method for the analysis of perchlorate with a detection limit of 4 ppb in natural waters. Lab and collaborator development of a low-level perchlorate analysis method by coupling liquid chromatography and tandem mass spectrometry technique (LC/MS/MS) is ongoing.
5. Identify points of treatment/control for legacy perchlorates.

6. Source reduction.
7. Replacement of effluent and sampling lines (where suspected radiological contamination exists) at the RLWTF.
8. Conduct public meeting to discuss known LANL perchlorate issues and collect public citizen concerns.

Long Term Needs

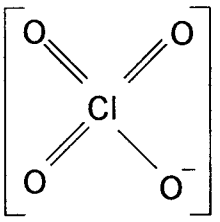
1. Establish up gradient/upstream surface and groundwater monitoring.
2. Develop an analysis for technological solutions/approaches.
3. Research and development for improved treatment options for legacy wastes.
4. Evaluation of where treatment is best applied.
5. Evaluation of perchlorate generation/formation in piping, ducts, filters, or sumps.
6. Evaluation of airborne discharges and their expected impact on subsequent surface contamination.
7. Coordination amongst perchlorate users to establish key facilities and appropriate controls.
8. Address treatment mandates that focus on contaminants on a species by species basis and anticipate future issues? Conduct additional characterization of historical perchlorate issues and the extent of contamination from releases.

Introduction

Perchlorate has become a national regulatory and public health concern due to the potential health effects of perchlorate in drinking water. In 1998, perchlorate was placed on the Environmental Protection Agency's (EPA) Contaminant Candidate List for consideration for possible regulation. In 1999, EPA required drinking water monitoring for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). EPA's guidance range is 4-18 ppb (parts per billion – ppb or μg/l). The state of New Mexico is proposing to add perchlorate to its list of toxic pollutants [groundwater and surface water] this year. Due to the extensive historical use and aqueous-and vapor-phase releases of perchlorate, or precursors to perchlorate, at Los Alamos National Laboratory (LANL) perchlorate is present in shallow, intermediate and deep ground waters underlying the Laboratory. The New Mexico Environmental Department/Oversight Bureau (NMED-OB), using an experimental LC/MS/MS method detected perchlorate at 0.5 ppb in one Technical Area 3 (TA-3) drinking water sample; this had not been confirmed by LANL sampling. In order to proactively address this problem, a team of experts from across the Laboratory has been pulled together to gather background information on perchlorate, the processes generating perchlorate waste streams, human health and environmental risks associated with perchlorate in the environment, technical options for elimination, and economic implications of any proposed plans and ideas. The team used a comprehensive approach to provide recommendations that may help eliminate future potential "problem" contaminants (e.g. other ions like perchlorate). Several internal and external organizations have already researched this issue and are providing technical solutions to the problem. Their research and recommendations are referenced at the end of this document

Perchlorate Structure and Nationwide Use

Perchlorate (ClO_4^-) is the soluble anion associated with the solid salts of ammonium, potassium, magnesium, and sodium perchlorate. Another common commercial form is perchloric acid ($HClO_4$).



Ammonium perchlorate (NH_4ClO_4) is manufactured as an oxygen-adding component in solid fuel propellant for rockets, missiles, explosives and fireworks. Solid rocket fuels typically consist of ammonium perchlorate (potassium perchlorate or sodium perchlorate may also be used), which serves as the oxidizer; aluminum, which serves as the fuel; a binder; and a plastic that serves to give the material its rigidity. Large-scale production of ammonium perchlorate began in the United States in the mid 1940's. Ammonium perchlorate has a limited shelf life, and must be periodically replaced in munitions and rockets, or in inventory. This has lead to the disposal of large volumes of the compound since the 1940's in Nevada, California, Utah, and likely other states. Examples of industrial sites contaminated with perchlorate are listed in Table 1. About 90% of perchlorate compounds produced by major U.S. manufacturers has been shipped as ammonium perchlorate for use as rocket fuel oxidizer.

Table 1. A Partial List of Characterized Perchlorate Contaminated Sites with Identified Co-Contaminants

Site	Contaminated Media	Other Identified Contaminates	Identified Perchlorate Degradation Products
Aerojet Facility, Rancho Cordova, CA	Groundwater	Tichloroethylene (TCE), N-nitrosodimethylamine (NDMA), nitrate, sulfate	
Aerojet Facility, San Gabriel, CA	Groundwater	Nitrate, TCE	
Big Dalton Well Site, Los Angeles, CA	Groundwater	Nitrate, sulfate	
La Puente, CA	Groundwater	NDMA, 1,4-dioxane, sulfate, volatile organic compounds (VOCs)	
Confidential site	Groundwater	Nitrate	Chlorate
DoD site, WV	Groundwater	Nitrate, sulfate	
Edwards Air Force Base, CA	Groundwater	Nitrate, sulfate	
Henderson, NV	Groundwater	Sulfate, sodium, calcium, magnesium, nitrate, boron, hexavalent chromium	Chlorate, chloride
Lawrence Livermore National Laboratory, Site 300, Livermore, CA	Groundwater	VOCs, nitrate, explosive compounds	
Pueblo Chemical Depot, CO	Soil, Groundwater	HMX, RDX, nitrate	

As can be seen in Table 1, the most common co-contaminants at sites are nitrate and sulfate. Co-contaminants may be significant for treatment option considerations (interference) and also for use as tracers at contaminated sites.

Potassium perchlorate ($KClO_4$), until recently was used to treat hyperthyroidism resulting from Grave's disease, and is still used diagnostically to test thyroid hormone production in some clinical settings. In addition, potassium perchlorate is used in breathing equipment on Air National Guard aircraft and in naval emergency escape equipment. Other uses of perchlorate salts include in nuclear reactors and electronic tubes, as additives in lubricating oil, in tanning and finishing leather, as a fixer for fabrics and dyes, and in electroplating, aluminum refining, rubber manufacture, and production of paints and enamels. Potassium perchlorate is believed to be the original source for a fraction of the perchlorate contamination found in the U.S., however, most of the contamination appears to have come from the legal discharge decades ago of then unregulated waste effluents containing high levels of ammonium perchlorate.

Perchlorate originates as a contaminant in ground water and surface waters when the salts of ammonium, potassium, magnesium, or sodium dissociate in water, as shown for ammonium perchlorate in equation 1.

$$NH_4ClO_4(s) \xrightarrow{water} NH_4^+(aq) + ClO_4^-(aq) \quad (1)$$

Salts of perchlorate have different solubility in water, with potassium perchlorate being the least soluble (Table 2). In groundwater, the perchlorate ion is highly mobile, migrating faster than many other ground water contaminants. It is repelled by the predominantly negatively-charged subsurface minerals, precluding adsorption reactions that serve to retain other uncharged or positively-charged contaminants. It can persist in the environment for many decades under typical ground water and surface water conditions because of its resistance to reactions with other available constituents.

Table 2. Properties of Perchlorate Compounds

Properties	Ammonium Perchlorate (NH_4ClO_4)	Potassium Perchlorate ($KClO_4$)	Sodium Perchlorate ($NaClO_4$)	Perchloric Acid ($ClHO_4$)
Chemical Abstract Service (CAS) #	7790-98-9	7778-74-7	7601-89-0	7601-90-3
Density/Specific Gravity	1.95 g/cm^3	2.53 g/cm^3	2.52 g/cm^3	1.67 g/cm^3
Solubility	200 g/L water @ 25°C	15 g/L water @ 25°C	2096 g/L water @ 25°C	Miscible in cold water
Sorption Capacity	Very low	Very low	Very low	Very low
Volatility	Nonvolatile	Nonvolatile	Nonvolatile	Volatile

Areas of natural occurrence of perchlorate are rare; however one natural source of solid perchlorate is found in potassium nitrate in Chile (Chile saltpeter), which may be used in chemical fertilizer originating from Chile. All types of nitrate products (nitric acid, etc.) were manufactured with Chilean Nitrate in years past. Today, it is mostly used for fertilizer. The United States Geological Survey (USGS) and the Air Force Research Laboratory have also found potassium perchlorate in samples of sylvite in New Mexico. Additional areas of natural occurrence of perchlorate have not been identified, but are speculated to exist, based on confirmed existence of several species of perchlorate-reducing microorganisms. In fact, perchlorate-reducers are increasingly predicted to be ubiquitous in nature, as they have been found in many locations, both contaminated and uncontaminated. The reason for their existence in uncontaminated soils is currently not known.

Releases of perchlorate to the environment have been reported in over 21 states nationwide. Many of the known releases are from sites that utilized one or more of the salts of perchlorate and include manufacturing sites, Department of Defense (DoD) sites, National Aeronautics and Space Administration (NASA) and associated sites, and industrial sites. The DoD sites associated with potential and known perchlorate releases are scattered across the United States (U.S.). These sites range from active military bases and ranges to some abandoned and formally

used sites reassigned to civilian use. NASA and some of its contractors use perchlorate in many operations. Industry also uses perchlorate compounds in the manufacture of various products and in processes to make products. Low levels of perchlorate contamination have also been found in association with certain nitrate plumes of agricultural origin. As further environmental testing for perchlorate is completed, more impacted areas may be found.

Contamination is extensive in California where perchlorate has been detected in 255 drinking water sources with 49 wells containing concentrations greater than 18 ppb. Two public water supply systems in New Mexico, Clovis and Deming, are reported to contain perchlorate concentrations greater than 4 ppb. At Clovis, a maximum perchlorate concentration of 5 ppb was reported and the Cannon Air Force Base has reported a perchlorate concentration of 24 ppb. Samples from the Deming water system were collected under the Safe Drinking Water (SDW) UCMR and perchlorate concentrations of 16 ppb were found. The sources of contamination at the Clovis and Deming sites have not been determined.

Health Issues

The toxicity of perchlorate is the subject of an active and ongoing research program. Perchlorate exerts its effect not by reacting with organs or cells, but by impeding another process. Cells in the thyroid gland (as well as the salivary and gastric glands), possess an iodide pump that brings iodide ions into the cell for subsequent generation of iodinated hormones. The pump discriminates among anions on the basis of size; consequently, perchlorate (and other large anions) interferes with this process by competing for uptake. However, unlike iodide, which is then incorporated into hormones, the perchlorate simply blocks iodide uptake. The result is lower intrathyroid-iodide and thus lower hormone output. As a result of decreased thyroid hormone production, the pituitary gland releases more thyroid-stimulating hormone (TSH), causing the thyroid to grow. The toxic effect of this perchlorate interaction is an active area of research, with most activity focusing on the above mentioned potential of perchlorate to hinder the synthesis of thyroid hormones and/or the subsequent consequences resulting from the decrease in thyroid hormones. In adults, the thyroid helps to regulate metabolism. In children, the thyroid plays a major role in proper development in addition to metabolism. Impairment of thyroid function in expectant mothers may impact the fetus and newborn and result in effects including changes in behavior, delayed development and decreased learning capability. Changes in thyroid hormone levels may also result in thyroid gland tumors.

In addition to the thyroid gland, perchlorate can also directly affect organs and tissues. The mouse mammary gland has a mechanism similar to the thyroid iodide pump that is inhibited by perchlorate; however, it is unclear whether this has any significance for human health. Much of what is known about perchlorate's effects on living organisms is derived from studies of acute toxicity over relatively short periods of time rather than chronic exposure to very low concentrations over a lifetime.

Applicable Drinking Water Regulations

Currently, no state or federal drinking water standard exists for perchlorate. EPA added perchlorate to its Contaminant Candidate List —a list of new contaminants being assessed for regulation—in 1998. In 1999, the EPA issued interim guidance for perchlorate recommending a provisional action level in the 4-18 ppb range. During this same year the EPA also initiated a

requirement for the monitoring of drinking water, for perchlorate, under the UCMR. Under the UCMR, all large public water systems and a representative sample of small public water systems are required to be monitored for perchlorate over the next two years to determine whether the public is being exposed to perchlorate in drinking water nationwide.

In March 2002, the EPA released the results of its long-awaited draft toxicity assessment for perchlorate. The draft assessment concludes that the potential human health risks of perchlorate exposure include (1) interference with iodide uptake and disruption of normal thyroid function, (2) impacts to the developing nervous system in the fetus and newborn, and (3) tumor formation. The draft assessment established a draft reference dose (RfD) for perchlorate in drinking water of 0.00003 mg/kg/day resulting in a derived Maximum Concentration Limit (MCL) of 1 ppb drinking water standard. The preliminary human health risk estimates established by the assessment are undergoing review and do not represent EPA policy at this time. In January 2003, the EPA reaffirmed their 4-18 ppb interim guidance as appropriate in the absence of a finalized risk benchmark for perchlorate. A final rule is not expected until 2004, at the earliest.

A 2002 perchlorate health effects assessment, conducted by the Oregon Health & Science University, Portland, OR, found EPA's proposed 1 ppb MCL standard to significantly understate how much perchlorate exposure is "safe". This analysis recommends a drinking water equivalent of 300 ppb as protective. Further information on this study is available at, http://ehpnet1.niehs.nih.gov/docs/2002/110p927-937greer/abstract.htm

Nationwide, many states have established action or advisory levels for perchlorate, but none has set enforceable standards. Current action/advisory levels range from 1 ppb in Maryland and Massachusetts, 4 ppb in California and Texas, 14 ppb in Arizona, to 18 ppb in Nevada. The State of New Mexico has proposed adding perchlorate to the Water Quality Control Commission Regulations as a toxic pollutant; toxic pollutants are not assigned a specific numerical limit or standard, but are risk-based contaminants (lifetime risk greater than one cancer per 100,000 exposed persons). A hearing on the adoption of perchlorate as toxic pollutant has been scheduled for June 2003 before the New Mexico Water Quality Control Commission.

Water Supply System Monitoring

Monitoring of the Los Alamos Water Supply System for perchlorate began in late 1997 following the discovery of perchlorate in California drinking water wells – two years prior to EPA guidance on testing requirements. Two rounds of sampling were conducted in 1997 and 1998 at the "entry points to the distribution system". All sample results in 1997 and 1998 were non-detect for perchlorate. All samples were analyzed using EPA Method 314 (Ion Chromatography). See Table 3.

Table 3. EPA Analytical Method 314 for Perchlorate

Analytical Method For Perchlorate		
Method	Method Detection Limit (ppb)	Reporting Limit/Practical Quantitation Limit (ppb)
Ion Chromatography (de ionized water)	1	NA
Ion Chromatography (natural water)	4	12

Beginning in 2000, many environmental water samples collected around LANL have been analyzed for perchlorate:

- All groundwater and many surface water samples collected at environmental monitoring stations;
- Samples from water supply wells operated by Los Alamos County, San Ildefonso Pueblo, and City of Santa Fe (2001); and
- Water samples from wells drilled for the Hydrogeologic Workplan.

In June 2000, a sample from water supply well Otowi-1 (O-1) was reported to contain 3.5 ppb perchlorate. In response, the Laboratory issued a press release regarding this discovery. Following the detection at O-1, the joint Laboratory-Los Alamos County Water Quality Steering Committee recommended monthly sampling of O-1. O-1 is a standby water supply well for Los Alamos County and the County is currently managing this well based on information provided by the LANL Water Quality Steering Committee.

Perchlorate was detected in 10 of the 14 samples collected from O-1 in 2000 at an average concentration of 2.48 ppb. Perchlorate was not detected in any of the other 11 water supply wells during 2000. All samples in 2000 were analyzed for perchlorate using EPA Method 314, Ion Chromatography.

Monthly monitoring and reporting to Los Alamos County for perchlorate was expanded in 2001 and 2002 to include water supply wells Pajarito Mesa–3 (PM-3) and PM-5, in addition to O-1. Also, semi-annual monitoring was instituted at the remaining nine water supply wells. During 2001 and 2002, perchlorate monitoring continued to confirm the presence of perchlorate in O-1 at concentrations between 2 ppb to 4 ppb. While estimated detections (<4 ppb) were reported at other water supply wells, none were repeatable and were attributed to deficiencies in the ion chromatography method; at concentrations between the method's reporting limit (12 ppb) and the detection limit (4 ppb) the ion chromatography method is imprecise due to interference by other ions in the sample matrix. Additional discussion on analytical methods is provided in the section, *Search for Lower Perchlorate Detection Limit.*

The Laboratory is continuing to conduct monthly monitoring at PM-3, PM-5, and O-1 and semiannual monitoring at the remaining nine water supply wells in 2003. Beginning in May

2003, water supply wells PM-1, PM-2, and PM-4 will be added to the monthly monitoring schedule.

In January 2003, the NMED-OB reported that a sample of tap water from TA-3 showed perchlorate at a concentration of 0.24 ppb. A follow-up sample showed perchlorate at a concentration of 0.5 ppb. Both samples were analyzed using a new, low-level analytical technique for perchlorate called liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS). The LC/MS/MS is an analytical method in development and has not been approved by the EPA for perchlorate analysis. It is discussed further in a later section.

Beginning in 2003, the NMED, Drinking Water Bureau, will begin monitoring the Los Alamos Water System for perchlorate under the SDW UCMR. Data collected under the UCMR provides the EPA with information on the occurrence of emerging contaminants and is used to support regulatory decision-making.

Detailed and complete water monitoring data can be found in the LANL Environmental Surveillance Reports, http://eshint.lanl.gov/publications.shtml#environmental.

Current Laboratory Perchlorate Use

Perchlorate is utilized at the laboratory in two forms, perchlorate salts (of various forms but primarily magnesium, sodium, potassium and some ammonium) and perchloric acid ($HClO_4$). Perchloric acid is used in actinide research because it is non-complexing and an excellent oxidant when heated.

Perchloric acid and actinide chemistry

The group of elements known as the actinides consists of the elements from actinium (element 89) to lawrencium (element 103), in the periodic table. All actinides are metals and all are radioactive. As a result, they dominate the study of nuclear chemistry. Fundamental understanding of actinides is needed to assess the nation's nuclear stockpile, help stem the clandestine proliferation of nuclear weapons, and to understand the implications of nuclear fuels' (such as enriched uranium) use and storage.

Stockpile stewardship, DOE's program for certifying the long-term safety and performance of the enduring stockpile without underground nuclear testing, has resulted in increased importance of assessing and predicting the long-term behavior of actinides. A major focus is on obtaining a better scientific understanding of the isotopes uranium-235 and, especially, plutonium-239; the two actinides of most interest to Los Alamos scientists.

Plutonium (Pu) is the most complex and perplexing element in the periodic table. The element's complexity stems in part from its mercurial nature. Depending on temperature, it assumes one of six different oxidation states, each with different density, volume and chemical properties. Virtually all plutonium is currently produced in a metallic state; as a consequence, initial solution preparation for research purposes involves dissolution of the metal. Because of its highly electropositive nature, plutonium metal is soluble in a number of mineral acids and plutonium ions in solution commonly exist in the (III), (IV), (V), and (VI) oxidation states, as Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_3^+, respectively. The oxidation state produced by dissolution of plutonium is

dependent on the acid employed and can be analytically determined by absorption spectrum. However, because perchloric acid tends to be non-complexing (spectra of perchloric acid solutions reflect plutonium ions containing only water molecules in the coordination sphere), and can sequentially oxidize plutonium, from oxidation state III through VI, by heating, it has been extensively used. In solutions containing more strongly complexing anions the spectra are generally different, complicating the interpretation of spectrometry results. The complexation tendencies of the more common anions were found to decrease in the order

$$F^- > NO_3^- > Cl^- > ClO_4^-$$

With perchloric acid, it is possible to prepare Pu(III), (IV), and (VI) solutions of greater than 99% purity, and Pu(V) solutions of 97 ± 3% purity.

Facilities and technical areas within the laboratory, with current perchloric acid chemical inventories include the CMR, TA-3; the Sigma Complex (Sigma building), TA-3; Radioactive Liquid Waste Treatment Facility (RLWTF), TA-50; Occupational Health, TA-59; Radiochemistry, TA-48; the Anchor East Site, TA-9; Health Research Lab, TA-43; and TA-46. See Table 4.

Table 4. LANL Technical Areas with Perchloric Acid Chemical Inventories

Technical Area	Building	Division	Group
TA-3	CMR	Chemistry	Actinide Analytical Chemistry (C-AAC)
TA-3	Sigma building	Materials Science and Technology	Materials Technology Metallurgy (MST-6) Structure/Property Relations (MST-8)
TA-9	0029	Dynamic Experimentation	Materials Dynamics (DX-2)
TA-43	0001	Bioscience	Langham Resource (B-2)
TA-46	217	Bioscience	Michelson Resource (B-4)
TA-48	0001	Chemistry	Isotope and Nuclear Chemistry (C-INC)
TA-48	0045	Chemistry	C-INC
TA-50	0001	Facilities and Waste Operations	Waste Facilities Management (FWO-WFM)
TA-59	0001	Chemistry	Actinide, Catalysis, and Separations Chemistry (C-ACS)

Ammonium perchlorate and explosives research

The Dynamic Experimentation (DX) Division is the Laboratory's primary experimental resource for high explosives research for maintaining a safe and reliable nuclear weapons stockpile in the absence of nuclear testing. DX Division personnel perform research, engineering, and experimentation on high explosives and dynamic processes essential to the success of the nation's Science-Based Stockpile Stewardship program. The division's stockpile management

responsibilities include the manufacture of production detonators for the stockpile and surveillance of stockpile detonators and energetic materials. The division operates and maintains a suite of explosives firing sites—both locally and at the Nevada Test Site—with state-of-the-art diagnostics that include world-class radiographic machines.

DX Division encompasses the following principal programs and facilities:

- AGEX I—hydrodynamic testing
- AGEX II—explosively driven pulsed-power physics and high-energy-density physics
- Detonator production
- High-explosives (HE) science
- Department of Defense Programs - advanced conventional munitions development
- PHERMEX—Pulsed High-Energy Radiographic Machine Emitting X-Rays
- DARHT—Dual-Axis Radiographic Hydrotest facility (under construction)
- U1a—Nevada Test Site facility for the underground testing of special nuclear materials

DX Division uses small amounts of perchlorate salts and perchloric acid to develop propellants. DX-2 is a group within the DX division at LANL concerned with all aspects of high explosives (HE) from cradle to grave. These aspects include chemistry, engineering, materials properties, and physics related to the synthesis, formulation, performance, and safety of explosives; monitoring and surveillance of explosives in the enduring nuclear stockpile; unique applications of explosives; and environmentally-conscious destruction/disposal of explosives and explosive devices. The two areas where perchlorate is used (in small amounts) are organic synthesis and propellants. The synthesis of new explosive compounds is the most chemical-intensive operation, involving an an almost unlimited number of small amounts of inorganic and organic chemicals. Most syntheses produce milligram quantities of new compounds. However, following testing, large quantities may be synthesized for use in pilot scale experiments. Larger quantities of chemicals and glassware are often needed for the preparation of precursors and intermediates in the synthesis process. Large fume hoods are required for this process.

Wastewater generated by DX is sent to the Engineering Sciences and Applications (ESA) High Explosives Waste Water Treatment Facility (HEWTF). An ion exchange installed at the TA-16 HEWTF (installed and operational as of May 23, 2003) provides treatment of liquid wastewater, contaminated with both HE and perchlorate, prior to discharge.

Technical areas within the laboratory, with current perchlorate (various) chemical inventories include the TA-3, 9, 35, 43, 46, 48, 50, 53, and 55. See Table 5.

Table 5. LANL Technical Areas with Current Perchlorate Salt (Various) Chemical Inventories

Technical Area	Building	Division	Group
TA-3	CMR	Chemistry	Actinide Analytical Chemistry (C-AAC)
TA-3	Sigma building	Materials Science and Technology	Materials Technology Metallurgy (MST-6) Electronic and Electrochemical

			Materials and Devices (MST-11)
TA-9	0021	Dynamic Experimentation	Materials Dynamics (DX-2)
TA-9	0029	Dynamic Experimentation	DX-2
TA-35	0085E	Bioscience	Szilard Resource (B-3)
TA-35	0085W	Chemistry	Applied Chemical Technologies (C-ACT)
TA-43	0001	Bioscience	Langham Resource (B-2)
TA-43	0001	Bioscience	McClintock Resource (B-1)
TA-43	0001	Materials Science and Technology	Superconductivity Technology Center
TA-46	0031, 0154, 0158	Chemistry	Physical Chemistry and Applied Spectroscopy (C-PCS)
TA-46	0041, 0154	Chemistry	Advanced Chemical Diagnostics and Instrumentation (C-ADI)
TA-46	0076	Chemistry	Actinide, Catalysis, and Separations Chemistry (C-ACS)
TA-46	0158	Bioscience	Michelson Resource (B-4)
TA-46	0250	Materials Science and Technology	Materials Integration Science Laboratory
TA-46	0250	Chemistry	C-ACT
TA-48	0001	Chemistry	Isotope and Nuclear Chemistry (C-INC)
TA-48	0001	Nuclear Materials Technology	Actinide Process Chemistry (NMT-2)
TA-48	0001	Chemistry	C-ACS
TA-48	0001	Chemistry	Division Office (C-DO)
TA-50	0001	Facilities and Waste Operations	Waste Facilities Management (FWO-WFM)
TA-53	0001	Physics	Neutron Science and Technology (P-23)
TA-53	0622	Los Alamos Neutron Science Center (LANSCE)	LANSCE-12
TA-55	0001	Nuclear Materials Technology	Actinide & Fuels Cycle Technologies (NMT-11)

Waste profile forms have identified perchlorate waste at the laboratory, which is packaged and transported to TA-54 for storage at Area L. For the fiscal years 2000 through 2002, the following table details the volume (in kilograms) of perchlorate containing waste disposed, by group. See Table 6.

Table 6. Perchlorate Waste Disposal

Group	FY 2000	FY 2001	FY 2002
B-DO			0.95
C-AAC			0.67
C-ACS		5.5	1.89
C-ACT		0.2	0.11
C-FM*		5499.5	35.8
C-SIC			0.91
DX-2	2.01	0.11	
E-ET	1.4	2.04	
ESH-5 (now HSR)		0.07	
FWO-SWO		2.04	
P-24		1.4	
MST-6	5.5	3.8	2.4
MST-7	5.9	0.6	0.2
MST-8	3.3		
MST-11	6.5	1.06	0.7
NMT-1	0.9		
NMT-7		0.57	5.8
Total	**25.51**	**5516.89**	**49.43**

*The FY 2001 and 2002 perchlorate waste generated by the Chemistry Division Facility Management Group (C-FM) was almost entirely contaminated ductwork, decon water, and duct wash down sludge from the perchlorate cleanup up at TA-48, building RC-1.

Successes in Managing Perchlorate Compound Risks (including shock sensitivity and environmental releases)

Replacement of HEPA Filters at CMR: Risk Reduced by Comprehensive Waste Characterization (LAUR-02-0339): The laboratory Chemistry and Metallurgy Research Facility (CMR) has been operating since 1952, providing actinide and analytical chemistry and materials characterization in support of stockpile surveillance, pit manufacturing, stockpile lifetime extension, and nuclear weapons certification. During this time, perchloric acid has been fumed as part of performing actinide chemistry at the CMR facility. This has resulted in the deposition of perchlorate in the ductwork of the facility's ventilation systems. Both the exhaust from glove boxes and fume hoods are discharged to a common duct that is filtered to remove airborne toxic and radioactive particulates before discharge. In March of 2001, LANL completed the replacement of 720 filters contaminated with perchlorate and radionuclides, at the CMR facility. Since that time, perchloric acid fuming has been limited to one (1) dedicated fume hood, located in Wing 5. A wet scrubber is installed in this hood as a practical technique for eliminating deposition of perchlorate salts in the ductwork and air emissions.

Perchlorate Fuming Operations at TA-48 and TA-59: Two buildings at TA-48 are used for actinide research, Radiochemistry 1 (RC-1) and RC-45. As was the case at the CMR facility, the RC-1 building also underwent perchlorate contamination cleanup of the ductwork beginning in 2001. Since that time a new Hazard Control Plan (HCP-CFM-010.2) was implemented for perchlorate work. Perchloric acid use is currently limited to approved, labeled hoods that exhaust to ductwork equipped with wash down systems. Wash down systems prevent the build up of perchlorate in the ductwork, but does not prevent the exhaust of perchlorate in the air stream. Hoods that are approved for perchloric fuming have labels stating "Perchloric acid fuming permitted. No organics permitted." Two types of wash downs are performed: hood wash downs and ductwork wash downs. The user performs the hood wash down following the fuming of perchloric acid in the hood. The Facility Coordinator performs the ductwork wash down following user hood wash downs (on the same day as perchloric acid fuming), and at least weekly (regardless of perchloric acid fuming) while the laboratories are in operational mode. Each hood and ductwork wash down is for a minimum of 10 minutes.

The facilities at RC-45 are currently rewriting HCP's and will specifically address perchlorate fuming in the new revisions. Currently, perchlorate fuming is handled under HCP-C-INC-004, and requires hood wash downs following use and routine wash downs of the facility exhaust ductwork, by the facility coordinator (note, at the time of this draft the schedule of the routine wash downs, by the facility coordinator, had not been specified). This facility processes approximately 1500 samples a year, and each sample requires 0.25 – 0.50 ml of perchloric acid.

Perchloric acid fuming has also been a required activity for sample preparation at TA-59. Historically, approximately 1 to 2 liters of perchloric acid were fumed a year. Two groups at TA-59 have conducted perchloric acid fuming for sample preparation in the past, Radiochemistry and Inorganic Analysis. Perchloric fuming of samples within the Inorganic Analysis team has been replaced by microwave digestion. The Radiochemistry team is currently evaluating alternative sample preparation methods also. One alternative method is high temperature muffling, to rid the samples of organics, and it would eliminate the use of perchlorate. Any perchlorate operations that currently occur are conducted in a dedicated fume hood with wash down procedures.

Wastewater from all of these facilities goes to the RLWTF at TA-50.

Testing Perchloric Acid Fume Scrubber at TA-59: The Isotope and Nuclear Chemistry Group (C-INC) are testing the performance of a perchloric acid fume scrubber. The use of fuming perchloric acid in chemistry operations is severely limited because of safety concerns about the buildup of potentially explosive perchlorate salts in fume hoods and ducts. Perchloric acid fuming operations are restricted to only a few approved hoods with wash down capability. Researchers from C-INC are testing an acid fume scrubber that removes the perchloric acid fumes before they enter the fume hoods and ductwork. The perchloric acid fumes pass through a water spray that captures the perchloric acid. The wastewater can then be disposed of normally or, if necessary, treated prior to disposal. The scrubber unit uses much less water than is presently required to wash down the fume hoods and ducts. The scrubber is portable and can be moved to wherever it is needed. Testing will take place at TA-59 and, if successful, the unit will be deployed at TA-48.

Perchlorate Reduction at TA-50 RLWTF (LAUR-01-6519): During the Spring of 2000, it came to the attention of the RLWTF management that the presence of perchlorate in the RLWTF effluent needed to be addressed. Typically, perchlorate concentrations in the RLWTF effluent were in the range of several hundred ppb. As a result, a perchlorate waste stream survey was performed to identify generators of perchlorate waste at LANL. Additionally, a best available treatment survey for perchlorate was performed. It was concluded from this survey that ion exchange would be the best option for the RLWTF waste stream. Pilot scale ion exchange tests were begun in September 2000 and continued until June 2001 to quantify the effectiveness of ion exchange removal of perchlorate and to identify the most effective ion exchange resin. Design and installation of the full-scale treatment system for the RLWTF effluent stream was completed in March 2002. Since March of 2002 the perchlorate in the effluent from the RLWTF has been less than 1 ppb.

Waste Minimization or Elimination Through Sustainable Building Design
The Characterization of High Energetic Materials (CHEM) Laboratory Building: An NNSA Waste Stream Elimination Case Study (LAUR-03-2317): Los Alamos National Laboratory management (Associate Director for Operations) has requested an evaluation of the impact of eliminating waste streams on Laboratory operations. A case study has been developed using the CHEM Laboratory Building, which is being proposed as part of the DX Strategic Facility Plan. This case study was undertaken to ascertain if sustainable building design could significantly reduce or eliminate waste streams. In particular, perchlorate or HE found in DX-2's wastewater. The CHEM Laboratory building is projected to cost approximately $20 million and typical operations would be expected to produce about 14,000 gallons of HE wastewater a year. At present this wastewater is treated at the HEWTF when it meets their Waste Acceptance Criteria (WAC). However, cumulative experience shows that operations are subject to shifting boundary conditions that make wastewater treatment uncertain: operations change with missions, and new or more stringent regulatory requirements have been applied. This leaves Lab national security research and development programs at risk, and can result in the suspension or reduction of operations until a suitable alternative can be identified and implemented. The results of this study indicate that DX's ability to manage HE wastewater begins in the earliest stages of building design and that adding operational flexibility into the building design provides significant future benefits. For example, having exposed drain lines located in a partial basement and readily accessible allows for the easy hook up of appropriate treatment processes where the water can be reused and/or evaporated. It is expected that with such a flexible building design, the HE wastewater could be significantly reduced if not eliminated entirely. It is expected that the discounted lifecycle savings (50 year life expectancy) would be about $2.2 million by the elimination or reduction of this waste through flexible design. This savings has a payback time of approximately nine years. Lifecycle savings would come from cost avoidance (e.g. the digging up of contaminated or leaking pipes), waste management cost, the isolation of particular wastewater that may need special treatment (no disposal path), and assure compliance with increasingly stringent environmental regulations.

Permeable Reactive Barrier Feasibility – Mortandad Canyon
A field-scale permeable reactive barrier (PRB) was installed in Mortandad Canyon in the winter of 2002 at a site downstream from the discharge point of the RLWTF, a National Pollutant

Discharge Elimination System (NPDES) -permitted outfall. Alluvial groundwater in Mortandad Canyon is being treated using a Multi-Barrier technology that consists of four different cells of materials (scoria basalt, hydroxyapatite, cotton seed meal and pecan shells, and limestone) arranged as a PRB. Among the targeted contaminants are perchlorate, nitrate, and strontium-90. The perchlorate removal mechanism in the Multi-Barrier is through microbial reduction to harmless chloride ion. The Multi-Barrier uses one cell that provides biological activity sufficient to reduce perchlorate to chloride. This cell is made of inexpensive waste materials including cottonseed meal and pecan shells. Both cotton seed meal and pecan shells are capable of supporting the growth of a microbial biofilm that is highly effective at reducing both nitrate and perchlorate to non-detectable levels as the groundwater flows through the barrier. Strontium-90 is removed from groundwater through adsorption processes involving hydroxyapatite. This project is a field-scale demonstration of the Multi-Barrier system that has multiple sampling points at strategic locations in each cell, and at sampling stations upstream and downstream from the PRB.

This summer, data from the PRB will be collected, and a report of the findings will be available in the fall of 2003.

Potential Perchlorate Sites and Sources

In September 1999, the NMED, Hazardous and Radioactive Materials Bureau, asked the Laboratory to conduct a survey to identify potential perchlorate-related sites. The survey findings, submitted to the NMED in December 1999, identified two areas at the Laboratory that contain potential perchlorate-related sites: the HE Corridor, and Mortandad Canyon.

High-Explosives Corridor

Wastewater generated within the HE corridor (since the early 1940's) has been discharged into Pajarito Canyon, Water Canyon, and Cañon de Valle, prior to the installation of the HEWTF. As a result, perchlorate has been sampled at Fishladder seep (in Fishladder Drainage) and the Fishladder 'waterfall' at the confluence of the Fishladder Drainage and Cañon de Valle – have detected perchlorate concentrations of 17 ppb and 7 ppb respectively. Cañon de Valle ultimately drains into Water Canyon.

In addition, soils from firing and rocket sites have become contaminated from past experiments and burning within the HE corridor. Stormwater contacting this contaminated soil may be another source and major transport mechanism.

Mortandad Canyon

Perchlorate was present in alluvial groundwater in Mortandad Canyon at values up to 280 ppb in 2000. The alluvial groundwater is separated from the regional aquifer by about 900 ft. Cores from four wells in Mortandad Canyon show that pore water perchlorate concentrations in the vadose zone beneath the canyon floor average 300 to 400 ppb down to at least 400 ft. This indicates a considerable inventory of perchlorate beneath the canyon floor as a result of 40 years of effluent discharge. At monitoring well, MCOBT-4.4 groundwater was observed between depths of 492 and 532 ft. The perched groundwater was encountered in the Puye Formation and Cerro del Rio basalt. Perchlorate was detected in this perched groundwater between

concentrations of 140 and 180 ppb. These are the highest concentrations of perchlorate observed in perched groundwater at the laboratory.

Three nearby regional aquifer monitoring wells have not shown perchlorate contamination, though analysis of several samples has produced analytical results that are near or below the detection limit of 4 ppb. None of the five surrounding Los Alamos County water supply wells (O-4, PM-1, -3, -4, -5) have detectable perchlorate contamination.

The LANL Integrated Groundwater Protection Strategy Team is conducting extensive evaluation and study of Mortandad canyon. This team is calculating the drinking-water ingestion risk (in terms of probability of exceeding 1 ppb perchlorate) associated with perchlorate moving from the TA-50 discharge point (since 1963) and the TA-35 discharge point (since approximately 1954), through the canyon alluvium, vadose zone, regional water-supply aquifer, and into the capture-zone of water-supply wells. The results will be then interpreted via traditional quantitative decision analysis methods to identify and rank (according to relative risk reduction per dollar spent) alternative actions to reduce the impact of perchlorate. The Mortandad Canyon risk-based decision analysis will be complete in early June. The other major sources (below) will be similarly addressed throughout the summer and fall.

Other Perchlorate Site

Rio Grande Springs

The NMED-OB has reported discovery of perchlorate in samples from some springs along the Rio Grande. Numerous follow up samples have not confirmed these findings, which remain mired in questions over analytical accuracy near the method detection limit. Samples analyzed by one of our analytical laboratories prior to April 25, 2001 showed many false positives due to lack of all the anion removal steps required in the EPA analytical method. Removal of other anions present in water prevents matrix interference in the analysis. Thus many of the apparent detections indicated in LANL data are not bona fide perchlorate detections.

Specific information on potential sources of perchlorate at the Laboratory is presented below.

Active Effluent Sources

The Laboratory has two active outfalls in the current National Pollutant Discharge Elimination System (NPDES) permit. NPDES Outfall 051 (RLWTF) and outfall 05A055 (HEWTF).

***Radioactive Liquid Waste Treatment Facility (RLWTF) at TA-50* (Mortandad Canyon).**

In 2000 and 2001, the annual average concentration of perchlorate in the RLWTF's effluent was 254 ppb and 169 ppb, respectively. In March 2002, the RLWTF began operating an ion exchange treatment system to remove perchlorate from the facility's effluent. Routine monitoring of RLWTF effluent since treatment began shows no detectable concentrations of perchlorate. In response to perchlorate reduction in the RLWTF effluent, by November 2002, the concentration nearest the outfall had dropped to near the detection limit of 4 ppb and concentrations at other stations were decreasing slowly.

***High Explosives Wastewater Treatment Facility (HEWTF)* at TA-16** (Cañon de Valle). Elimination of 19 NPDES-permitted HE outfalls was completed in 1997. All water from HE operations is now collected and treated at the HEWTF, which discharges into Fish Ladder Drainage and ultimately Cañon de Valle. Analysis of holding tank and effluent samples at the HEWTF shows a range of perchlorate concentrations from 4 to 58 ppb. The primary perchlorate source has been tracked to a single contributing facility at TA-9, Anchor East Site. An ion exchange system was installed on May 23, 2003 and is currently operational.

Perchloric Acid Fuming, TA-48 and TA-59
The majority of perchlorate release is associated with operations requiring fuming of perchloric acid. It has been estimated that 70% of the perchloric acid used is discharged as gaseous effluent in fume hoods. These fume hoods have wash downs and the exhaust ducts are also washed down regularly. The remaining 30% is released as liquid effluent via the radioactive liquid waste drains, which are treated at the RLWTF. There is however, considerable uncertainty in the relative percentages of gaseous release versus liquid effluent release.

Programs that utilized these operations, in order of perchloric acid use, are the Weapons Test Program, Environmental Sample Analyses Programs, Miscellaneous Programs (generally short term programs), Iridium Anomalies Study, Rover Program, and Natural Analogs Program.

Potential Uncharacterized Source
Commercial perchlorate is prepared electrochemically, from treatment of aqueous chlorides with sufficient voltage to prepare adequate concentrations (typically several tens of percent by weight) of perchlorate (either as acid or salts). However it is possible to prepare perchlorate chemically and by other means, which may lead to the low concentrations of perchlorate being observed in systems where it has not been added. In general, any chlorine-containing species (e.g., hydrochloric acid, hypochlorites, chlorites, chlorates, and perhaps even some organic chlorides) may react with strong acids, oxidizing agents such as peroxides, ozone (whether naturally or artificially produced), ultraviolet light/air, etc. to produce small amounts of perchlorate on the order that can be detected by more sensitive chemical analysis. It must be noted that while perchlorate has been in use since the early 1800s, the technology to detect it at ppb levels has only existed in the last decade.

Since perchlorate is an environmentally (and chemically) stable species, it is important to understand its adventitious production to discriminate between so-called 'natural' or unintentional sources and that arising from perchlorate-contaminated waste. However, this has been difficult to determine, as the wastewater contamination is intermittent and sporadic, even sampling the same piping and sumps.

Inactive Effluent Sources - probable discharges of perchlorate

***TA-1, TA-45* (Acid Canyon and Pueblo Canyon).**
Acid Canyon, a small tributary of Pueblo Canyon, was the original disposal site for liquid wastes generated by research on nuclear materials for the World War II Manhattan Engineer District atomic bomb project at TA-1 (Los Alamos townsite). Acid Canyon received untreated radioactive industrial effluent from 1943 to 1951. The TA-45 treatment plant was completed in 1951, and from 1951 to 1964 the plant discharged treated effluents that contained residual

radionuclides into nearby Acid Canyon. Based on similarity of processes to TA-50 (including nuclear chemistry research), the effluents probably contained similar amounts of perchlorate.

As indicated previously, perchlorate is present in water supply well O-1 (Pueblo Canyon) at concentrations of about 2 to 4 ppb. Though these values are below the ion chromatography detection limit, results of numerous analyses are consistent enough to support the conclusion that perchlorate is present. Los Alamos County only uses this well as a stand-by supply.

***TA-21* (DP Canyon).**
An industrial liquid waste treatment plant that served the old plutonium processing facility at TA-21 discharged effluent containing radionuclides into DP Canyon, a tributary to Los Alamos Canyon, from 1952 to 1986. Based on similarity of processes to TA-50 (including nuclear chemistry research), the effluents probably contained similar amounts of perchlorate.

Recent evaluation of core from well # LADP-4, drilled down gradient of the former radioactive liquid effluent outfall at TA-21, revealed perchlorate concentrations of 200 to 1000 ppb. Rock core samples from this well were sampled to a depth of 800 ft. with the deepest perchlorate concentration observed at a depth of 280 ft. The regional aquifer in this area is at a depth of 1000 ft. These perchlorate concentrations indicate a residual foot print in the rock above the saturated zone, which warrants more evaluation. These concentrations are similar to those in the vadose zone beneath Mortandad Canyon.

There may be several buildings at TA-21, including those still standing, that had outfalls other than the sanitary sewage treatment plant. Further evaluation of the complete TA-21 situation is warranted.

***TA-9* (Pajarito Canyon).**
Since 1950, operations at Anchor East Site have discharged wastewater from high explosives synthesis and testing operations. The Anchor East Site, TA-9, was identified as a significant perchlorate contributor. A recent analysis of wastewater, from this facility, showed it contained over 500 ppb of perchlorate, which is used as an oxidizer in high explosives. While outfalls from these buildings were shut down by 1997, and wastewater is now hauled to the HEWTF, discharge from these outfalls entered upper Pajarito Canyon for the previous 45 years. This area warrants further evaluation.

TA-46, TA-48, TA-59 outfalls (Mortandad Canyon)
Nuclear (actinide) chemistry research has been ongoing at these faculties. Prior to the installation of the RLWTF, untreated radioactive industrial effluent was most likely discharged into the nearby Mortandad Canyon.

TA-35, and Ten Site Wastewater Treatment Plant (Mortandad Canyon and Ten Site Canyon)
Numerous accidental waste spills and intentional releases of waste materials occurred at TA-35. Experimentation with several radionuclides, especially plutonium and tritium, were conducted at TA-35 in the 1950s and 1960s. Waste liquids, generated by washing of hot cells used in TA-35-2, were stored in four 50,000 gallon concrete tanks (TA-35-10) to allow decay of the short-lived radionuclides. The wastewater was then discharged into Mortandad Canyon. The discovery that

other radionuclides with longer half-lives were also stored in the tanks, and were being concentrated in these wastes, necessitated construction of a wastewater treatment plant. From 1951 to 1963 this facility treated radioactive wastes produced by various reactor and hot cell experiments at TA-35. The wastewater treatment plant was constantly beset by problems, and inadvertent spills of insufficiently-treated wastewater into Ten Site Canyon (tributary to Mortandad Canyon) occurred frequently. The potential for perchlorate releases exist due to chemistry's, similar to actinide research, which may have been used.

Search for Lower Perchlorate Detection Limit

With potential State and/or Federal regulations setting discharge limits in the range of 1-18 ppb perchlorate, the accuracy and sensitivity of perchlorate detection methods is extremely important. The EPA has approved one analytical method for the analysis of perchlorate, Method 314 using Ion Chromatography. This method has a detection limit of 4 ppb in natural waters, with a practical quantitation limit (the lowest concentration that can be reliably determined) of 12 ppb. These detection limit values are based on several verification studies using natural groundwater. However, careful screening or cleanup steps are required with the current IC analytical method to lessen the occurrence of interference from other ions. Frequently these steps have not been used by all analytical laboratories, resulting in interference from other ions (inherent in real, environmental matrices), particularly sulfate, chloride, nitrate and carbonate, which produce random and highly-variable noise in the baseline at the known perchlorate retention time on the chromatogram. This can result in a significant background signal above zero and "false positives" in the range of 1 to 4 ppb. In addition, as mentioned previously, the potential for a drinking water standard below 4 ppb creates a need for an analytical method with a lower detection limit.

The Department of Energy's (DOE) National Nuclear Security Administration (NNSA) Albuquerque Operations Office Analytical Management Program (NNSA-AL AMP) is collaborating with LANL in evaluating a low-level perchlorate analysis method by coupling liquid chromatography (LC) and a tandem mass spectrometry (MS) technique (LC/MS/MS). The two MS steps serve as a confirmation for the presence and level of perchlorate. The first MS detects ClO_4^- and in the process strips one oxygen from the ion, the second MS then detects ClO_3^-, and the two concentrations must balance. In addition, because the chlorine atom exists in two forms, of different masses (75% as Cl^{35} and 25% as Cl^{37}), corroboration of the number and type of chlorine atoms detected by each MS ensures specificity for perchlorate analysis. EPA's Office of Water is also interested in the method. See Table 7.

Table 7. New Analytical Method for Perchlorate (Proposed)

Analytical Method For Perchlorate (Proposed)		
Method	Method Detection Limit (ppb) (proposed)	Reporting Limit/Practical Quantitation Limit (ppb) (proposed)
Liquid Chromatography/ Mass Spectrometry/Mass Spectrometry	0.05	0.15

The method works well across a range of natural water chemistry, but has suffered from problems with the internal standard. These problems have previously resulted in erroneously high analytical results and have plagued the perchlorate LC/MS/MS method from the beginning. General Engineering Laboratories (GEL) completed work on their internal standard in early April of 2003. Work on the analytical method was also completed by GEL and they were ready to receive samples by early April of 2003. GEL plans on submitting this updated analytical method to the EPA Office of Water (no date available).

A consensus was also reached at the January 9th meeting that NMED-OB, DOE, NNSA and LANL would jointly perform a performance evaluation of the LC/MS/MS method prior to the Laboratory employing it for low-level perchlorate analysis. Los Alamos area environmental water samples will be part of the evaluation. Design of the performance evaluation, with input from the NMED-OB, Los Alamos Department of Public Utilities, and the DOE has occurred. Also, 116 water samples have been collected (May 12 – 15, 2003) and submitted to GEL (May 29, 2003) with results are expected back to the LANL Environmental Surveillance Team, Risk Reduction and Environmental Stewardship (RRES) Division Water Quality & Hydrology (WQH) Group, by June 30, 2003. Following data validation and approvals from all of the entities involved, the data will be available for review.

Treatment

Treatment of perchlorate contamination in water is complicated because the perchlorate anion does not respond to typical water treatment technologies due to its fundamental physical and chemical nature. The perchlorate tetrahedron itself is structured such that the four oxygen atoms surround the central chlorine atom, effectively blocking reductants from directly attacking the chlorine. The perchlorate anion is soluble and very mobile in aqueous systems. It can persist in the environment for many decades under typical groundwater and surface water conditions because of its resistance to react with other available constituents. While perchlorate is thermodynamically a strong oxidizing agent, with the chlorine in the +7 oxidation state, the kinetics of reduction are generally very slow. Common reducing agents do not reduce perchlorate, and common cations do not coordinate with or precipitate it. Consequently, standard practices of water treatment will neither remove it physically nor destroy it chemically.

Perchlorate treatment technologies may be generally classified into categories of removal or reduction technologies. Physical removal processes include anion exchange, membrane filtration (including reverse osmosis and nanofiltration), and electrodialysis, which all require subsequent disposal of removed perchlorate. Reduction processes include biological reduction, chemical reduction, and electrochemical reduction. It must be noted that because of the newly emerging nature of perchlorate contamination and the associated cleanup concerns, that nearly all treatment techniques remain to be demonstrated for effectiveness. Further, little or no cost or performance data is available.

The optimum treatment technology for a given perchlorate occurrence may depend on several factors, including perchlorate concentration, the presence and concentration of co-contaminants, other water quality parameters (pH, alkalinity, natural organic matter (NOM), total dissolved

solids, metals, etc.), and geochemical parameters (nitrate, sulfate, chloride, dissolved oxygen, redox potential, etc.).

Physical Removal Processes, Treatment options identified

1. *Ion Exchange* – Ion exchange is a technology for the treatment of groundwater, surface water, and leachate. It works on perchlorate by capturing perchlorate anions on a positively charged resin and releasing a harmless chloride ion in its place. The exchange resin can be made from natural or synthetic organic, inorganic, or polymeric material that contain functional ionic groups.

   Ion exchange is energy-intensive due to the "pump and treat" nature of its operation. It requires frequent changing or regeneration of exchange resins and generates a problematic residual waste in the form of brine or contaminated resins that still contain the perchlorate. The secondary wastes generated during treatment would require additional treatment or disposal. It is possible that a treatment train using ion exchange and *ex situ* biological treatment of the secondary waste could be used to treat low levels of perchlorate contamination in surface waters and wetlands

   Private sector organizations have been successfully applying ion exchange for many years for different applications. This success has extended to continuous ion exchange units that have effectively demonstrated the ability to reduce perchlorate to below 4 ppb in remediation and drinking water applications.

   The DoD has been investigating the use of ion exchange to treat perchlorate-contaminated groundwater at Edwards Air Force Base, California. Edwards Air Force Base (AFB) will soon begin field-testing a new class of anion exchange resins in a conventional fixed-bed ion exchange system. Pilot-scale tests of the system were completed in June 2001 and were proven successful at treating contaminated groundwater.

   Capital and operational cost of ion exchange systems vary depending on a number of factors, such as discharge requirements, the volume of water to be treated, contaminant concentration, the presence of other contaminants, resin and regenerant utilization, brine disposal, and site-specific hydrological and geochemical conditions.

2. *Membrane Filtration* – Membrane filtration, reverse osmosis and nanofiltration, are established treatment technologies used for the removal of contaminants such as salts, disinfection by-product precursors, nitrates, and selected pesticides. While it is anticipated that these processes may be effective for the removal of perchlorate, there is little to no peer-reviewed data that demonstrates their applicability to perchlorate contamination at concentrations of 1000 ppb and lower. Influent perchlorate concentrations would have to be below 400 ppb to have permeate concentrations below 18 ppb. Two examples offered from Azita Yazdani, (President) & Fred Reinhard (VP/Senior Engineer) of Exergy Technologies Corporation are:

   - *Membrane Electrolysis (ME)* - large variety of recovery and maintenance applications of chemical process solutions, but also equipped with patented pending design, latest proprietary ion exchange membranes and electrodes.

- *Advance Reverse Osmosis (ARO)* - utilizes selected reverse osmosis membranes to allow process water/chemical recovery at elevated total dissolved solids concentrations and an expanded pH range from 0.5 to 13.

Also, treatment of the perchlorate-concentrated secondary stream will need to be addressed.

3. *Electrodialysis* – Electrodialysis systems separate ionic species from aqueous solutions using an applied direct current potential across ion-permeable and selective membranes. No known demonstration projects were found.

4. *Exergy Technologies Corporation*- This Company has technologies to address perchlorate as well as other organic issues. An example of a technology that is used to eliminate perchlorates in the wastewater is the Continuous Electrodeionization. This technology combines ion exchange/membrane/electrolysis technologies and utilizes unique proprietary ion exchange membranes and electrodes to replace conventional ion exchange systems in industrial recovery applications.

5. *Ultraviolet and Ozone Peroxide System* - This approach has the dual advantage of eliminating perchlorates and other organics from waste wastewater while conserving water usage. Hydrothermal and other wet oxidation technologies were evaluated for their efficacy in destroying these contaminants. Wet oxidation converts the organic materials present to carbon dioxide and water and the inorganic contaminants to their common salts (nitrates, chlorides, sulfates, etc.). After destruction is completed, the salts can be removed with standard deionization resins and recycled. Literature indicates that mixtures of ozone and hydrogen peroxide coupled with ultraviolet light offers the most effective treatment. A pilot project conducted at C-Division to test the efficacy of using an UV/Ozone/Peroxide treatment process indicated that it would destroy 95% of the contamination within a single pass.

Chemical/Biological Removal Processes, Treatment options identified

1. *Anaerobic Bioremediation* – Studies have shown that perchlorate can be successfully biodegraded to the chloride ion, but only under anaerobic conditions. The *in situ* (in place) anaerobic bioremediation of perchlorate is a promising technology in which naturally occurring microorganisms are used to reduce perchlorate to innocuous chloride upon addition of a carbon source. For *in situ* bioremediation to occur, an electron donor (i.e. carbon-source) is added to perchlorate-contaminated groundwater or soil. A variety of electron donors have been used to stimulate perchlorate reduction, including alcohols, organic acids, edible oils and some sugars. The carbon source stimulates aerobic microorganisms to remove oxygen and nitrate, resulting in redox conditions amenable to reduction of perchlorate *in situ*. However, *in situ* bioremediation requires careful consideration of environmental conditions, hydraulic flow, and residence time of the contaminated water in the underground reactive zone. Because perchlorate reduction only occurs in the absence of oxygen and nitrate, initial research into the use of *in situ* bioremediation as a means of treating perchlorate-contaminated groundwater has focused on developing and optimizing anaerobic bioremediation techniques.

More than 30 different strains of perchlorate-reducing microbes have been isolated from diverse environments. In this reductive process, bacteria utilize the perchlorate ion as a terminal electron acceptor. A carbon or hydrogen electron donor (e.g., acetate) is normally necessary to drive the reaction sequence for optimal remediation rate. It is now generally accepted that microbial reduction of perchlorate proceeds according to the following:

$$\underset{\text{(Perchlorate)}}{ClO_4^-} \rightarrow \underset{\text{(Chlorate)}}{ClO_3^-} \rightarrow \underset{\text{(Chlorite)}}{ClO_2^-} \rightarrow \underset{\text{(Hypochlorite)}}{ClO^-} \rightarrow \underset{\text{(Chloride)}}{Cl^-} + O_2$$

As can be seen, perchlorate is ultimately completely converted into chloride and oxygen through the anaerobic reduction process. The perchlorate-to-chlorate step is thought to be the rate-limiting step, being considerably slower than the other steps. Buildup of toxic intermediates, specifically chlorite, does not occur because the chlorite-to-chloride step proceeds at a rate on the order of 1000 times that of the accepted rate-limiting step.

Current approaches for the remediation of perchlorate-contaminated groundwater typically involve long-term pump-and-treat solutions. Comparison of cost estimates for *in situ* versus *ex situ* treatment for perchlorate plumes at several DoD field cases suggests that *in situ* bioremediation cost between 50 to 75 percent of *ex situ* treatment costs. The ability to jointly treat perchlorate and common co-contaminants such as nitrate and chlorinated solvents via *in situ* bioremediation will also increase cost savings.

Laboratory-, and pilot-scale studies of *in situ* anaerobic bioremediation for treating perchlorate-contaminated groundwater are ongoing. A summary of projects is shown in Table 8.

Table 8. Summary of *In Situ* Bioremediation Projects

Project Name	Location/Funding Source	Scale/ Media	Status of Project
Bioreduction and Removal of Ammonium Perchlorate	Carbondale, IL / SERDP[1]	Lab/W	In-Progress
Bioremediation of Perchlorate	Lawrenceville, NJ / SERDP[1]	Lab/GW	Complete FY01
Bioremediation of Perchlorate-Impacted GW	Six SERDP[1] test sites; 1) Edwards Air Force Base, CA 2) DOD site, West Virginia 3) Rocket Manf., CA 4) Aerojet Superfund Site, CA 5) U.S. Navy, CA 6) Industrial Site, Nevada	Lab/Pilot GW	Complete FY01
Treatability Studies on GW from Henderson, NV	Panama City, FL / Kerr-McGee Chemical LLC	Lab/GW	Complete (2000)
Insoluble Organic Substrates (Edible Oils) for Degradation of	Edwards AFB, CA / AFCEE[2]	Pilot/GW	In Progress

Perchlorate			

[1] Strategic Environmental Research and Development Program (SERDP) – DoD's corporate environmental R&D program.
[2] Air Force Center for Environmental Excellence.

2. *Permeable Reactive Barriers* – The Permeable Reactive Barrier (PRB) is a groundwater cleanup technology that consists of a wall of reactive material installed in the path of a flowing contaminated groundwater plume to treat pollutants as they penetrate through the wall. The PRB contains materials that target specific contaminants and chemically and/or biologically treats them. As with any biological treatment system, PRBs require careful control of environmental conditions within the reactive zone to maintain the anaerobic conditions that encourage the bacteria to biodegrade the perchlorate. The regular addition of nutrients and electron donors may be necessary depending on the efficiency of the PRB system and the reactive material used.

   PRBs are increasingly being used to treat a variety of groundwater contaminants and are recognized as a cost-effective, passive remediation method.

   The DoD has successfully used PRBs to treat perchlorate at the Naval Weapons Industrial Reserve Plant in McGregor, Texas. The system is believed to represent the first full-scale *in situ* bioremediation of perchlorate. Pilot- and full-scale studies of PRBs for treating perchlorate-contaminated groundwater are ongoing. A summary of projects is shown in Table 9.

Table 9. Summary of Permeable Reactive Barrier Projects

Project Name	Location/Funding Source	Scale/ Media	Status of Project
Insoluble Organic Substrates (Edible Oils) for Degradation of Perchlorate	Edwards AFB, CA / AFCEE[2]	Pilot/GW	In Progress
Permeable Reactive Barrier Feasibility	Los Alamos, NM / U.S. DOE, LANL	Pilot/GW	In Progress
In situ GW Remediation	McGregor, TX / U.S. Navy	Full Scale/GW	In Progress

3. *Phytoremediation* – Phytoremediation is a treatment technology that uses natural plant processes and microorganisms associated with the root system to remove, contain, or degrade environmental contaminants in soil, sediment, and water. There are several processes associated with phytoremediation. Depending on the contaminant to be treated and site-specific conditions, these processes may work together, with the entire plant acting as a single system to remove the contaminant, or they may work individually with certain processes having a greater influence on contaminant removal.

   Several recent studies have shown that plants are capable of taking up, and at least partially reducing perchlorate. Research funded by the Air Force Aeronautic Systems Center and the

US Army Operations and Support Command have confirmed the ability of phytoremediation to remove perchlorate from contaminated water and soils. The two most important phytoremediation processes for perchlorate involve the uptake and subsequent phytodegradation of the chemical in branches and leaves, and rhizodegradation. Phytodegradation uses naturally occurring plant enzymes to degrade contaminants within the plant tissues. Rhizodegradation, on the other hand, occurs in the soil surrounding plant roots. Natural substances released by the plant roots serve as substrates for the microorganisms present in the rhizoshpere and speed up contaminant degradation.

Pilot- studies of phytoremediation for treating perchlorate-contaminated groundwater are ongoing. Defensible data on cost and performance need to be developed. See Table 10.

Table 10. Summary of Phytoremediation Projects

Project Name	Location/Funding Source	Scale/ Media	Status of Project
Longhorn Army Ammunition Plant	Karnack, TX / US Army Operations, US Air Force	Pilot/GW	In Progress
Phytoremediation – Greenhouse Testing	Athens, GA / US Air Force, Wright Patterson AFB	Lab/GW, soil	Complete FY 2000
Phytoremediation By Native Salt cedar	Las Vegas, NV / U.S. EPA	Field /GW	Complete FY 2000

4. *Bioreactors* – Bioreactors are an *ex situ* form of biological treatment in which contaminated process wastewater or extracted groundwater is pumped into an above ground reactor vessel (bioreactor), and placed into direct contact with microorganisms. These microorganisms remove perchlorate by reducing it in the presence of a food source. Careful control of environmental conditions (pH, temperature, oxygen content, nutrient sources, etc.), hydraulic flow, and residence time of the contaminated water supply in the bioreactor is necessary to support the growth of microorganisms and ensure complete reduction of the perchlorate. Common system designs include fluidized bed reactors (FBR), continuous-stirred tank or suspended growth reactors, and fixed film or packed bed reactors.

   Despite widespread use of bioreactors in the treatment of municipal and industrial wastewater, only in the past decade have studies been performed to evaluate the effectiveness of bioreactors in treating contaminated groundwater. In addition, because it has been determined that perchlorate can be successfully reduced to the harmless chloride ion under anaerobic conditions; initial research into using bioreactors to treat perchlorate-contaminated water has focused on the development and optimization of anaerobic bioreactors.

   The Air Force Research Laboratory (AFRL) Materials and Manufacturing Directorate (Tyndall Air Force Base, Florida) has led the way in developing bioreactor systems to treat process wastewater containing very high levels of perchlorate. Since 1997, a bioreactor based on the AFRL design has been treating wastewater from rocket motor production and demilitarization operations at a defense contractor facility near Brigham City, Utah.

A large, full-scale FBR system has also been operating at a site in Rancho Cordova, CA, since 1998. This system was integrated into the sites overall groundwater extraction and treatment plant to remediate perchlorate contaminated groundwater.

The first DoD facility to install a functional bioreactor for treating perchlorate-contaminated groundwater was the former Longhorn Army Ammunition Plant (LHAAP) in Karnack, Texas. Past activities at this site led to the construction of a groundwater pump-and-treat system, in 1997, for the site's production and disposal areas. However, the groundwater treatment plant was designed to extract and treat metals and volatile organic compounds, not perchlorate. After assessing the cost and technical feasibility of alternative technologies, LHAAP opted for a bioreactor, specifically an FBR, as an add-on device to the existing groundwater treatment system.

Aerojet, a significant user of ammonium perchlorate, is developing a proprietary *ex situ* bioremediation system to remediate perchlorate-contaminated groundwater. Pilot-scale testing of the biological process is taking place at the San Gabriel Valley Superfund Site. The purpose of the test is to determine whether the bioreactor, if followed by filtration and other post-bioreactor treatment, could produce potable water. The test was completed in December 2000, and in April 2002 the California Department of Health Services accepted the technology for use in the production of drinking water (Phase 2 Treatability Study Report *Aerojet GET E/F Treatment Facility, Sacramento, CA, September 2001*). Additional information on this technology, including a report describing the pilot-scale test results, is available from EPA Region 9. Four full-scale bioreactors, in operation since 1998 at Aerojet's northern California facility, have consistently reduced perchlorate levels from about 2,500 ppb to non-detectable levels (< 4.0 ppb).

Interim Conclusions

1. As soon as the issue of perchlorate health effects was raised, LANL began monitoring and reporting sources and concentrations.
2. Since 2001, NPDES monitoring & reporting to EPA, DOE, & NMED for TA-50 RLWTF & TA-16 HEWTF
3. Active sources of perchlorate contamination have been identified, mediated and virtually eliminated.
4. Perchlorate reduction activities completed or underway at LANL include:
    a. Replacement of HEPA Filters at the CMR Facility.
    b. Ductwork replacement and cleanup at TA-48.
    c. Perchlorate fume hood and ductwork wash down procedures implemented at TA 48 and TA-59.
    d. Ion exchange installed at TA-50 RLWTF to remove perchlorate. Successfully decreased perchlorate in its effluent to <1 ppb.
    e. Ion exchange at TA-16 HEWTF to remove perchlorate completed May 23, 2003.
    f. Field-scale (feasibility study) installation of permeable reactive barrier in Mortandad Canyon.
5. Integration of activities related to measuring, monitoring and treatment is occurring.
6. Technical options for long-term mitigation of contamination are being identified and evaluated.

7. Improvement of the resolution of detection methods is in progress.

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Acronyms

AFB - Air Force Base
AFRL - Air Force Research Laboratory Materials and Manufacturing Directorate
AGEX I - Hydrodynamic testing
AGEX II - Explosively driven pulsed-power physics and high-energy-density physics
ARO - Advance Reverse Osmosis
B-1 - Bioscience Division McClintock Resource Group
B-2 - Bioscience Division Langham Resource Group
B-3 - Bioscience Division Szilard Resource Group
B-4 - Bioscience Division Michelson Resource Group
CAS - Chemical Abstract Service
C-DO - Chemistry Division
C-AAC - Chemistry Division Actinide Analytical Chemistry Group
C-ACS - Chemistry Division Actinide, Catalysis, and Separations Chemistry Group
C-ACT- Chemistry Division Applied Chemical Technologies
C-ADI - Chemistry Division Advanced Chemical Diagnostics and Instrumentation
C-INC - Chemistry Division Isotope and Nuclear Chemistry Group
C-PCS - Chemistry Division Physical Chemistry and Applied Spectroscopy
CHEM - Characterization High Energetic Materials Laboratory
CMR - Chemistry and Metallurgy Research Facility
DARHT - Dual-Axis Radiographic Hydrotest Facility
DOE-NNSA - Department of Energy National Nuclear Security Administration
DoD - Department of Defense
DoD-SERDP - Department of Defense Strategic Environmental Research and Development Program
DX-DO - Dynamic Experimentation Division
DX-2 - Dynamic Experimentation Division Materials Dynamics Group
EMRTC - Energetic Materials Research and Testing Center
EPA - Environmental Protection Agency
ESA - Engineering Sciences and Applications
FBR-Fluidized bed reactors
FWO-WFM - Facilities and Waste Operations Division Waste Facilities Management Group
GEL - General Engineering Laboratories
HCP - Hazardous Control Plan
HE - High Explosives
HEWTF - High Explosives Waste Water Treatment Facility
HSR - Health, Safety, and Radiation Protection (HSR) formerly ESH
Kg - Kilograms
LANSCE-12 - Los Alamos Neutron Science Center
LANL - Los Alamos National Laboratory
LAUR - Los Alamos unlimited releases
LC/MS/MS - Liquid chromatography and tandem mass spectrometry technique
LHAAP - Longhorn Army Ammunition Plant
MCL - Maximum Concentration Limit
ME - Membrane Electrolysis
MST-6 - Materials Science and Technology Division Materials Technology Metallurgy Group
MST-7 – Materials Science and Technology Division The Polymers and Coatings Group
MST-8 - Materials Science and Technology Division Structure/Property Relations Group
MST-11 - Materials Science and Technology Division Electronic and Electrochemical Materials and Devices
NASA - National Aeronautics and Space Administration
NDMA - N-Nitrosodimethylamine

NMED-OB - New Mexico Environmental Department/Oversight Bureau
NMT-2 – Nuclear Materials Technology Division Actinide Process Chemistry
NMT-7 – Nuclear Materials Technology Division Waste Management / Environmental Compliance
NMT-11- Nuclear Materials Technology Division Actinide & Fuels Cycle Technologies
NNSA-AL AMP - Department of Energy National Nuclear Security Administration Albuquerque Operations Office Analytical Management Program
NPDES - National Pollutant Discharge Elimination System
O - Otowi
P-23 - Physics Division Neutron Science and Technology Group
P-24 - Plasma Physics Group
PHERMEX - Pulsed High-Energy Radiographic Machine Emitting X-Rays
PM- Pajarito Mesa
ppb - Part per billion
PRB - Permeable Reactive Barrier
Pu - plutonium
RC - Radiochemistry
R&D - Research and Development
RfD - Draft reference dose
RLWTF - Radioactive Liquid Waste Treatment Facility
RRES-WQH - Risk Reduction and Environmental Stewardship Division Water Quality & Hydrology Group
SDW - Safe Drinking Water
TA - Technical Area
TCE - Trichloroethylene
Ula - Nevada Test Site facility for the underground testing of special nuclear materials
UCMR - Unregulated Contaminant Monitoring Rule
USGS - U.S. Geological Survey
VOCs - Volatile organic compounds
WAC - Waste Acceptance Criteria
TSH - Thyroid-stimulating hormone

Comments on NM Environment Department Hazardous Waste Bureau presentation "Perchlorate Occurrence at RCRA Facilities in New Mexico" June 3, 2002, the following slides pertain to Los Alamos National Laboratory:

Slide #26 – No comments

Slide #27 – Discusses the Radioactive Liquid Waste Treatment Facility.

NMED	**Los Alamos**
Wastewater entering RLWTF perchlorate concentration ~ 500 ppb	2000 – 2001 average annual effluent perchlorate concentration was 254 and 169 ppb
Treatment: Reverse Osmosis	Treatment: Ion Exchange
Perchlorate effluent concentration after treatment: 24 to 66 ppb	Perchlorate effluent concentration after treatment: non detect (Method EPA 314)
December 1999 alluvial GW perchlorate concentration at 80-220 ppb	2000 alluvial GW perchlorate concentration at 280 ppb

Slide #28 – Perchlorate in Mortandad Canyon

NMED	**Los Alamos**
Pore water from rock core collected from 50 to 400 ft depth in Borehole R-15	Pore water from four wells in Mortandad Canyon down to at least 400 ft
Perchlorate concentration 100-600 ppb	Perchlorate concentration average 300 to 400 ppb
Pore water collected from deep perched zone at 740 ft (Borehole R-15)	At monitoring well, MCOBT-4.4 perched groundwater was observed between depths of 492 and 532 ft
Perchlorate was detected at 1,662 ppb	Perchlorate was detected in this perched groundwater between concentrations of 140 and 180 ppb

Slide #29 – No comments

Subject: **Perchlorate Paper**
Date: Fri, 13 Jun 2003 11:15:34 -0600
From: Denny Hjeresen <dlh@lanl.gov>
To: julie_wanslow@nmenv.state.nm.us
CC: bramsey@lanl.gov, "Paul B. Schumann" <schumannp@lanl.gov>

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>
>Julie - My name is Denny Hjeresen and I was asked by Beverly Ramsey
>the Risk Reduction and Environmental Stewardship Division Director
>to lead a data collection effort on the perchlorate issues at the
>Lab. This is an interim effort since we are still researching many
>aspects of the contamination and response but it is a good summary
>of what we know to date. I am copying you on the paper because of
>your interest in the subject. I saw a copy of your presentation to
>the ITRC and applaud the comprehensive look you have taken at the
>problem across the state. I did note that some of our numbers differ
>on some specific points and have also attached a comparison of these
>points. Most are just clarifications and in some cases our numbers
>are higher than yours. I'd be happy to talk with you about the paper
>and our efforts at your convience. I know you are out the rest of
>this week and I'll be at boy scout camp all but Wednesday next week
>but we can certainly start by e-mail.
>
>Denny Hjeresen
```


```
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##################################
Dr. Dennis L. Hjeresen
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Risk Reduction and Environmental Stewardship
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(505) 665-7251/FAX 5-8118
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##################################
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"One touch of nature makes the whole world kin"
William Shakespeare. Troilus and Cressida.

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Comments_on_NMED_viewgraphs.doc	**Name:** Comments_on_NMED_viewgraphs.doc **Type:** WINWORD File (application/msword) **Encoding:** x-uuencode