New Jersey
Drinking Water Quality Institute

Maximum Contaminant Level Recommendation for Perchlorate

October 7, 2005

SUBMITTED TO:

Commissioner Bradley M. Campbell

State of New Jersey
Department of Environmental Protection

ACKOWLEDGEMENTS

The New Jersey Drinking Water Quality Institute (Institute) would like to acknowledge the efforts of the staff of the New Jersey Department of Environmental Protection (DEP) and the New Jersey Department of Health and Senior Services (NJDHSS) in the development of the Institute's recommendation.

The Institute would like to recognize the following DEP and NJDHSS personnel who prepared this document:

The health-based document was prepared primarily by Dr. Perry Cohn (NJDHSS), Dr. Gloria Post, Leslie McGeorge, and Karen Fell (DEP). Contributors to the development of the report on analytical methods include Stephen Jenniss (NJDHSS), Dr. Lee Lippincott, Karen Fell, and Michele Mooney (DEP). Participation on the Treatment Subcommittee was made by Dr. Lee Lippincott, Barker Hamill and Dr. Eileen Murphy (DEP).

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Drinking Water Quality Institute Membership

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Gene Golub, NJIT, Civil and Environmental Engineering

Statutory Authorization of Development of Drinking Water Standards

The authority for the development of drinking water standards comes from the state's Safe Drinking Water Act and subsequent amendments. Below are some excerpts from the act.

58:12A-1 . Short title

This act shall be known and may be cited as the "Safe Drinking Water Act."
L.1977, c. 224, s. 1, eff. Sept. 17, 1977.

58:12A-2. Legislative findings and declarations

The Legislature finds and declares that it is a paramount policy of the State to protect the purity of the water we drink and that the Department of Environmental Protection shall be empowered to promulgate and enforce regulations to purify drinking water by filtration or such other treatment method as it may require, prior to the distribution of said drinking water to the public; that the maintenance of high-quality potable water is essential in order to safeguard the health and welfare of the people of the State; that the Federal Safe Drinking Water Act provides a comprehensive framework, at a minimum, for establishing standards, providing technical assistance, and for regulating the collection, treatment, monitoring, storage, and distribution of potable water, and for consolidating and improving existing State law regarding potable water; and that it is in the best interests of the people of the State for the State, through its Department of Environmental Protection, to assume primary enforcement responsibility under the Federal Safe Drinking Water Act. L.1977, c. 224, s. 2, eff. Sept. 17, 1977. Amended by L.1983, c. 443, s. 12, eff. Jan. 9, 1984.

58:12A-6. Knowledge of contaminant in or likely to enter water system; actions by commissioner

The commissioner, upon receipt of information that a contaminant which is present in or is likely to enter a water system may present an imminent and substantial endangerment to the health of persons, may take such actions as he may deem necessary in order to protect the health of such persons. Such actions may include, but shall not be limited to: a. issuing such orders as may be necessary to protect the health of persons who are or may be users of such system, including travelers; and b. commencing a civil action for appropriate relief, including a restraining order or permanent or temporary injunction.

58:12A-20. Drinking water quality institute

a. There is established in the department the Drinking Water Quality Institute. The institute shall comprise 15 members as follows: the Commissioner of Environmental Protection, the Commissioner of Health, and the Chairman of the Water Supply Advisory Council, the Director of the Division of Water Resources in the department, the Director of the Office of Science and Research in the department and the Director of the Office of Occupational and Environmental Health in the Department of Health, all of whom shall serve ex officio; and nine appointed members, three of whom shall represent the water purveyors, at least one of which has as its primary water source an underground source; three of whom shall represent the academic scientific community and three of whom, having backgrounds in environmental health issues, shall represent the public, with one of each group of three set forth hereinbefore to be appointed by the Governor, the President of the Senate and the Speaker of the General Assembly. Of the members first appointed, three shall serve for terms of three years, three for terms of two years and three for terms of one year. Thereafter, all terms shall be for three years. Each member shall serve for the term of his appointment and until his successor shall have been appointed and qualified. Any vacancy shall be filled in the same manner as the original appointment for the unexpired term only. Any member of the institute may be removed by the appointing authority, for cause, after public hearing.

b. Members of the institute shall serve without compensation, but the institute may, within the limits of funds appropriated or otherwise made available to it for such purposes, reimburse its members for necessary expenses incurred in the discharge of their official duties.

c. The institute shall meet at such times and places as may be determined by its chairman, who shall be designated by the Governor. A majority of the membership of the institute shall constitute a quorum for the transaction of business. Action may be taken and motions and resolutions adopted by the institute at any meeting by the affirmative vote of a majority of the full membership of the institute.

d. The institute shall make recommendations for the implementation of the Drinking Water Quality Program by the department. These recommendations shall consist of:

(1) The development of a list of contaminants for which testing shall be required;

(2) The development of maximum contaminant levels;

(3) The development of appropriate testing techniques to measure maximum contaminant levels;

(4) The development of testing frequencies;

(5) The review of all activities undertaken pursuant to the "Safe Drinking Water Act" and any amendments or supplements thereto.

e. The Drinking Water Quality Institute shall have the authority to call to its assistance and avail itself of the services of the employees of any State, county or municipal department, board, commission or agency that may be required and made available for such purposes.

Executive Summary

The New Jersey Drinking Water Quality Institute (NJDWQI), established by the 1983 amendments to the New Jersey Safe Drinking Water Act (N.J.S.A. 58:12A1 et seq., P.L. 1983, c. 443), is responsible for developing maximum contaminant levels (MCL) or standards for hazardous contaminants in drinking water and recommending these standards to the Commissioner of the N.J. Department of Environmental Protection (DEP). The standard setting process was established within the 1983 amendments to the New Jersey Safe Drinking Water Act. In 1987, the Institute recommended MCLs for 16 of the 22 hazardous contaminants listed in the 1983 amendments which were adopted by DEP in 1989. In 1994, the Institute recommended six additional contaminants for regulation in drinking water and MCLs for these contaminants based on their presence in New Jersey waters and the frequency of occurrence. These recommendations were adopted by DEP in 1996.

There are fifteen members of the Institute. Six members serve ex officio and 9 members are appointed three each by the Governor, the President of the Senate, and the Speaker of the Assembly. The appointed members are from the academic scientific community, the public or the regulated public water supply systems. The Governor designates the Chairman of the Institute. The first meeting of the Institute was held in March 1985.

In addition to recommending drinking water standards to the Commissioner of DEP, the Institute is responsible for making recommendations for the implementation of the drinking water quality program. Three subcommittees were established to address the main areas of concern outlined in the legislation. The **Health Effects Subcommittee** is responsible for recommending health-based levels for the contaminants listed in the legislation and for developing an additional list of drinking water contaminants based on occurrence in New Jersey drinking waters. For carcinogenic contaminants, the statutory goal is to establish a standard that would not, within the limits of medical, scientific and technological feasibility, permit cancer in more than one in one million persons ingesting the contaminant over a lifetime. For noncarcinogens, the statutory goal is to establish a standard, which would not result in any adverse physiological effects following ingestion within the limits of practicability and feasibility. The **Testing Subcommittee** is responsible for reviewing and evaluating appropriate analytical methods to measure levels as close to the health based levels as possible and developing appropriate monitoring frequencies. The **Treatment Subcommittee** is responsible for evaluating best available treatment technologies for removal of the hazardous contaminants from drinking water, as well as overall program review.

The NJDWQI was requested by the DEPartment of Environmental Protection (DEP) to investigate the need to establish a regulatory limit for perchlorate in drinking water. Perchlorate is an inorganic ion that has been detected in drinking water supplies not only in New Jersey but nationally. It is used as an oxidizer in explosives, is found in fertilizer from Chile, and may also occur naturally. The adverse effects of perchlorate arise from inhibition of iodine uptake into the thyroid gland, which may lead to disturbance of thyroid function at sufficient doses. Pregnant women and infants are considered to be sensitive subpopulations for perchlorate's effects, as hypothyroidism can have serious consequences on neurodevelopment.

This report discusses the development of the MCL for perchlorate. The derivation of a health-based level, review of analytical methodologies and assessment of treatment techniques for perchlorate are provided and a maximum contaminant levels (MCL) of 5 µg/L is recommended.

Health Effects

The adverse effects of perchlorate arise from inhibition of iodine uptake into the thyroid gland, which may lead to disturbance of thyroid function at sufficient doses. The evidence from clinical and epidemiological studies indicate that there is sufficient data to support the establishment of a No Observed Effect Level (NOEL) from the low dose group in a radioiodine uptake study and to support the protectiveness of a Reference Dose (RfD) that is ten times lower. Inhibition of iodide uptake is not considered in itself to be an adverse effect, and effects on TSH and T4 were not observed in the dose range used in clinical studies or in an occupational cohort. Thus, it appears that the margin between the NOEL and adverse effects is at least two orders of magnitude or more in healthy adults. Therefore, the RfD of 0.0007 mg/kg/day provides about 3 orders of magnitude protection and should be protective of the sensitive populations, including neonates and fetuses.

It is proposed that the health-based MCL for perchlorate be based upon the Reference Dose recommended by NRC (2005) of 0.0007 mg/kg/day, which has also been incorporated in the EPA IRIS database. A health-based Maximum Contaminant Level (MCL) of 5 ug/L for perchlorate is proposed. This health-based MCL is anticipated to be protective for chronic exposure to perchlorate. Pregnant women and infants are considered to be sensitive subpopulations for perchlorate's effects, as hypothyroidism can have serious consequences on neurodevelopment.

Analytical

The Testing Subcommittee evaluated current testing technologies toward the goal of making appropriate recommendations to specify the preferred analytical procedure(s) to be utilized by the certified laboratory community for the analysis of perchlorate in drinking water samples.

Based upon the information discussed and documented in this report, the Testing Subcommittee recommends that EPA Method 314.0 be used as the analytical method of choice for the determination of perchlorate in drinking water. This method is proven to be accurate, precise, and rugged; is currently used by the certified drinking water laboratory community; and can measure perchlorate, with an accepted degree of confidence, at the low concentration levels being considered by the Health Effects Subcommittee.

Method 314.0 operated "as currently written" is sufficient to measure perchlorate to a reporting limit (RL) of 2.7 ppb. This is more than adequate to meet the health-based Maximum Contaminant Level (MCL) of 5 ppb being recommended by the Health Effects Subcommittee. If it is determined that there is a need to report perchlorate at levels lower than this, the Testing Subcommittee recommends the adoption of Massachusetts Department of Environmental Protection's (MADEP) additional laboratory method performance criteria to Method 314.0. It has been demonstrated that MADEP's added requirements are effective in lowering the certified laboratory communities' RL to 1.0 ppb.

Treatment

Recently, two comprehensive documents were released that evaluate the various water treatment technologies available to reduce perchlorate levels. In February 2005, the EPA released, "Perchlorate Treatment Technology Update – DRAFT, February 9, 2005", and in March, the Interstate Technology and Regulatory Council Perchlorate Team issued their "Technology Overview – Perchlorate". The information presented in these documents indicates that perchlorate can be reduced in drinking water to levels below detection (reported in general as 4 ug/L). Therefore, the Treatment Subcommittee of the NJ Drinking Water Quality Institute has decided to use these documents as its basis and background in recommending a level of 4 ug/L as the level to which perchlorate can be reliably and consistently removed from drinking water.

Health Effects Subcommittee

Executive Summary

Perchlorate is an inorganic ion which has been detected in drinking water supplies. It is used as an oxidizer in explosives, is found in fertilizer from Chile, and may also occur naturally. The adverse effects of perchlorate arise from inhibition of iodine uptake into the thyroid gland, which may lead to disturbance of thyroid function at sufficient doses. Pregnant women and infants are considered to be sensitive subpopulations for perchlorate's effects, as hypothyroidism can have serious consequences on neurodevelopment.

The evidence from clinical and epidemiological studies indicate that there is sufficient data to support the establishment of a **No Observed Effect Level (**NOEL) from the low dose group in a radioiodine uptake study and to support the protectiveness of an Reference Dose (RfD) that is ten times lower. **Inhibition of iodide uptake is not considered in itself to be an adverse effect, and** effects on TSH and T4 were not observed in the dose range used in clinical studies or in an occupational cohort. Thus, it appears that the margin between the NOEL and adverse effects is at least two orders of magnitude or more in healthy adults. Therefore, the RfD of 0.0007 mg/kg/day provides about 3 orders of magnitude protection and ought to be protective of the sensitive populations, including neonates and fetuses.

It is proposed that the Health-based MCL for perchlorate be based upon the Reference Dose recommended by NRC (2005) of 0.0007 mg/kg/day, which has also been incorporated in the EPA IRIS database. A health-based Maximum Contaminant Level (MCL) of 5 ug/L for perchlorate is proposed. This Health-based MCL is anticipated to be protective for chronic exposure to perchlorate.

Background Information

Physical and chemical properties

CAS Numbers:

Perchlorate ion	14797-73-0
Ammonium perchlorate	7790-98-9
Lithium perchlorate	7791-03-9
Potassium perchlorate	7778-74-7
Sodium perchlorate	7601-89-0

Chemical structure: ClO_4^-

Molecular Weight:

Perchlorate ion	99.45
Ammonium perchlorate	117.49
Lithium perchlorate	106.40
Potassium perchlorate	138.55

Sodium perchlorate	122.44

Physical State:

Ammonium perchlorate and sodium perchlorate	White orthorhombic crystals
Potassium perchlorate	Colorless crystals or white crystalline powder

Melting/Decomposition Point:

Ammonium perchlorate	439^{o}C (decomposition)
Potassium perchlorate	400^{o}C (decomposition), 525^{o}C (melting)
Sodium perchlorate	480^{o}C (decomposition)

Water Solubility

Ammonium perchlorate	249 g/L (25^{o}C)
Lithium perchlorate	597 g/L (25^{o}C)
Potassium perchlorate	21 g/L (25^{o}C)
Sodium perchlorate	2096 g/L (25^{o}C)

Uses

Perchlorate is a strong oxidizer, and is thus used in the solid propellant for rockets, missiles, and fireworks; these are primary uses within the United States. It has also been used in inflators for air bags, as well as in other applications. Large amounts of perchlorate have been disposed of throughout the United States since the 1950s. The current annual production of perchlorate is not available, as it is classified as a strategic compound. Nitrate fertilizer from Chile also contains perchlorate. In one study, the concentrations were 0.15-0.16 mg/g (Urbansky et al., 2001).

Perchlorate has been found in lettuce (FDA, 2004), and it is thought that it is taken up from irrigation water contaminated with perchlorate. This process has not yet been fully characterized. Perchlorate has also been detected in dairy milk and human breast milk samples from throughout the United States (Kirk et al., 2005). Recent studies suggest that perchlorate is found in many rain and snow samples and may be formed naturally in the atmosphere; this may account for its widespread presence at low levels (Dasgupta et al., 2005) Perchlorate was used in the past to treat thyroid disease, but is currently rarely used for this purpose.

Environmental Fate and Occurrence

Perchlorate (ClO_4^-) in water supplies originates from the dissolution of salts, such as ammonium, potassium, magnesium, or sodium. The perchlorate salts are highly water soluble, and the health effects of perchlorate salts are therefore considered identical to the effects of the perchlorate ion. The perchlorate ion is very mobile in water and is persistent in ground and surface water.

Large public water systems and a sample of small public water systems in the U.S. were required to monitor for perchlorate between January 2001 and December 2003 as part of the Unregulated Contaminants Monitoring Rule (UCMR) requirements set by the Environmental Protection Agency (EPA). As of May 2004, perchlorate was detected above the minimum reporting level (MRL) of 4 ppb in 1.9% of the 28,179 nationwide samples reported. The maximum concentration reported was 200 ug/L and the median concentration above the MRL was 6.4 ppb. As of September 2004, perchlorate has been detected in water supplies in 35 states. Improvements in analytical capabilities may lower this minimum reporting limit to below 1 ug/L in the near future.

In New Jersey, 123 public water systems were required to monitor as part of the Unregulated Contaminant Monitoring Rule. Perchlorate was detected at or above the minimum reporting level of 4 ppb in six of those systems. The minimum concentration detected was 4 ppb and the maximum concentration detected was 13 ppb.

In order to further evaluate the occurrence of perchlorate in New Jersey, DEP conducted additional perchlorate sampling between 2003 and early 2005. Public water systems were chosen based on their potential vulnerability to perchlorate contamination. Reasons for sampling included proximity to military installations and unexploded ordnance, and proximity to previous UCMR-tested sites that showed perchlorate detections. In a few circumstances, DEP sampled some of the individual public wells that had tested high in the original UCMR sampling. Samples were collected from both community and non-community water systems. Most, but not all, of these samples were taken before treatment. A small number of these were point of entry (POE) samples. The samples were also analyzed using EPA Method 314.0. For this study, the laboratory was able to achieve a minimum reporting level (MRL) of 1 ppb or lower, while the EPA had used an MRL of 4 ppb as part of the UCMR sampling, in part because of method improvements over the period. The summary from the DEP sampling can be found in Table 1 below.

Table 1. DEP Perchlorate Sampling

Number of Public Water Systems Analyzed	Number of Analyses (includes repeats)	Number of Detections greater than or equal to 1 ppb and includes repeats	Number of Public Water Systems with Detections greater than or equal 1 ppb	Maximum Concentration Detected (ppb)
67	114	21	11	23

Health Effects

Overview

The adverse effects of perchlorate arise from its action as an inhibitor of the uptake of iodide into the thyroid gland by a thyroid cell surface molecular pump, the sodium-iodide symporter (NIS) protein. In the thyroid, iodine is bound to certain constituent amino acids of the protein thyroglobulin that are subsequently converted into the thyroid hormones, triiodothyronine (T3) and thyroxine (T4). At sufficiently high concentration, inhibition by perchlorate can lead to a decrease in the production of the thyroid hormones, triiodothyronine (T3) and thyroxine (T4). In normal individuals who have adequate iodide in their diets, a decrease in the production of these hormones is compensated for increased production of thyroid stimulating hormone (TSH or thyrotropin) by the pituitary, which leads to stimulation of the thyroid gland to bring production of T3 and T4 back to normal. Over stimulation can lead to enlargement of the thyroid, referred to as "goiter". Pregnant women, infants, and children are particularly sensitive to the effects of insufficient thyroid hormones, because hypothyroidism (low thyroid hormone levels) can affect the development of the central nervous system and the skeleton (Haddow et al.,1999; Pop et al., 1999, 2003; Smith et al., 2000).

Genotoxicity

Results of genotoxicity studies on perchlorate were summarized in EPA (2002). Genotoxicity studies on perchlorate have included Ames testing, with and without metabolic activation, in two independent laboratories; mouse lymphoma gene mutation assay, with and without metabolic activation; micronuclei formation in mice and rats. All of these tests were negative, indicating that perchlorate is not mutagenic or clastogenic.

Pharmacokinetics

Perchlorate is almost completely absorbed after oral exposure, and is excreted primarily unchanged in the urine. A study of elimination in exposed workers indicates that the half life in humans is about 8 hours (OEHHA, 2004). Therefore, perchlorate does not accumulate in the body over time.

Carcinogenicity

Perchlorate has been found to increase the incidence of tumors of the thyroid gland in several studies in rats and mice (reviewed by EPA, 2002 and NRC, 2005). The tumors occurred at doses high enough to disrupt thyroid function. The NRC and EPA conclude that perchlorate is unlikely to pose a risk of thyroid tumors to humans, at least below the high doses needed to alter thyroid hormone homeostasis. Although high doses of perchlorate caused an increase in thyroid tumors in rodents, the mechanism by which these tumors occur has been well characterized as an adaptive physiological mechanism to effects arising from the prolonged inhibition of iodide uptake. Perchlorate is considered to cause tumors in animals through a mechanism for which a threshold exists, in contrast to the non-threshold mechanism assumed for genotoxic carcinogens. Perchlorate is not genotoxic and does not increase the risk of cancer at low doses (unlike many other environmental chemicals of concern). Additionally, humans are considered to be less sensitive than rats to the disruption of thyroid function, and are therefore unlikely to develop thyroid tumors from perchlorate exposure.

Animal Studies

In contrast to many other environmental chemicals of concern, human data on iodide uptake into the thyroid, the biochemical step which is the precursor to adverse effects, is available for perchlorate. Additionally, although the basic mechanisms involved in the function and regulation of the thyroid in rats are qualitatively similar to those in humans, differences in binding proteins, binding affinities of the proteins for the hormones, turnover rates of hormones, and thyroid stimulation by placental hormones lead to important quantitative differences between the two species. These differences between rats and humans affect their responses to thyroid inhibitors, such as perchlorate. Therefore, although studies in rats provide useful qualitative information on potential adverse effects of perchlorate exposure, they are limited in their utility for quantitatively assessing human health risk associated with perchlorate exposure.

It is beyond the scope of this document to review all of the animal studies conducted on perchlorate, particularly since the risk assessment focuses on human data. The animal studies are reviewed comprehensively by EPA, 2002 and NRC, 2005. A few key findings were reviewed by EPA (2005) and are summarized below:

> In a study conducted by Argus (2001), female rats (dams) were exposed to perchlorate during gestation and lactation. This study provides a comprehensive evaluation of perchlorate impacts on rat development. Ammonium perchlorate was administered in drinking water at concentrations that provided doses of 0, 0.01, 0.1, 1.0 and 30 mg/kg/day. Administration began 2 weeks before mating and extended through postnatal day 22. The offspring were exposed to perchlorate in utero, through their mother's milk, and through any consumption of the perchlorate contaminated water provided to their mothers.
>
> There were dose-related increases in serum TSH and dose-related decreases in serum total T4 and T3 in the dams, fetuses, and pups. Serum T4 was decreased significantly in dams at all doses during gestation. A downward trend was observed in serum T3 in the dams, but was not statistically significant during gestation until the highest dose group. Serum TSH was substantially increased in the pregnant dams at all doses. Statistically significant changes in thyroid hormones and TSH were noted in the fetuses and pups, although the changes tended to be more modest than those in the dams.
>
> Argus (2001) also conducted histological evaluations of the thyroid gland at the same time as the thyroid hormone and TSH measures. In dams, histological examination revealed colloid depletion, follicular-cell hypertrophy, and follicular-cell hyperplasia. These effects were mainly restricted to the highest dose group (30 mg/kg/day), although colloid depletion and follicular-cell hyperplasia were increased at 1.0 mg/kg/day on postnatal days 10 and 22, respectively. In rat fetuses and pups, colloid depletion of the thyroid was the most consistent histological finding, observed consistently in the highest-dose animals and, to a smaller extent, in the 1.0 mg/kg/day group. The thyroid morphology of the two lower-dose groups of animals (0.01 and 0.1 mg/kg/day) was similar to that of controls.
>
> The effects of maternal perchlorate exposure on offspring brain development in Sprague-Dawley rats were also examined by Argus Laboratories (Argus, 2001). Dams were

exposed to the above noted perchlorate doses (Argus, 2001). Pups were sacrificed at several post-natal ages and their brains fixed and sectioned for histological evaluation. The thickness of various brain regions was measured (morphometry). Statistical analyses revealed a number of significant effects, most notably an increase in the thickness of the posterior corpus callosum. However, questions and concerns about the studies have been raised, including apparent systematic differences in the plane of section among treatment groups, lack of clear and consistent dose-response relationships, doubts about the biologic plausibility of the changes observed, and concerns that the measures used were relatively insensitive and would be unlikely to pick up subtle differences in neurodevelopment. On the basis of its review of the data, the NRC (2005) committee concluded that the evidence in Argus (1998, 2001) was inadequate to determine whether or not a causal relationship exists between maternal perchlorate exposure and pup neurodevelopmental abnormalities.

The NRC (2005) committee also noted that perchlorate could theoretically produce several types of adverse immunological reactions. Based on their evaluation of the animal data, the NRC (2005) did not conclude that ingestion of perchlorate causes immunotoxic effects in animals.

Human Data

Human data include several epidemiological studies conducted in Arizona, California, Nevada, and Chile, as well as several clinical studies of the effect of perchlorate on radioiodine uptake. The North American studies were based on populations exposed to 0-10 ppb in drinking water, while in the Chilean study area exposure was in the 0-120 ppb range. Various difficulties in interpretation of the epidemiology were discussed in NRC (2005).

The key study upon which NRC (2005) and several other risk assessments have focused is that of Greer et al. (2002) in which groups of healthy men and women were administered perchlorate in water at 0.007, 0.02, 0.1 and 0.5 mg/kg/day for fourteen days. The results of this study are consistent with several smaller human studies on the effects of perchlorate (reviewed by NRC, 2005). The endpoint in this study was iodide uptake by the thyroid, as this is the first step in the production of thyroid hormones, and is the key event that precedes all other possible effects of perchlorate relating to the thyroid, including developmental effects. Inhibition of iodide uptake is not considered an adverse effect, per se, but can potentially lead to the adverse outcome of hypothyroidism in sensitive individuals. Thyroid uptake of radioiodide was measured at 8 and 24 hours after radioiodide administration at baseline, on days 2 and 14 of perchlorate administration, and 15 days after cessation of dosing.

On day 14 of administration, the mean 24-hour radioiodide uptake was 98.2% of the baseline value in the seven subjects given 0.007 mg/kg/day, a non-statistically significant decrease. Decreases in iodide uptake at day 14 at the three higher doses were statistically significant: 83.6% of the baseline value in the 10 subjects given 0.02 mg/kg/day: 55.3% of the baseline value in the 10 given 0.1 mg/kg/day; and 32.9% of the baseline value in the 10 given 0.5

mg/kg/day. The effects of perchlorate were very similar on day 2 and day 14 of perchlorate dosing. At 15 days after exposure ended, iodide uptake was very similar to baseline, indicating that perchlorate's effects are not persistent. The results were similar in the women and men.

Radioiodine uptake data for the individual participants in the Greer (2002) study is shown in Figure 2 of the paper. The 24 hr baseline averages for radioiodine uptake in the various dose groups were in the 18-21% range (Table 1), but individually they ranged from 10-35%, while the normal range for 24-hour thyroidal radioiodide uptake is 10-30% in the U.S. Thus, a 16% change in the 0.02 mg/kg/d group, resulting in an average of 15% radioiodine uptake versus the average 18% radioiodine uptake in the baseline measurements for that dose group, does not necessarily represent a shift outside the clinically normal range. However, the 0.1 mg/kg/d dose group reduced iodine uptake to the margin of normal (11% average uptake) and the 0.5 mg/kg/d high dose group reduced iodine uptake to 6-7%. Nevertheless, even at 70% inhibition of radioiodine uptake in the 0.5 mg/kg/d high dose group, there were no changes in serum T4, T3 and TSH except for a very small decrease in serum TSH concentrations (not an increase, as would be expected if thyroid secretion decreased).

There are several other small corroborating studies of radioiodine uptake with healthy euthyroid individuals exposed to perchlorate doses near the Greer et al. (2002) low dose. Lawrence et al. (2001) found that approximately 0.04 mg/kg/d given to 8 men caused a 10% non-statistically significant decrease of 24 hr thyroidal iodine uptake measured after 14 days of exposure, which was less than the 16% decrease found in the 0.02 mg/kg/d dosage group by Greer et al. (2002). At 0.14 mg/kg/day Lawrence et al. (2000) reported that there was a 40% decrease after 14 days among 9 euthyroid males, but no effect on T4 or TSH. Braverman et al. (2004) gave 0.007 mg/kg/d to 5 healthy individuals and 0.04 mg/kg/d to 4 individuals for 6 months. No statistically significant changes occurred at either dose in thyroidal iodine uptake or serum T4 and TSH at 3 and 6 months after the start of exposure or as compared to 4 controls. Although individual study groups were small, the results were highly consistent within each treatment group in that the variance of the group during exposure was similar to or less than the baseline variance. In addition, study of an occupational cohort (Braverman et al., 2005), discussed more at length below, indicated that thyroidal radioiodide uptake at the end of 3 consecutive days with 12 hour shifts also yielded similar results.

Greer et al. (2002) derived linear regression models to describe the overall data. Using one of those models they estimated that a 5% benchmark effect level (benchmark dose-5% effect level, BMD05) was 0.009 mg/kg/d for the 24-hour radioiodine uptake measurement on the 14th day of exposure. The 0% benchmark effect level calculated by Greer et al. (2002) was estimated to be 0.006 mg/kg/d. California OEHHA (2004) also calculated a BMD05 and BMDL05 (lower 95th percentile confidence interval of the 5% effect level) from the date of Greer et al. (2002) using a different mathematical model. California's BMD and BMDL05 are 0.007 and 0.004 mg/kg/day, respectively. These estimates are all close to the actual lowest dose in the study (0.007 mg/kg/day), indicating that using the low dose as the starting point (NOEL) is a public health protective approach.

There are no dose controlled exposure studies analogous to Greer et al. (2002) in children, but TSH levels were not increased among neonates and 6-8 yr olds in Chile exposed to drinking water levels of 100-120 micrograms/L (in the town of Taltal) (Crump et al., 2000).

Recently, Tellez et al. (2005) reported that there is no effect on TSH levels in pregnant women (approximately 12 and 33 weeks gestation) and postpartum women (approximately 12 weeks after delivery) in Taltal when compared to similar women in towns with low or no perchlorate. Although only a few of the pregnant women studied by Tellez et al. (2005) had perchlorate doses exceeding the Greer et al. NOEL developed by NRC of 0.007 mg/kg/day, many had doses approaching the NOEL, and there was no discernable tendency toward hypothyroid findings as perchlorate dose increased. Among the pregnant women studied by Tellez et al. (2005), 90% of the women from Taltal exceeded the RfD of 0.0007 mg/kg/day, yet there was no tendency toward hypothyroidism in either mothers during pregnancy or their infants at birth. (With regard to iodine nutrition during pregnancy in the Chilean studies, the pregnant women studied had median urinary iodine levels of 269 µg/L, which is somewhat higher but not too dissimilar to 174 µg/L in pregnant women in the U.S. recently surveyed by the Centers for Disease Control and Prevention (CDC) (Campbell et al., 2005; see below).)

Crump and Gibbs (2005) modeled BMDL05s for the TSH results from the Greer et al. (2002) data, although neither T4 nor TSH were affected (i.e., BMDs were undefined). With a choice of several modeling assumptions, the Greer et al. study yielded BMDL05s for free serum T4 were approximately 0.5 mg/kg/d, while those for TSH were more varied, in the 0.6 – 0.8 mg/kg/d range. They also modeled data from an occupational cohort (Lamm et al., 1999; Braverman et al, 2005). In these data T4/T3 levels were statistically significantly increased and TSH levels were marginally (but not statistically significantly, $p = 0.14$) increased when comparing workers ($N = 29$) at the end of their 4 day time off period (pre-exposure) with the same workers at the end of their 3 consecutive day-12 hour per day work period (exposed). Serum and urine perchlorate levels were also measured before and after the 3 consecutive day shifts, and it was estimated that the average exposure over the three consecutive days was 0.33 mg/kg/d or half of that when averaged over 6 days (3 days on, 3 days off) Compared with community controls ($N = 12$), T4/T3 were marginally higher at the end of exposure, but TSH was statistically significantly lower. The levels for BMDL05 were 0.2-0.5 mg/kg/d.

At the highest clinical study doses tested, Brabant et al. (1992) studied five healthy male volunteers pretreated with iodine for four weeks before perchlorate exposure. Volunteers were given 3 x 300 mg/day (approximately 13 mg/kg/d) of perchlorate for another four weeks. At the end of the four-week perchlorate-dosing period, perchlorate treatment had no effect on total serum T3 or T4 levels or on thyroid gland volume. However, serum free T4 and TSH levels were significantly diminished by treatment, and serum thyroglobulin levels were almost doubled, indicating the stress of the treatment on thyroid hormone homeostasis. Notably, TSH was decreased rather than increased.

Reference: Dose and Health-Based MCL Derivation

The Perchlorate Reference Dose Recommended by NRC

The NRC (2005) recommends using the Greer et al. (2002) study discussed above as the basis for the Reference Dose. The results of the Greer et al. (2002) study are consistent with several previous smaller human studies on the effects of perchlorate. As mentioned above, the endpoint in this study, inhibition of iodide uptake by the thyroid is not considered an adverse effect, per se, but can potentially lead to the adverse outcome of hypothyroidism in sensitive individuals. For this reason, this endpoint is considered to be a conservative, health-protective approach.

The Reference Dose recommended by NRC (2005) for perchlorate is 0.0007 mg/kg/day. This was derived by applying an uncertainty factor of 10 to the lowest dose (0.007 mg/kg/day) given in the controlled human 14 day study. In this study, 0.007 mg/kg/day was considered to be the No Observed Effect Level (NOEL) for inhibition of iodide uptake by the thyroid, in contrast to the No Observed Adverse Effect Level (NOAEL) typically used as the endpoint for Reference Dose development. NRC states that this RfD will be protective for sensitive populations, such as fetuses of pregnant women with low thyroid function or iodide deficiency, as the uncertainty factor of 10 will be sufficient to protect these sensitive individuals.

The NRC (2005) discussed the rationale for deciding that an additional uncertainty factor to account for the short length of the study (14 days) was not needed. Chronic exposure to perchlorate is not expected to have greater effects than short term exposure, because the inhibition of iodide uptake occurs within a short time frame. Actually, prolonged exposure in adults may have less effect than short term exposure, because the thyroid has compensatory mechanisms to deal with iodide deficiency by increasing iodide uptake. Additionally, perchlorate does not accumulate in the body even with chronic exposure.

The NRC (2005) estimated that healthy adults would have to be exposed to levels greater than 0.4-0.5 mg/kg/day (approximately two to three orders of magnitude above the Reference Dose) for an extended period of time before measurable decreases in levels of serum T4 and/or increases in TSH. Importantly, these levels may exhibit statistically significant changes, but only when these changes exceed a critical level do they become clinically significant in adults.

Since perchlorate is a competitive inhibitor of the NIS protein, one can calculate a level of dietary iodine that would counterbalance the effect of perchlorate. Although the only data available is goiter incidence, it is instructive, since elevated TSH levels are a necessary step to goiter formation. Delange and Ermans (2000) noted that humans chronically exposed to thiocyanate, an inhibitor of thyroidal iodine transport in cabbage and cruciferous vegetables, can maintain thyroid function without increasing the frequency of goiter with dietary iodine of $\geq$ 3 µg iodide per 1 mg thiocyanate. Since perchlorate is 20 times more potent than thiocyanate as an inhibitor of iodine uptake (Greer et al., 1966), and adjusting for the relative molecular weights of the two compounds, it is calculated that the ingestion of 36 µg of iodine per mg of perchlorate should be sufficient to avoid goiter (Greer et al., 2002). (The range of perchlorate-thiocyanate equivalency estimates in the literature is 10-100x, but 20x is about the middle (Dohan et al., 2003).) Daily intake of perchlorate at the Greer et al. low dose would require about 10 times less iodine than in the median diet, estimated as 200 µg/day from the NHANES III data (NAS, 2000). Intake at the RfD would require only 1% of the iodine in an average diet to prevent the goitrogenic effect of perchlorate.

Perchlorate Reference Doses Developed by Other Agencies

References doses for perchlorate differing from the one developed by NRC (see above) have been derived by several other agencies, including EPA (2002, draft), California EPA, and Massachusetts DEP. The basis for these Reference Doses are summarized in the table below:

Table 2. Perchlorate Reference Doses Developed by Various Agencies

	EPA (2002) Draft	**Massachusetts (2004) Draft***	**California PHG (2002)**	**NAS/EPA IRIS**
Study	Rat developmental (Argus, 2001)	Argus (2001) and other rat studies/(Greer (2002))	Greer (2002)	Greer (2002)
Basis	Pups – brain morphometry and thyroid effects. Dams - hypothyroidism	Rat developmental/ (Greer (2002))	Human Iodide Uptake	Human Iodide Uptake
Dose	0.01 mg/kg/day LOAEL	0.0085 mg/kg/day (rat) LOAEL (0.007 mg/kg/day (Greer) LOAEL)	0.004 mg/kg/day BMDL 05	0.007 mg/kg/day NOEL
Uncertainty Factors	300 –Total: 3-Intraspecies (PK model used to calculate human equivalent dose) 10 – LOAEL to NOAEL 3-Tumors in F1 Pups 3 – Database Deficiency (Immunotoxicity)	100- Total: 10- Intraspecies 10 – LOAEL to NOAEL 3 – Animal to human (300 – Total 10 –Intraspecies 3 – LOAEL to NOAEL 10 – Database deficiency)	10- Intraspecies	10 - Intraspecies
Reference Dose	0.00003 mg/kg/day	0.00003 mg./kg/day (0.000023 mg/kg/day)	0.0004 mg/kg/day	0.0007 mg/kg/day

**Mass. Reference Dose is based on convergence of several risk assessments based on animal and human data. The information shown in parentheses, based on human data, was not the actual value chosen, but was used to confirm the final Reference Dose of 0.00003 mg/kg/day.*

EPA, in a draft risk assessment dated January 2002, determined that the Lowest Observed Adverse Effect Level for perchlorate is 0.01 mg/kg/day, based on effects on brain morphometry in exposed rat pups, hypothyroidism in the mothers of the pups, and histopathological and hormonal thyroid effects in the pups (Argus, 2001). Based on a human equivalent exposure calculated via a pharmacokinetic model and application of an uncertainty factor of 300, a Reference Dose of 0.00003 mg/kg/day was derived. The uncertainty factor of 300 is composed of the following components: a factor of 3 for intraspecies variability, a factor 10 to extrapolate the LOAEL to the NOAEL, a factor of 3 to account for concern about tumors observed in F-1 pups, and a factor of 3 for inaccurate characterization of immunotoxicity, based on additional data from more recent studies about these effects. This draft Reference Dose has since been superseded, as EPA has accepted the Reference Dose recommended by NRC (2005) as its consensus Reference Dose in its IRIS database

California has finalized a drinking water Public Health Goal (OEHHA, 2004) of 6 µg/L, based on the human study of Greer et al. (2002). Data on uptake of iodide by the thyroid were analyzed using a benchmark dose with mathematical modeling based on the Hill equation. The 95% lower confidence limit on the benchmark dose of 0.0037 mg/kg/day and an uncertainty factor of 10 to account for intraindividual variation was used to arrive at a Reference Dose of 0.0004 mg/kg/day. The exposure factors used by California to arrive at its final Public Health Goal (similar to Health-based MCL) differ from the standard approach used by New Jersey and EPA, and are discussed below.

The draft final risk developed by the Massachusetts Department of Environmental Protection (2004) is based on analysis of both animal and human data. Massachusetts determined a LOAEL of 0.0085 mg/kg/day for the perchlorate ion (equivalent to 0.01 mg/kg/day for ammonium perchlorate) for effects observed in rat studies, including Argus (2001). For human data, 0.007 mg/kg/day was considered to be the LOAEL in the Greer et al. (2002) study. A range of possible uncertainty factors was applied to these NOAELs – 300-1000 to the 0.00085 mg/kg/day animal LOAEL and 100-300 to the 0.0007 mg/kg/day human LOAEL. The resulting Reference Doses span 0.0000085 mg/kg/day to 0.00007 mg/kg/day, and the animal-based and human-based assessments overlap at 0.000023 and 0.00003 mg/kg/day, and Massachusetts chose 0.00003 mg/kg/day as its final Reference Dose.

The low dose in Greer et al. (2002) was not considered a NOEL by some because 1) the draft assessment by EPA (2002) estimated the study power at the low dose to be 0.1, in contrast to study power greater than 0.9 in the higher dose groups, and 2) the low dose group contains individuals with high baseline RAIU that is decreased after 14 days of exposure.

The first concern is an important criticism of designating the low dose as a NOEL. However, as noted above, several studies, though small, observed a similar dose-response and two found no decrease of radioiodine uptake at the 0.007 mg/kg/day. Furthermore, the power at the low dose matters much less for computations generating a BMDL curve or regression equation.

In general and particularly noticeable in lower dose groups, individuals with low baseline radioiodine uptake were not affected or had slightly increased uptake. In contrast, the decrease in radioiodine uptake by some individuals in the low dose group may in part be due high baseline uptake in those with marginal iodine insufficiency, as noted by Greer et al. (2002). It is also clear that daily/weekly changes in dietary iodine (e.g., between 150 and 250 µg/day, 50 µg/day above or below the NHANES III median) can also affect radioiodine uptake by 15-20% on the basis of direct competition by non-radioactive iodine (Franklyn and Shephard, 2000). Day-to-day intra-individual urinary iodine excretion and dietary iodine intake, has been shown to vary by as much as 3-fold in Denmark (Rasmussen et al., 1999), corresponding to a larger change in radioiodine uptake. While a sequential study of radioiodine uptake in normal individuals could not be found, 15-20% variability is regarded as a reasonable estimate of normal week-to-week variability.

Since the low dose in Greer et al. (2002) (0.007 mg/kg/day) is only 1.8 times higher than the California BMDL05 (0.004 mg/kg/day), and since the lowest 95th percentile of the dose resulting in a 5% effect based on regression equations generated by Greer et al. (2002) is only 0.006 mg/kg/day, the factor of three applied by Massachusetts to account for the use of a LOAEL is probably an over application of that uncertainty factor.

It is probably not necessary to apply an uncertainty factor for database deficiency to the human data of Greer et al. (2002) because radioiodine uptake must be affected before any adverse effect can occur. However, concerns have been raised about the incomplete understanding about how perchlorate acts on the thyroid and other organs and about possible perchlorate accumulation in the thyroid and other organs (e.g., mammary gland and breast milk), as well as the lack of studies on immunotoxicity. Concerns have also been raised about the toxic effects of long-term high doses of perchlorate in the clinical environment and because the Greer et al. study incorporated only 14 days of exposure. There were no adverse effects among the nine individuals exposed for 6 months in the Braverman et al. (2004) study and there were few adverse effects among adults who had received perchlorate during long-term clinical treatment with the lower clinical dose range (NAS, 2005), but some of the patients at the higher end of the clinical dose range did exhibit serious side effects. None appeared to involve immunotoxicity. There was also the concern that thyroid hormone levels in rats exposed for 90 days were more sensitive to perchlorate than after 14 days. However, humans have a clearly better homeostatic thyroxine response than rats.

Of more critical concern is the small reserve of thyroxine and thyroxine precursor in neonatal human thyroids. From an autopsy series study of thyroids from preterm neonates (van den Hove et al., 1997) it was estimated that newborns that are 34-41 weeks of gestation (moderately preterm) at birth have daily T4 production that is sufficient for that day. In comparison, an adult has several months worth of stored iodinated thryoglobulin. By two weeks after birth the full term infant has sufficient thyroidal maturity to begin storing iodinated thyroglobulin. There are two concerns with this autopsy series study: 1) the unclear effect of the various causes of death (including cardiovascular and respiratory problems) on thyroid homeostasis and 2) the low iodide level in Belgian nutrition at that time.

On the other hand, the robustness of the neonatal thyroid is demonstrated by a series of studies of preterm neonates in the Netherlands (van Wassenaer et al., 1997, Briet et al., 2001, van Wassenaer et al., 2002). Supplementation with thyroxine only improved the neurodevelopmental process in infants born before 27 weeks of gestation, based on subsequent neurobehavioral testing through age 6-7 years old. Infants born older than 27-28 weeks of gestation displayed no additional improvement and, apparently, negative neurodevelopmental effects.

Another study showed that preterm neonates of 27-30 weeks gestational age are in negative iodine balance (indicative of thyroidal stress) during the first week after birth (Ares et al., 1997). However, by 4 weeks after birth the premature neonate is in well in positive iodine balance.

Neonates born with a congenital thyroid problem are efficiently detected in a universal screening system in New Jersey, and they receive prompt treatment with synthetic hormone. Notably, even in infants with congenital hypothyroidism, maternal thyroxine supplies approximately 20-40% of normal levels at the time of birth (Vulsma et al., 1989).

The NAS considered the 0.0007 RfD protective for infants in part because pharmacokinetic (PK) modeling, particularly the “area under the curve” (AUC) for exposure of the thyroid to perchlorate, shows that delivered dose in neonates is similar to or less than adults. Since the AUC for perchlorate in serum of neonates and adults appears to be similar in rats (Clewell et al., 2003), the PK portion would need little additional uncertainty factor to protect infants, leaving only pharmacodynamic (PD) uncertainty as the primary focus for an uncertainty factor to protect infants. Such information would include the functional maturity of the NIS protein, its associated cellular mechanisms, and the hypothalamo-pituitary-thyroid feedback axis. Although there is no PD data on RAIU for human infants, rodent studies indicate that the sensitivity of neonatal thyroid radioiodine uptake to perchlorate is not significantly different (and probably less than) from the adult (Clewell et al., 2003), and that the dose-response curve for perturbations of TSH and T4/T3 in neonatal rats is relatively flat in comparison with adult rats (Lewandowski et al., 2004). The uncertainty factor of 10 used by the NAS would seem sufficiently protective for infants, despite the vulnerability due to low thyroid storage of thyroxine and thyroxine precursor, mentioned above. Indeed, the study of neonatal screening in Chile (described above) with 0-120 µg/L perchlorate in the water supply did not find any decrease of T4 or elevation of TSH at the higher exposure levels.

Fetuses may represent the most vulnerable population. Evidence from PBPK modeling (Clewell et. al., 2003) predicted that thyroidal iodine uptake inhibition due to perchlorate in rat fetuses is approximately twice that of the adult. At a maternal rat dose of 0.01 mg/kg/d, their model predicted 4% inhibition of radioiodine uptake in the fetus. This contrasts with a model predicted 0.4% inhibition in neonatal rats.

Human fetuses start secretion of thyroxine by 18-20 weeks of gestational age and maternal production is the major supply until late in pregnancy. A study of 2,000 pregnant women at 4 months of gestation in Maine found that 2.2% were subclinically hypothyroid (elevated TSH only), while 0.3% were overtly hypothyroid with decreased levels of T4/T3 (Klein et al., 1991). This is similar to the 0.25% categorized as overtly hypothyroid in a study of the subsequent effect on intelligence (Haddow et al., 1999)

Since subclinical hypothyroidism is defined as elevated TSH and normal T4/T3 , the effect of perchlorate on T4/T3 at the NAS RfD would be expected to be minimal for most of this potentially sensitive population. However, there is greater fetal risk among the fraction of the overtly hypothyroid women who are not diagnosed since pregnancy screening is not universally practiced.

Although iodine sufficiency has been raised as a concern during pregnancy, T4 and TSH were not affected in pregnant women with low urinary iodide measured in the 1988-1994 CDC National Health and Nutrition Examination Survey (NHANES III) (Soldin et al., 2005). Recently, a meta-analysis of six European studies showed only a minimal effect of iodine supplementation on thyroid hormones in areas with marginally sufficient iodine intake (Zimmerman, 2005).

(The NHANES III data showed a significant decline in urinary iodine (UI) compared to the 1970-1974 NHANES I data (Hollowell et al., 1998). Analysis of recently released raw data from the 2000-2001 NHANES indicates that UI in pregnant women is noticeably higher than the 1988-1994 levels (Caldwell et al., 2005; P Cohn, personal communication). Median creatinine adjusted UI was 173 µg/g versus 132 µg/g during the 1988-1994 period. The NAS report sums it up as, "… the data indicate that iodide deficiency in the U.S. population is mild, if it exists…")

Reference Dose Summary and Conclusions

A Reference Dose (RfD) of 0.0007 mg/kg/day is recommended, based on application of an uncertainty factor of 10 to the No Observed Effect Level (NOEL) for inhibition of radioiodide uptake, 0.007 mg/kg/day. Although minimal inhibition is observed in some euthyroid individuals at this dose, this inhibition is not associated with adverse outcomes and may be due to variations in dietary intake of iodine over time. Effects which are considered adverse, such as increased TSH or decreased T4, were not observed in the dose range used in clinical studies or in an occupational cohort. It appears that the NOEL for iodide uptake is about two orders of magnitude below the dose at which adverse effects begin (NOAEL, No Adverse Effect Level). Thus, the data from clinical and epidemiological studies support the establishment of a NOEL of 0.007 mg/kg/day from radioiodine uptake studies and to support the protectiveness of an RfD of 0.0007 mg/kg/day that is ten fold lower than the NOEL. Therefore, the RfD of 0.0007 mg/kg/day is about three orders of magnitude below the threshold for adverse effects, and is expected to be protective of the sensitive populations, including neonates and fetuses.

RfD <---(10 x) --→ NOEL <---------(~100 x) ----------→ NOAEL

Derivation of Health-based MCL for Perchlorate

It is proposed that the Health-based MCL for perchlorate be based upon the Reference Dose recommended by NRC (2005) of 0.0007 mg/kg/day. This Reference Dose has also been incorporated in the EPA IRIS database. As discussed extensively above, this Reference Dose is considered to be health protective since it is based on a No Observed Effect Level for an effect which is not adverse, with the application of an appropriate uncertainty factor for intra-individual variation. As discussed above, the results of the study which forms the basis for this Reference Dose is based, Greer et al. (2002), are confirmed by the results of several similar smaller studies. The Reference Dose is also supported by the lack of effects on thyroid function in Chilean children exposed to perchlorate in drinking water at much higher doses, and by the recent analysis of the benchmark dose for effects on T4 and TSH by Crump and Gibb (2005).

The Health-based MCL or Health-based Ground Water Criterion from the Reference Dose would be as follows:

$$\frac{0.0007\ \text{mg/kg/day} \times 70\ \text{kg} \times 0.2}{2\ \text{Liters/day}} = 0.0047\ \text{mg/L or}\ 5\ \text{ug/L}$$

Where:
0.0007 mg/kg/day = Reference Dose
67 kg = assumed body weight of pregnant adult (see explanation below)
0.2 = Relative Source Contribution factor (see explanation below)2 Liters/day = Assumed daily water ingestion

For perchlorate, the health-protective approach is to use the body weight of a pregnant woman, instead of the 70 kg default, as pregnant women may represent a sensitive subpopulation. EPA Office of Water (2004) currently recommends 67 kg as the value to be used for pregnant women.

The Relative Source Contribution factor of 0.2 or 20% is included to account for other sources of exposure to the contaminant, such as food or air. EPA guidance, which is followed by DEP in its risk assessments, suggests 20% as a default, in the absence of specific information. Additionally, 20% is recommended as the “floor” so that a lower factor (e.g. 10%) is not recommended even if less than 20% of exposure comes from drinking water. As discussed above, available information indicates that perchlorate is present in the food supply, including cows milk and lettuce, so that the use of the 20% default is appropriate for the Health-based MCL.

Health-based Drinking Water Values Developed by Other Agencies

EPA has not proposed a Maximum Contaminant Level Goal (MCLG, equivalent to Health-based MCL) for perchlorate, although it has finalized the perchlorate Reference Dose in its IRIS data base. Massachusetts has issued a health-based guidance value of 1 ug/L, apparently based upon Drinking Water Equivalent Level derived from the draft EPA (2002) risk assessment based on rat developmental effects. This guidance does not incorporate a Relative Source Contribution Factor in its derivation.

California OEHHA (2004) used a somewhat different exposure approach in developing its perchlorate Public Health Goal of 6 ug/L. The estimated ratio of body weight and daily water consumption for the 95th percentile of pregnant women, 25.2 kg-day/L, was used. The equivalent ratio using the New Jersey assumptions would be 33.5 kg-day/L. However, California used a Relative Source Contribution Factor of 0.6, rather than the recommended floor of 0.2, which would be three-fold more conservative. California justifies the use of 0.6 by stating that available data suggests that more than half of exposure to perchlorate is from drinking water, with less than half of exposure from food.

Consideration of Exposure Assumptions for Infants

Infants are considered to be a sensitive subpopulation for perchlorate's effects. Additionally, adverse effects from perchlorate would occur during a short timeframe, in contrast to many other chemical, such as carcinogens, for which chronic exposure is the primary concern. Therefore, an evaluation of the health-based drinking water concentration based on exposure parameters for infants was undertaken.

For 3 month old infants an alternative Drinking Water Equivalent Level (DWEL) (serving only as comparison) could be calculated using data from the EPA Exposure Factors Handbook (1997). The 95th percentile tap water ingestion for < 6 months of age is 0.8 L/d and the 3 month age average weight is 5.7 kg (male and female) in Tables 3-6 and 7-1. The DWEL would be:

$$0.0007 \text{ mg/kg/d} \times 5.7 \text{ kg} \ / \ 0.8 \text{ L/d} = 0.005 \text{ mg/L or } 5 \text{ ug/L},$$

or the same as for adults. For the infant the total daily dose of perchlorate would be 0.004 mg.

The last step in developing an MCLG is to multiply the DWEL by a factor for Relative Source Contribution (RSC). For bottle-fed infants drinking exclusively powdered or concentrated formula, the RSC is 1 or 100%, because the only source of perchlorate is through tap water. The resulting MCLG would be the same as the DWEL.

For those infants drinking only ready-to-feed formula (to which no tap water is added), the RSC is immaterial, as it is for exclusively breastfed infants. Use of an RSC of 1 is also valid for mixed exposure to tap and to breast milk for infants under approximately 4-6 months of age if it is assumed that perchlorate is present in breast milk and tap water at the same concentration. This is so because infants under 4-6 months consume only liquid (formula or breast milk), and the total volume of fluid ingested is expected to remain constant regardless of the proportion of formula or breast milk.

Available information on perchlorate in breast milk is very limited and can only be considered preliminary at this time (Kirk et al., 2005). Although it has been shown that perchlorate is present in breast milk samples, not enough data is available to develop estimates of the mean and range for perchlorate in breast milk which can be used in risk assessment. If breast milk perchlorate concentrations are actually greater than the alternative DWEL for infants calculated above, the RSC would be affected in risk assessments for infants. For example, if breast milk perchlorate concentration is assumed to be 0.01 mg/L (twice the alternate infant DWEL), a 5.7 kg infant ingesting only breast milk would be exposed to 0.008 mg/d. A 50-50 mixture of tap water and breast milk require perchlorate in tap water to be zero, so that the total daily perchlorate ingestion would be no more than 0.004 mg:

0.0 mg/L x 0.4 L/d + 0.01 mg/L x 0.4 L/d, = 0.0040 mg/d.

Thus, if the breast milk concentration is twice the DWEL, the RSC is effectively zero for mixtures in which tap water volume is less than breast milk.

There is no clear methodology in federal or state standard setting procedures by which to approach setting an RSC for neonates consuming both formula made up with contaminated tap water and contaminated breast milk. A situation in which the RSC changes from 1.0 to zero because of a two-fold increase in breast milk concentration is not easily amenable to regulatory application, especially when the information about breast milk levels is minimal. Under this logic an infant is more at risk the less tap water is consumed. Clearly, a specialized approach needs to be instituted if further studies of perchlorate in breast milk indicate concentrations higher than the health-based drinking water concentrations.

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Testing Subcommittee

Executive Summary

The NJ Drinking Water Quality Institute (NJDWQI) was requested by the DEPartment of Environmental Protection (DEP) to investigate the need to establish a regulatory limit for the presence of perchlorate in drinking water. A subcomponent of this investigation involves an assessment of available testing technologies and their impact, if any, on the establishment of regulatory limits. Subsequently, the NJDWQI charged the Testing Subcommittee with the task of evaluating current testing technologies and making appropriate recommendations to specify the preferred analytical procedure(s) to be utilized by the certified laboratory community for the analysis of perchlorate in drinking water samples.

Based upon the information discussed and documented below, the Testing Subcommittee recommends that United States Environmental Protection Agency (EPA) Method 314.0 be used as the analytical method of choice for the determination of perchlorate in drinking water. This Method is proven to be accurate, precise, and rugged; is currently used by the certified drinking water laboratory community; and can measure perchlorate, with an accepted degree of confidence, at the low concentration levels being considered by the Health Effects Subcommittee.

Method 314.0 operated "as currently written" is sufficient to measure perchlorate down to a reporting limit (RL) of 2.7 ppb. This is more than adequate to meet the health-based Maximum Contaminant Level (MCL) of 5 ppb being recommended by the Health Effects Subcommittee. If it is determined that there is a need to report perchlorate at levels lower than this, the Testing Subcommittee recommends the adoption of Massachusetts Department of Environmental Protection's (MADEP) additional laboratory method performance criteria to Method 314.0. It has been demonstrated that MADEP's added requirements are effective in lowering the certified laboratory communities' RL to 1.0 ppb.

Technical Considerations and Historical Approach to Method Assessment

When establishing a MCL for a particular chemical that will be used to regulate the quality of drinking water, it is important that the chemical of concern be measured:

- By a well defined test procedure that has been proven to be accurate, precise and rugged;
- By a test procedure that can be used by the certified drinking water laboratory community; and
- At the MCL with some degree of confidence.

In the past, the Testing Subcommittee has focused on the use of EPA approved methodologies as the preferred approach for recommending analytical methods for the analysis of drinking water samples. These methods have been assessed by the EPA and the method's performances documented through the use of intra- and inter- laboratory method performance studies. In this way, the method's precision, accuracy and ruggedness have been well documented. In addition, these methods have been available to and for the most part, are already in use by the certified drinking water laboratory community.

The next step in the Testing Subcommittee's approach to evaluating the appropriateness of potential analytical procedures was to obtain preliminary information from the Health Effects Subcommittee on the anticipated MCL that may be recommended to the NJDWQI. This information was then used as the target level by which a method should be able to detect and measure the chemical of concern within some degree of confidence. Ideally, the candidate method was developed specifically for the analysis of the chemical of concern and the anticipated MCL fell within the candidate method's calibration curve. In this case and provided the method's documented precision and accuracy was found to be acceptable, the candidate method could be recommended as the method of choice for drinking water analysis. Historically, however, this was not the case. Of particular difficulty to the Testing Subcommittee were those instances when:

- There was no applicable EPA approved methods;
- Candidate EPA approved methods existed but the anticipated MCL fell below the method's calibration curve or even, the statistically derived Method Detection Limit (MDL); and
- Candidate EPA approved methods existed, but required modification in order to achieve the detection level of the anticipated MCL.

Depending upon the instance, the Testing Subcommittee has recommended the following:

- The research and development of new test methods;
- The use of certain methods with specific modifications that would enable the method to detect and measure the chemical of concern at the anticipated MCL;
- The evaluation of the candidates' method performance at concentrations below the published method reporting limit; and
- The establishment of the lowest level a method could detect and measure the chemical of concern with some degree of confidence, the Practical Quantitation Limit (PQL).

Approach and Findings

As a first step, a meeting of the Testing Subcommittee (Appendix A, Testing Subcommittee Members) was scheduled for the purpose of initiating the process of: (1) reviewing background information associated with monitoring for perchlorate in drinking water; (2) identifying the target testing level that a candidate test procedure should be capable of achieving, (3) canvassing available testing methods/technologies that might be applicable for this application; (4) identifying available data, if any, on the candidate analytical method performance in drinking water testing laboratories; and (5) assessing and recommending applicable perchlorate test methods.

a. Background on Monitoring for Perchlorate in Drinking Water

The first significant sampling for perchlorate undertaken in New Jersey was done as part of the requirements of the Unregulated Contaminant Monitoring Rule (UCMR), which is part of the Federal Safe Drinking Water Act. The Federal Safe Drinking Water Act required community water systems and non-transient non-community water systems that serve more than 10,000 persons (large systems) to monitor their water for the presence of certain unregulated compounds between 2001 and 2003. Over 120 large public water systems in New Jersey met this criterion. In addition, the EPA randomly selected some small water systems nationwide to be sampled, including 16 small water systems in New Jersey. The purpose of the UCMR monitoring was to collect data to support EPA decisions regarding whether or not to regulate certain contaminants, such as those on the Drinking Water Contaminant Candidate List, to protect public health. Sampling was done at the "point of entry" (POE) which would be after any treatment that may be performed at the system. Each ground water POE was monitored twice over a one year period between 2001 and 2003, and each surface water system was monitored four times over a one year period between 2001 and 2003. There were provisions to combine POEs and reduce the number of samples in some circumstances. A total of 123 water systems in New Jersey conducted sampling.

The results of UCMR sampling for perchlorate are summarized in Table 3 below.

Table 3. UCMR Perchlorate Summary

Number of Public Water Systems Analyzed	Number of Analyses	Number of Detections	Number of Public Water Systems with Detections	Minimum Concentration Detected (ppb)	Maximum Concentration Detected (ppb)
123	986	10	6	4.0	13

EPA Method 314.0 was used for the analysis of samples collected under this program, with a listed reporting limit of 4 ppb.

In order to further evaluate the occurrence of perchlorate in New Jersey, DEP conducted additional perchlorate sampling between 2003 and early 2005. Public water systems were chosen based on their potential vulnerability to perchlorate contamination. Reasons for sampling included proximity to military installations and unexploded ordnance, and proximity to previous

UCMR-tested sites that showed perchlorate detections. In a few circumstances, DEP sampled some of the individual public wells that had tested high in the original UCMR sampling. Samples were collected from both community and non-community water systems. Most, but not all, of these samples were taken before treatment. A small number of these were POE samples. The samples were also analyzed using EPA Method 314.0. For this study, the laboratory was able to achieve a minimum reporting level (MRL) of 1 ppb or lower, while the EPA had used an MRL of 4 ppb as part of the UCMR sampling, in part because of method improvements over the period. The summary from the DEP sampling can be found in Table 4 below.

Table 4. DEP Perchlorate Sampling

Number of Public Water Systems Analyzed	Number of Analyses (includes repeats)	Number of Detections greater than or equal to 1 ppb and includes repeats	Number of Public Water Systems with Detections greater than or equal 1 ppb	Maximum Concentration Detected (ppb)
67	114	21	11	23

b. Target Level for Reporting of Perchlorate Results

Documentation from the Health Effects Subcommittee indicates that the subcommittee will be recommending a MCL of 5 ppb. In January 2005, the National Academy of Sciences released a report that set a reference dose of up to 0.0007 milligrams per kilogram of body weight of perchlorate per day that would not result in adverse human health affects. If standard risk assessment protocols were applied, the Subcommittee has concluded that the Health-based number is 5 ppb.

The DEP believes perchlorate may behave similarly to nitrate in ground water. As a result, it is possible that the DEP may want to set a trigger for reduced or increased monitoring for a public water system at half the maximum contaminant level. Being able to measure to 1 ppb would allow the Department the ability to set a trigger for reduced or increased monitoring at half the MCL.

Understanding that the Health Effects Subcommittee may be recommending a perchlorate MCL of 5 ppb and considering the possibility that the DEP may want all perchlorate compliance data reported down to 1 ppb, the Testing Subcommittee elected to use the 5 ppb as their primary reporting level for a method's performance assessment, while keeping in mind the possible need to report values down to 1 ppb.

c. Method Detection Limit (MDL) and Minimum Reporting Limit (MRL)

The EPA defines a MDL as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero (40 CFR 136 Appendix B). This value reflects a method's lower limit to detect, but not necessarily measure, a given analyte. Both the EPA and DEP require certified laboratories to determine this statistically derived value for most water testing procedures.

The concept of a method's MRL has not been clearly defined by the regulatory agencies and therefore, is a concept that is not used in a consistent manner by laboratories. In some cases, laboratories may use the lowest standard in their calibration curve as their MRL or it may only be a value that has been selected by a laboratory that represents their lowest "comfort level" for reporting data. EPA Method 314.0 does, however, define a MRL as being "the minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met."

Within the past year, the EPA Region 2 Laboratory Certification Team audited the State Department of Health and Senior Services' Environmental and Chemical Laboratory Service (ECLS) as part of the DEP's drinking water primacy requirements. A finding of this audit directed the ECLS to establish a MRL for each analyte for each water test method and that the MRL shall be the lowest calibration point on the method's calibration curve. In general, the statistically derived MDL is usually less than the MRL. It is anticipated that this standard will eventually be a standard applied uniformly to all certified environmental laboratories for all environmental test methods.

In some cases, the MRL data reported in this assessment is undefined and therefore, should be treated as only an indication of a laboratory's lower limit for quantifying the concentration of a given analyte.

d. Available Test Methods

Analytical methodologies for perchlorate are discussed briefly below. Table 5 provides a comparison of the primary analytical methodologies in use. Of the methods listed, the only one currently approved by the EPA for drinking water compliance testing is Method 314.0 and is a test procedure currently in use by the certified drinking water testing laboratory community.

Table 5. Perchlorate Analytical Laboratory Methods Comparison

Method (Technique)	Applicability	Analytical Limitations	Aqueous Reporting Limits (ppb)
EPA 314.0 (IC)	• Mandatory for drinking water samples reported under UCMR I • Aqueous samples with low dissolved solids (conductivity < 1 mS/cm TDS) and chloride, sulfate, and carbonate concentrations < 100 mg/L each	• Analysis is subject to false positives due the unspecific nature of the conductivity detector • Method has been validated in drinking water only; no guidance provided for use with soils, biota, etc. • The lower reporting limit of 0.5 ppb is achievable only in samples with very low TDS • Inappropriate for use in samples with high TDS	0.5 – 5
EPA 314.1 (“Improved” IC)	• Aqueous samples with up to 10 mS/cm TDS • Planned option for UCMR II	• False positives will be reduced but not eliminated • No published EPA Method	0.5 -1
SW9058 (“Improved” IC)	• Aqueous samples with up to 10 mS/cm TDS • Soil samples	• False positives will be reduced but not eliminated • EPA Method currently under revision	0.5 -1
SW6850 (LC/MS)	• Aqueous samples to include those with high TDS • Soil samples • Biota samples	• No published EPA Method	0.1
EPA 331.0 (LC/MS/MS)	• Method limited to aqueous samples to include those with high TDS • Planned option for UCMR II • Technique has also been documented to analyze soil, milk and biota samples	• Pretreatment recommended in Winkler, et al., 2004 method • Draft EPA Method available	0.02
EPA 332 (IC/MS)	• Method has been used on aqueous samples, including those with high TDS and on milk and biota samples • Planned option for UCMR II	• False positives will be substantially reduced but may not be eliminated • EPA Method to be released in early 2005	0.1
EPA 332 (IC/MS/MS)	• Method has been used on aqueous samples, including those with high TDS • Planned option for UCMR II • Technique has also been documented to analyze soil, milk and biota samples.	• No published EPA Method	0.02
FDA Method (IC/MS/MS)	• Fruits and vegetables, bottled water, and milk	• None noted in literature	0.5 (LOQ)

Current published EPA methods are limited to Method 314.0, approved by the EPA for drinking water testing and Method SW9058, though new methods are slated for release later in 2005. A description and the identified limitations of each method are provided below.

EPA Method 314.0 – Ion Chromatography

Method 314.0 is the only method for perchlorate promulgated by the EPA and was developed for drinking water. Aqueous samples are introduced into an ion chromatograph (IC). The perchlorate ion is separated and measured using a system comprised of an ion chromatographic pump, sample injection valve, guard column, analytical column, suppressor device, and conductivity detector. The conductivity detector is non-specific; ions are differentiated based solely on retention times.

Sample matrices with high total dissolved solids (TDS) and high concentrations of common anions such as chloride, sulfate and carbonate can destabilize the baseline in the retention time window for perchlorate. These can be indirectly assessed by monitoring the conductivity of the matrix. Therefore, the laboratory must determine its instrument-specific Matrix Conductivity Threshold (MCT) and all sample matrices must be monitored for conductivity prior to analysis. When the MCT is exceeded, sample dilution and/or pretreatment must be performed. A weakness in this test method is that sample dilution leads to elevated reporting limits and pretreatment may reduce the actual perchlorate content of the sample at low concentrations.

Method 314.0 has also been used as the basis for laboratories reporting to sub-ppb levels despite the method's documented lower reporting limit of 4.0 ppb. The Massachusetts Department of Environmental Protection's laboratory accreditation program requires a "Demonstration of Capability" involving very rigid quality control (QC) requirements and successful participation in proficiency evaluation studies in order for laboratories to verify their ability to detect and report at the sub-ppb levels.
(See http://www.mass.gov/dep/brp/dws/files/perchlor.doc)

Method 314.1 – "Improved" IC

Several options have been explored to improve Method 314.0, including sample enrichment/isolation techniques intended to improve sensitivity, such as increased sample size and pre-concentration/pre-elution and resolution and analysis improvement strategies, such as heart-cutting/column switching, noise suppression, and the use of dual channels. Laboratories employing these improvements/alterations report their results as Method 314.0 analyses as the changes are not considered to be outside the method.

EPA is currently revising Method 314.1 for publication as an "Improved IC" method. This method is intended to add increased sensitivity, better tolerance of TDS, and better selectivity through use of a confirmation column and in-line concentration. Method 314.1 is scheduled for publication sometime in 2005. No additional details of the EPA revision are available at this time.

Method SW9058- “Improved” IC

Method SW9058 is the EPA’s Office of Solid Waste (OSW) method for ion chromatography. The method is substantially the same as Method 314.0, although the MCT requirement is not included. The method is stated to perform adequately on water samples with conductivities up to 1000 µS/cm and is potentially applicable to surface water, mixed domestic water, and industrial wastewaters. The limitations described above for Method 314.0 apply similarly to Method SW9058.

USEPA OSW is in the process of revising the November 2000 version of Method SW9058 given the known interferences and the high probability of false positive and false negative results. The areas being considered for the optimization of the method are: to include an extraction procedure for solids; to broaden the scope so that the method is applicable for aqueous samples having high total dissolved solids; to lower the level of detection for perchlorate at sub-ppb level; to have better separation; and to minimize false positive and negative results. Revisions to this method were not available at this time.

Emerging Determinative Laboratory Methods

The remaining test methods, SW6850 (LC/MS), EPA 331.0 (LC/MS), EPA 332 (IC/MS), EPA 332 (IC/MS/MS) and FDA (IC/MS/MS), are new, emerging test procedures that utilize structural identification and natural isotopic abundance to provide unique and high-confidence quantitation of perchlorate. These include ion chromatography (IC) or liquid chromatography (LC) instruments paired with either a mass spectrometer (MS) or tandem mass spectrometers (MS/MS).

QC requirements are similar for most of the determinative laboratory methods. Some of the QC evaluations that are unique to these analyses include the analysis of a suppression standard (500 mg/L bicarbonate, carbonate, chloride, and sulfate) spiked at the practical quantitation limit (PQL), comparison of the isotopic ratio for chlorine in the perchlorate to natural isotopic abundance, and the use of an 18O4-labeled perchlorate internal standard. Analysis via the determinative methods is more sophisticated than for the IC methods, requiring more education/training for both the analysts and the data reviewer. However, IC/MS/MS, LC/MS and LC/MS/MS are more expensive than ion chromatography methods alone.

EPA is currently working on three determinative methods – Methods SW6850, 331.0 and 332. The Office of Solid Waste is currently evaluating Method SW6850 (LC/MS). The Office of Water is preparing Methods 331.0 (LC/MS and LC/MS/MS) and 332.0 (IC/MS and IC/MS/MS), which are currently available[i, ii]. The Food and Drug Administration (FDA) has published one draft method using LC/MS/MS intended for bottled water, lettuce, and milk (CFSAN, 2004). Only SW6850 will address environmental matrices other than drinking water.

e. Test Method Assessment

Emerging Determinative Laboratory Methods

The Testing Subcommittee conducted a preliminary review of the perchlorate test methods listed in Table 6 and concluded that the Emerging Determinative Laboratory Methods (SW6850 (LC/MS, EPA 331.0 (LC/MS), EPA 332 (IC/MS), EPA 332 (IC/MS/MS) and FDA (IC/MS/MS)) were inappropriate for application to regulatory monitoring of perchlorate in drinking water. Although these methods may prove to be of benefit for regulatory programs in the future, their application for regulatory drinking water compliance monitoring at this time would be pre-mature.

The rationale for excluding the Emerging Determinative Laboratory Methods was based upon the developmental stage of many of these procedures and the lack of familiarity of these testing techniques in the NJ certified laboratory community. In some cases, the test methods are still in draft form and lack peer-reviewed documentation on the method's performance by "typical" environmental laboratories. In addition, these procedures employ sophisticated analytical techniques that are not only costly to procure, but also require specialized analyst skills to operate the instrumentation. The Testing Subcommittee contacted several instrument vendors to obtain an estimate of the cost associated with this type of analytical instrumentation. The current cost of IC/MS and LC/MS, instruments used with EPA 332 and SW6850, is in the range of $175,000 to $200,000 per instrument. The use of tandem mass spectrometers (MS/MS) even further adds to the cost of the instrumentation. Ion chromatographs, employed with Methods 314.0 and 314.1, cost in the range of $40,000 to $75,000. These instruments are currently used in the NJ certified laboratory community as indicated by the 13 laboratories currently certified to perform Method 314.0.

Input from the DEP Office of Quality Assurance, responsible for the agency's laboratory certification program, found that these testing techniques (IC/MS, LC/MS, IC/MS/MS etc.) are not readily available in the certified drinking water laboratory community. Therefore, the Testing Subcommittee elected not to consider these procedures for this regulatory application.

Method SW9058- "Improved" IC

Review of Method SW9058, developed for the EPA solid waste program, found it to be similar to Method 314.0 with no real advantage for application to drinking water monitoring. Like Method 314.0, a new revision is being developed to address the issues of interferences and false positive and negative detections, but draft copies of these revisions are still not available from the EPA. Therefore, the Testing Subcommittee chose not to consider this analytical approach for application to drinking water regulatory monitoring.

EPA Method 314.0 – Ion Chromatography

The Safe Drinking Water Act (SDWA), as amended in 1996, directs the EPA to publish a list of contaminants (referred to as the Contaminant Candidate List, or CCL) to assist in priority-setting efforts. Perchlorate was placed on the CCL in 1998. EPA developed regulations for monitoring certain unregulated contaminants in 1999. These contaminants are listed in the UCMR. The CCL Occurrence Priority list is the primary source of contaminants for the unregulated monitoring list, which must not exceed 30 contaminants.

Perchlorate was placed under the UCMR in 1999. The UCMR requires hundreds of large and small public water systems to monitor for perchlorate for several years. Ten states have established “action levels” for perchlorate that range from 1 to 35 ppb. MA and CA have established Drinking Water Public Health Goals (PHGs) of 1 and 6 ppb, respectively.

The current federally approved method for perchlorate analysis of drinking water is EPA Method 314.0. This procedure uses Single Column - Ion Chromatography. There are documented interference problems with samples having high total dissolved solids and there can be false positive/negative results due to interferences. Accuracy must be measured in each sample. False positives may occur using Method 314.0 because the conductivity detector is sensitive to any substance that can carry an electric current in water. Method 314.0 can not reach the sensitivity required to provide results below 1 ppb.

In general, Ion Chromatography is a testing technique that is familiar to the certified drinking water laboratory community. The DEP currently certifies thirteen (13) laboratories for the usage of EPA Method 314.0. The DEP Office of Quality Assurance provided MDL information for Method 314.0, shown in Table 6, reported by the certified laboratories.

Table 6. Perchlorate Method Detection and Reporting Data for EPA Method 314.0

NJ Laboratory ID Number	Method Detection Limit (MDL) Determined (ppb)	Reporting Limit (RL) (ppb)	Policy PQL (MDL times 5)	Ratio of the Reporting Limit to MDL	Maximum Conductivity Threshold (MCT)
CA005	0.339	4	1.7	11.8	1500 ppm
PA010	1.09	4	5.5	3.7	3456 ppm
MD671	0.43	1	2.2	2.3	700 µs/cm
IN598	0.2	1	1.0	5.0	2730 µmho/cm
12129	0.82	3	4.1	3.7	4100 µmho/cm
MO002	2	4	10.0	2.0	3000
FL002	0.935	10	4.7	10.7	not provided
CA008	0.5	2	2.5	4.0	3230 µs/cm
GA769	0.3	1	1.5	3.3	1636 µs/cm
CO003	2.63	4	13.2	1.5	3400 µs/cm
VT972	0.3	1	1.5	3.3	2710 µs/cm
20012	0.2	0.5	1.0	2.5	3000 ppm TDS or 5000 µs/cm
TN001	0.35	1	1.8	2.9	1400 µs/cm
Average	**0.8**	**2.8**	**3.9**	**4.4**	
Median	**0.5**	**2.7**	**4.1**	**3.8**	

It should be noted that the DEP Office of Quality Assurance also had available information concerning each listed laboratory’s calibration curve. In eleven (11) out of twelve (12) cases, the laboratory's lowest standard on their calibration curve was at or below their reporting limit. In the case of TN001, this information was not available. Bracketing reported values between calibration standards of a linear calibration curve strengthens the reliability of the reported value. This adds weight to the routine achievability of the listed reporting limits.

The average MDL value and Median MDL values for this data showed that the distribution of detection levels were skewed low or left censored which is normal for most inter-laboratory detection level determinations. The average detection level was 0.8 ppb perchlorate with a median value of 0.5 ppb. This indicates that half of the certified laboratory community would show a detection of perchlorate in drinking water of 0.5 ppb.

For a majority of the laboratories, reporting limits ranged from 1 ppb to 10 ppb with a median value of 2.7 ppb. Assuming that the maximum conductivity of the sample did not exceed the values listed in the right most column of Table 4, the NJ certified laboratories would have sufficient control of the accuracy from calibration data to reliably report to a level of 2.7 - 2.8 ppb, based upon the current analytical method requirements.

In the past, the Department has used a multiplier of five (5) times the MDL to determine a PQL. This was done in the absence of collaborative study data of sufficient quantity to allow robust statistical analysis. In Table 4, the column, Policy PQL, shows that by multiplying the MDL by 5 yields an average value of 3.9 ppb and a median value of 4.1 ppb that would be the Department's calculated value for regulatory consideration using the available data. If one looks at the ratio of the reporting limit (RL) to the MDL, we arrive at an average value of 4.4 ppb and a median value of 3.8 ppb that represents the theoretical multiplier from this limited data set. Statistically speaking, the more laboratories reporting data in a collaborative study, the larger the statistical spread of the data and the greater the uncertainty. This is why the Department adopted the convention of multiplying by a factor of five (5) which is slightly more conservative than the analytical data illustrates.

The NJ certified drinking water laboratories have demonstrated the ability to use EPA Method 314.0 and are, in general, capable of detecting and measuring perchlorate down to a lower level of 2.7 - 2.8 ppb. Although this is acceptable to achieve the Health Effects Subcommittee's 5 ppb recommendation, it would be preferable if laboratories using this method could achieve a reporting limit of 1.0 ppb or lower. An RL of 1.0 ppb could be achieved by requiring laboratories to follow the Massachusetts Department of Environmental Protection specific standards of performance for analyses of perchlorate (discussion follows in Section e.).

<u>EPA Method 314.1</u>

The Testing Subcommittee obtained verbal feedback from research contract laboratories that have seen and are evaluating the draft Method 314.1. Although it has been indicated that this revision of Method 314.0 shows promise as the next best procedure for the certified laboratory community to use when performing perchlorate analysis on drinking water samples, this revised method is still under development and is not yet ready for assessment by the certified laboratory community, let alone adoption as a EPA approved method. Therefore, the Testing Subcommittee elected to place this method on hold until such time that the EPA releases its draft revisions for review and assessment.

e. State of Massachusetts' Approach to Perchlorate Testing Regulation

The Massachusetts Department of Environmental Protection (MADEP) is investigating the occurrence of perchlorate in public water supplies (PWSs) in the state and is determining the need for a drinking water standard or MCL for this chemical. Their interim guidance is for PWSs to test their drinking water down to a level of 1.0 ppb. A detection at or above this level triggers a response action by the PWS. This requires that laboratories be capable of accurately measuring perchlorate at the 1.0 ppb level.

To achieve this testing sensitivity, the MADEP adopted specific standards of performance that the certified laboratory must achieve in order to obtain and maintain their certification to perform perchlorate testing (see http://www.mass.gov/dep/brp/dws/files/perchlor.doc). This criteria consists of the following:

1. The laboratory must perform an initial demonstration of accuracy and precision using seven laboratory fortified blanks (LFBs) at a perchlorate concentration of 5.0 ppb or lower. In addition, the MDL must be determined using seven LFBs at a perchlorate concentration of 1.0 ppb, the matrix conductivity threshold (MCT) must be determined at a perchlorate concentration of 5.0 ppb or lower; and a perchlorate MRL of 1.0 ppb must be verified by recovering 70-130% of 1.0 ppb perchlorate spiked in a mixed common anion solution displaying a conductivity within ± 10% of the MCT. The laboratory must be able achieve a perchlorate MRL of 1.0 ppb with a perchlorate MDL approximately 1/3 of the MRL.

2. The laboratory is also required to run a 0.5 ppb perchlorate MDL-check standard daily and obtain perchlorate recoveries of 70-130%. The lowest initial calibration standard must be at a perchlorate concentration of 1.0 ppb or lower. The LFBs must be spiked at a perchlorate concentration of 1.0 ppb and analyzed at the frequency of one per batch of 20 or fewer field samples; perchlorate recovery for the LFB must be 85-115% as specified in the method.

3. The conductivity of each field sample must be measured, documented, and reported along with the perchlorate concentration (note: the conductivity meter calibration must be verified or established, and documented with each analysis batch as specified in Section 10.4 of the method).

4. The laboratory fortified sample matrix (LFM) must be performed on the field sample having the highest conductivity within the analysis batch. The LFM must be spiked at a perchlorate concentration of 1.0 ppb and analyzed at the frequency of one per batch of 20 or fewer field samples (perchlorate recovery for the LFM must be 70-130%). If the 1.0 ppb perchlorate spike is less than the measured native perchlorate level of the unfortified sample matrix, the laboratory

must repeat the LFM spiked with perchlorate at a concentration approximately equal to its native perchlorate concentration.

5. All field samples with measured native perchlorate concentrations between 0.8 ppb and 2.0 ppb must be retested with and without a perchlorate spike approximately equal to the native perchlorate concentration. The perchlorate concentration in the initial test and retest of the field sample as well as the perchlorate spike concentration and recovery must be documented and reported.

Dr. Lee Lippincott contacted the MADEP, Division of Environmental Analysis, Senator William X. Wall Experiment Station and spoke with the designated member of the MADEP Quality Assurance office. Mr. John Bardzik informed him of a study entitled, "Summary Report of the First Low-Level Perchlorate Proficiency Test Study Conducted by the Massachusetts Department of Environmental Protection." The conclusion of that study stated; "These results clearly demonstrate that, in a water matrix with a conductivity typical of most MA drinking water supplies, 15 of the 17 participating laboratories (including all MADEP-approved laboratories) reliably detected and quantitated perchlorate at a concentration of 1 µg/L without incurring false positives at 0.5 µg/L or higher." After a detailed technical discussion with Mr. Bardzik, Dr. Lippincott concluded that EPA analytical method 314.0, utilizing the quality control criteria imposed by MADEP, was capable of reliably reporting concentration levels of perchlorate at 1 ppb.

Subcommittee Recommendations on Analytical Methods

Based upon the findings above, the Testing Subcommittee recommends that EPA Method 314.0 be used as the analytical method of choice for the determination of perchlorate in drinking water. This method, operated as currently written, is proven to be accurate, precise, and rugged; is used by the certified drinking water laboratory community; and can achieve an RL of 2.7 ppb which supports an MCL of 5.0 ppb with a certain degree of confidence.

If it is determined that there is a need to report perchlorate at levels lower than this, down to a minimum of 1.0 ppb, the Testing Subcommittee recommends the adoption of MADEP's additional laboratory method performance criteria to Method 314.0. This will enable laboratories to achieve an RL of 1.0 ppb.

Treatment Subcommittee

Charge to the Subcommittee

The NJ Drinking Water Quality Institute (DWQI) was requested by the DEPartment of Environmental Protection (DEP) to investigate the need to establish a regulatory limit for the presence of perchlorate in drinking water. A subcomponent of this investigation involves an assessment of available technologies to reduce perchlorate levels in drinking water. Toward this end, the DWQI charged the Treatment Subcommittee with the task of evaluating current treatment technologies and making appropriate recommendations on the preferred water treatment technology for use in NJ and the anticipated levels to which perchlorate can be reliably and consistently removed from drinking water.

Summary

Perchlorate is an inorganic ion that has been detected in drinking water supplies. It is manufactured and used as an oxidizer in explosives and is found in natural deposits used in the production of fertilizer from Chile.

Reports from the Health Effects and Testing Subcommittees describe the health effects and analytical capabilities for perchlorate. This report focuses on water treatment removal capabilities for perchlorate in drinking water.

Recently, two comprehensive documents were released that evaluate the various water treatment technologies available to reduce perchlorate levels. In February 2005, the EPA released, "Perchlorate Treatment Technology Update – DRAFT, February 9, 2005", and in March, the Interstate Technology and Regulatory Council Perchlorate Team issued their "Technology Overview – Perchlorate". The information presented in these documents indicate that perchlorate can be reduced in drinking water to levels below detection (reported in general as 4 ug/L). Therefore, the Treatment Subcommittee of the NJ Drinking Water Quality Institute has decided to use these documents as its basis and background in recommending a level of 4 ug/L as the level to which perchlorate can be reliably and consistently removed from drinking water.

Background Information

Chemical Characteristics

Perchlorate is an inorganic chemical compound formed of one chlorine attached to four oxygen atoms. Perchlorate is relatively soluble and mobile in water and is quite stable (does not degrade readily). Perchlorate does not bind well to soil.

Uses

Perchlorate is a strong oxidizer, and is thus used in the solid propellant for rockets, missiles, and fireworks. It is also used in inflators for air bags, as well as in other applications. Large amounts of perchlorate have been disposed of throughout the United States since the 1950s. The current annual production of perchlorate is not available, as it is classified as a strategic compound. There are natural sources of perchlorate. For instance, perchlorate has been detected as a natural contaminant in fertilizer deposits in Chile at levels 0.15-0.16 mg/g (Urbansky et al., 2001) and may exist in similar deposits elsewhere in the world.

Perchlorate has been found in lettuce (FDA, 2004) and in dairy milk. Perchlorate has recently been detected in human breast milk samples from throughout the United States including New Jersey (Kirk et al., 2005). Recent studies suggest that perchlorate is found in many rain and snow samples and may be formed naturally in the atmosphere; this may account for its widespread presence at low levels (Dasgupta et al., 2005) Perchlorate was used as a pharmaceutical in the past to treat thyroid disease, but is currently rarely used for this purpose.

Environmental Fate and Occurrence

Perchlorate (ClO_4^-) in water supplies originates from the dissolution of salts, such as ammonium, potassium, magnesium, or sodium. The perchlorate salts are highly water soluble, and the health effects of perchlorate salts are therefore considered identical to the effects of the perchlorate ion. The perchlorate ion is very mobile in water and is persistent in ground and surface water.

Large public water systems and a sample of small public water systems were required to monitor for perchlorate between January 2001 and December 2003 as part of the Unregulated Contaminants Monitoring Rule requirements. As of May 2004, perchlorate was detected above the minimum reporting level (MRL) of 4 ppb in 1.9% of the 28,179 samples reported. The maximum concentration reported was 200 ug/L and the median concentration above the MRL was 6.4 ppb. As of September 2004, perchlorate releases have been confirmed in 35 states including New Jersey. Improvements in analytical capabilities may lower this minimum reporting limit to below 1 ug/L in the near future.

Areas that have been identified with high concentrations of perchlorate contamination (in the thousands of ppb or more) have involved manufacturing, testing or disposal of solid rocket propellant or other types of industrial activity. Areas with lower levels of perchlorate have been linked to small spills and/or to inadvertent contamination through the use of naturally-contaminated fertilizer.

Occurrence of Perchlorate in New Jersey Water Supplies and Private Wells

The first significant sampling for perchlorate undertaken in New Jersey was done as part of the requirements of the Unregulated Contaminant Monitoring Rule (UCMR), which is part of the Federal Safe Drinking Water Act. The Federal Safe Drinking Water Act required community water systems and non-transient non-community water systems that serve more than 10,000 persons (large systems) to monitor their water for the presence of certain unregulated compounds between 2001 and 2003. Over 120 large public water systems in New Jersey met this criterion. In addition, the EPA randomly selected some small water systems nationwide to be sampled, including 16 small water systems in New Jersey. The purpose of the UCMR monitoring was to collect data to support EPA decisions regarding whether or not to regulate certain contaminants, such as those on the Drinking Water Contaminant Candidate List, to protect public health. Sampling was done at the "point of entry" (POE) which would be after any treatment that may be performed at the system. Each ground water point of entry was monitored twice over a one-year period between 2001 and 2003, and each surface water system was monitored four times over a one-year period between 2001 and 2003. There were provisions to combine points of entry and reduce the number of samples in some circumstances. A total of 123 water systems in New Jersey conducted sampling.

The results of UCMR sampling for perchlorate are summarized in Table 7 below.

Table 7. UCMR Perchlorate Summary

Number of Public Water Systems Analyzed	Number of Analyses	Number of Detections	Number of Public Water Systems with Detections	Minimum Concentration Detected (ppb)	Maximum Concentration Detected (ppb)
123	986	10	6 (5)	4.0	13

EPA Method 314.0 was used for the analysis of samples collected under this program, with a listed reporting limit of 4 ppb.

In order to further evaluate the occurrence of perchlorate in New Jersey, DEP conducted additional perchlorate sampling between 2003 and early 2005. Past sampling at about 120 large community water systems in New Jersey under the federal Unregulated Contaminant Monitoring Rule from 2001 to 2003 found levels of perchlorate from 4 to 7.1 parts per billion in six different water systems. Subsequent sampling by DEP at these six systems, around military bases and other munitions facilities also found sporadic perchlorate contamination in drinking water wells ranging from below detection to 23 parts per billion. Public water systems were chosen based on their potential vulnerability to perchlorate contamination. Reasons for sampling included proximity to military installations and unexploded ordnance, and proximity to previous UCMR-tested sites that showed perchlorate detections. In a few circumstances, DEP sampled some of the individual public wells that had tested high in the original UCMR sampling. Samples were collected from both community and non-community water systems. Most, but not all of these samples were taken before treatment. The summary from the DEP sampling can be found in Table 8 below.

Table 8. DEP Perchlorate Sampling

Number of Public Water Systems Analyzed	Number of Analyses (includes repeats)	Number of Detections greater than or equal to 1 ppb and includes repeats	Number of Public Water Systems with Detections greater than or equal 1 ppb	Maximum Concentration Detected (ppb)
67	114	21	11	23

Park Ridge System

Initial sampling by Park Ridge at five Points of Entry (POE) which were considered to be representative of the system was conducted under the Unregulated Contaminant Monitoring Rule on November 26, 2002. The POE representing Wells 9 and 15 had a concentration of Perchlorate of 5.1 PPB. The four other POE had non-detectable results. Follow-up sampling conducted July 7, 2003 yielded a result of 13 PPB at the Wells 9 and 15 POE, and ND at the remaining POE. DEP sampling performed on March 3, 2004 showed a concentration of 6 PPB at the Wells 9 and 15 POE. Well 10 had a concentration of 23 ppb in what appears to be its first sampling event for UCMR compounds. Several additional sampling events led Park Ridge to conclude that Wells 10 and 15 were contaminated with perchlorate. Sampling conducted from June though December 2004 yielded average raw water concentrations of perchlorate of 24.8 ppb in Well 10 and 6.13 ppb in Well 15. Table 9 shows the results through May 2005.

Table 9. Perchlorate Sampling at Park Ridge.

Sample Location	Date of Sample	Concentration (µg/L)
Well #9 & #15, effluent	11/26/02	5.1
Well #9 & #15, effluent	7/7/03	13
Well #9 & #15, effluent	3/3/04	6
Well #10	3/3/04	23
Well #10	June-Dec. 2004	24.8 average
Well #15	June-Dec. 2004	6.12 average
Well #9, influent	5/12/05	3.9
Well #9, effluent	5/12/05	ND*
Well #15, influent	5/12/05	8.0
Well #15, effluent	5/12/05	ND
Well #9 & #15, effluent	5/12/05	ND

* *Detection Level 0.02 (µg/L)*

Well #10 was put out of service upon discovery of the contamination until the source could be identified and a suitable treatment system installed at the well. The Park Ridge Board of Public Works conducted an investigation into potential source of perchlorate not only in the Park Ridge system but also in surrounding private wells.

A report prepared by the borough consultants, Leggette, Brashears and Graham, Inc., indicate that a water soluble fertilizer used at a nearby greenhouse in Woodcliff Lake could be a potential source of the contamination. According to the report, perchlorate was present in all of the fertilizer products tested and was found to be particularly elevated in a mixing tank containing Scotts/Peters Excel 15-2-20 Plus 3.75% Ca and 2% Mg Pansy, Salvia and Vinca Formula. The report asserts that the concentration of perchlorate in this tank was sufficient to be considered a probable source of perchlorate contamination of the local ground water. It recommends additional sampling and investigation to establish the connection between this source and contamination detected at well #10.

Private Wells

The sampling of perchlorate in private wells was initiated as a response to finding perchlorate in the Park Ridge community water system (described above). Both the local health department and the DEP sampled residential wells in the surrounding area. Private wells were sampled in the Boroughs of Saddle River, Park Ridge and Woodcliff Lake. As of June 6, 2005 fifty-five (55) private wells were sampled with seventeen (17) wells showing levels over the detection level of 4 ppb. The highest concentration of perchlorate detected was 110 ppb. The extent of the perchlorate contamination has not been determined. DEP is planning additional sampling rounds of private wells.

Overview of Treatment

There is extensive background material related to the remediation of perchlorate from national Department of Energy and Department of Defense sites for perchlorate. Of the available treatment technologies that are currently employed to reduce the concentration of perchlorate contamination in the ground water, only three types of treatment technologies are sufficiently developed and proven for use in public water systems, and fewer still for private wells. These technologies include; Ion Exchange, Granular Activated Carbon, and Membrane technologies. The most widely used physical process is ion exchange, either through a conventional method or a more perchlorate-selective method.

In addition to Ion Exchange, Granular Activated Carbon, and Membrane technologies, considerable progress has been made in the last few years to bring about innovative physical processes in the removal of perchlorate from drinking water, groundwater, and surface water. Some technologies are proven and commercially available, while others are still in the research and development phase. Physical removal processes have been proven to be successful for remediation; however, all require subsequent disposal of removed perchlorate.

Other physical processes that are perhaps not as widely used but have continued potential include modified granular activated carbon, reverse osmosis, captive deionization, electrodialysis, and nanofiltration/ultrafiltration. Each of these processes is discussed in the following sections.

Water Treatment Techniques: Community Supplies

Ion Exchange

Ion exchange is the most commonly used ex-situ process for treatment of perchlorate-impacted water. Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. Similar to adsorption or chemical reactions, ion exchange is an equilibrium process that depends upon several variables, including the presence and concentrations of competing ions.

During ion exchange, perchlorate, which is a negatively charged ion (anion), is exchanged with another anion, typically chloride (Cl^-). The ion exchange medium consists of a polymer (ion exchange resin) containing a positively charged functional group (e.g., a quarternary amine, R_4N^+) with a strong preferential affinity to the perchlorate ion. With an influent stream passing through the system, perchlorate anions in the water attach themselves to the resin and release the bound chloride ions. The leakage of undesired ions eventually reaches the point where product water is not of an acceptable quality and resin has to be regenerated.

Ion exchange, however, is not a destructive process; it generates a brine wastewater containing high perchlorate and total dissolved solids that require further treatment or destruction.

Conventional Ion Exchange

Conventional Ion Exchange is a technology that is used in the treatment of drinking water (softening and deionization) and other industrial processes. Commercial cation and anion exchange products prepared as resins have been successfully applied to water treatment processes since the 1940s. While in-situ and other ex-situ processes are being evaluated, the implementation of ion exchange, a proven and publicly accepted technology, is available to meet existing treatment goals. Since perchlorate is an anion and conventional ion exchange has been proven, this process was one of the first technologies considered as a remediation alternative for removal of perchlorate.

In the ion exchange process, many other anions besides perchlorate commonly present in groundwater will compete with the perchlorate ion for this reaction. These include sulfate (SO42–), nitrate (NO3–), bicarbonate (HCO3–), carbonate (CO32–), and bromide (Br–). Trace ions can also compete with the perchlorate ion for the resin surface (e.g., chlorate, bromate [BrO3–-], arsenate, etc.). Water that contains high total dissolved solids values can significantly hinder ion exchange effectiveness and can become cost-prohibitive to treat.

There are three basic operating methods for conventional ion exchangers: batch, column and moving bed operations. Batch operations consist of adding resin and solution into a tank, mixing and allowing for equilibrium, and then filtering the solution. Resin is then prepared for the next cycle. This process is limited by the selectivity of the resin under equilibrium.

Column operation is essentially several batch reactors in series. Several ion exchange column equipment designs are currently employed including fixed bed downflow or upflow contactor systems that can be operated in either concurrent or countercurrent (service flow in the direction opposite to the regeneration), continuous moving bed systems, and continuous multi-port rotating distributor systems. Moving bed operations may be the most economical beds of the three because the resin is contacted counter-currently with the exhausting stream and regenerated stream.

During the treatment process, perchlorate-impacted water is passed through the equipment stored with resins. In conventional ion exchange equipment, as the ion exchange capacity of resins is progressively exhausted, the water produced deteriorates in quality. At that point, the resin is regenerated.

Although regeneration of ion exchange resins is widely practiced in general, the management of the regenerant brine containing high levels of perchlorate in the presence of high chlorides and other anions poses significant challenges. The specialized disposal and/or treatment of the perchlorate-laden saline waste stream generated as a by-product of the process is a primary concern surrounding the use of conventional ion exchange. Brine treatment (biological, physical-chemical, electrochemical) could potentially eliminate the costly and specialized disposal and treatment of a concentrated waste stream, minimize the volume of waste discharged, minimize impact to the environment through perchlorate and nitrate destruction, and prepare for possible future regulations that might require brine pretreatment prior to disposal.

Selective Ion Exchange

The ion exchange technology discussed above removes sulfate, nitrate, perchlorate, and arsenic; all of them require the use of a sodium chloride regenerant to restore chloride in the system. Thus, they all produce the brine wastewater byproduct. Some newer resin designs, however, take advantage of a greater selectivity for perchlorate, making it possible to operate the ion exchange unit for a protracted period of time while removing only the problematic perchlorate, and not all of the other ions in the influent stream. However, very strong binding of selective ion exchange means that removal of that ion for regeneration of the resin may be difficult. The concentration required for the regenerating ion and the cost will be less if a resin is selected that is adequate for the task but does not hold the ion too tightly.

Certain nitrate-selective resins have been developed, because nitrate has ion exchange properties similar to perchlorate, and these resins preferentially exchange nitrates over sulfates to remove perchlorate. As the resin bed reaches saturation, these selective resins prevent sulfates from displacing nitrate anions or perchlorate.

The University of Tennessee, Rohm and Hass Corporation, and Oak Ridge National Laboratory (ORNL) have developed bi-functionalized resins that have the highest selectivity for perchlorate. One of these is marketed under the brand name Purolite A-530E (Purolite, 2004). The quaternary ammonium groups (C6) combined with small (C2) alkyl groups afford these bi-functional resins high perchlorate selectivity and highly favorable exchange kinetics. These resins can be disposed or taken for off-site regeneration. The associated operational costs for these selective resins are the highest of all of the ion exchange alternatives. Additionally, the chemistry of the treated ground water is not negatively impacted by the removal of other ions but can cause the treated water to be corrosive.

Other ion exchange resins are being developed including the polymeric ligand exchanger (PLE). Less than 2% of breakthrough was observed after 12,000 bed volumes (BV) when the PLE was used to treat simulated water containing 200 ppb perchlorate$^-$ and high concentrations of three other anions. Nearly 90% of exhausted perchlorate capacity was recovered after regeneration.

Modified Granular Activated Carbon

Modified Granular Activated Carbon (GAC) has a limited capacity for removing perchlorate because GAC is an inorganic ion rather than the organic constituents for which it is more ideally suited. Numerous efforts are under way to improve the efficacy of GAC in removing perchlorate. Ongoing work conducted at Pennsylvania State University, the EPA, the American Water Works Association Research Foundation (AWWARF), and at Calgon Carbon relates to adding enhancements (e.g., monomers, polymers, organic iron complexes or quaternary amines) to improve the capacity of GAC for perchlorate.

On-going studies conducted by the AWWARF have indicated when GAC was tailored with cetyltrimethyl ammonium chloride (CTAC), the GAC was found to adsorb perchlorate 30 to 35 times longer than virgin GAC. The most successful treatment was preloading the GAC with CTAC. At on operating system, this extended the time to initial perchlorate breakthrough from 1,200 BV for virgin GAC to 34,000 BV for CTAC tailored GAC. Preliminary cost estimates indicate that when using a quaternary amine monomer preloading protocol, the costs for the tailored and polishing GAC media installations and replacements could be 1/4 to 2/3 the cost of ion exchange resin-based treatment.

Reverse Osmosis

Reverse Osmosis (RO) membrane filtration has long been used to remove ions from drinking water supplies. It is commonly used for the treatment of groundwater with high total dissolved solids levels. In the RO process, the influent stream is driven, under pressure, through a semi-permeable membrane that does not allow contaminants to pass. In this case, the perchlorate is removed from the process in a concentrate or brine, which requires further treatment or destruction. Also, the lack of ionic selectivity in the semi-permeable membrane can alter the pH of the effluent stream and make it corrosive. Membrane resilience may also be a performance issue in treating perchlorate.

Based on its size (hydrodynamic radius), perchlorate is selectively rejected over chloride through size exclusion. Membranes are classified by the size of the particle that the membrane removes. Membrane filters in the RO process have pore sizes that remove nearly all ions in source water (range of 0.0001 micron in diameter and smaller) to produce a high-purity water, but requires a higher operating pressure than other membrane treatment technologies.

A protocol to evaluate drinking water treatment devices for perchlorate-reduction performance has been added to National Sanitation Foundation/American National Standard Institute (NSF/ANSI) Standard 58: Reverse Osmosis Drinking Water Treatment Systems. The protocol requires a reverse osmosis unit to be able to reduce 130 ppb perchlorates to 4 ppb or less in the treated water supply.

Nanofiltration/Ultrafiltration

Nanofiltration and Ultrafiltration are two other membrane treatment technologies like reverse osmosis discussed in the previous section. In these technologies, the synthetic porous material of membranes acts like a shield, preventing particles of a defined size or larger from passing through as water pressure pumps water through the membrane.

Membranes classifications for these two technologies are as follows:

- Nanofiltration (NF): Also known as "membrane softening," this membrane has a pore size of 1 nm and is used for hardness reduction or removal of organics.

- Ultrafiltration (UF): Developed to fractionate and concentrate solutions with colloidal and high-molecular-weight material, this membrane removes most nonionic material and passes most ionic material, depending on its size.

Nanofiltration is a special process selected when reverse osmosis and ultrafiltration are not ideal choices for separation. Nanofiltration can perform separation applications that are not otherwise economically feasible. In concentration of organic solutes, suspended solids, and polyvalent ions, the permeate contains monovalent ions and low-molecular-weight organic solutions. The nanofiltration process removes particles in the 300 to 1000 molecular weight range and can reject selected salts. The particles removed by nanofiltration are generally greater than 10 angstroms. Since the perchlorate molecule is 3.5 angstroms, nanofiltration is not expected to work well in separating perchlorate from water.

Ultrafiltration is a selective fractionation process utilizing pressures up to 145 pounds per square inch (psi). It concentrates suspended solids and solutes with high molecular weights. The permeate of this process contains low-molecular-weight organic solutes and salts. The ultrafiltration process removes particles in the 0.002 to 0.1 micron range. As ultrafiltration targets compounds that are larger than those removed by nanofiltration, ultrafiltration fails to remove perchlorate from water. However, surfactant modified ultrafiltration has been tested to modify a negatively charged membrane to enhance perchlorate rejection.

All of the membrane filtration technologies discussed in this section have high energy requirements and produce brines equal to 20% of the volume of ground water treated. The brine will contain high total dissolved solids and perchlorate concentrations requiring treatment or further disposal. Currently, AWWARF is funding ongoing research to investigate the feasibility of membrane filtration technology for perchlorate removal in water sources of different quality.

Water Treatment Techniques: Private Wells

Possible water treatment techniques for private wells include the treatment techniques listed in the previous section for community supplies. However, due to the fact that the treatment systems will be in residential homes, there are many more limitations that make the implementation of some of these techniques infeasible. For instance, homeowners are less likely to monitor the water with the frequency that is required of a community system. Hazardous substances used with some community supply treatment techniques such an acidic or caustic chemicals can not be stored in a home. Also backwash water that would contain elevated concentrations of perchlorate poses a disposal problem because in most cases it will be discharged to a septic.

There are two basic types of water treatment that can be used for contaminant removal in a residential dwelling served by a private well: 1) point-of-entry treatment (**POET**) systems treat the water for the entire household; and 2) point-of-use (**POU**) systems treat the water at the kitchen tap.

In general a Point of Entry Treatment (POET) system that treats all the water entering a home needs to be to meet the following criteria. It must reliably and effectively remove perchlorate below the drinking water standard. The unit must be simple to maintain and ideally will have an extended service life of approximately one year or more. Finally the POET alternative selected should meet the above criteria and be cost effective to install and maintain.

Limited research has been conducted to determine the most reliable, efficient, and cost effective treatment system for the removal of perchlorate from private wells. Based on studies from community systems, some of the available treatment techniques seem to be applicable to private wells. Ion exchange resins appear to be the most promising treatment technique for the use in a POET system. Specifically, ion selective resins such as the ResinTech SIR 110-HP may be the most appropriate treatment for residential wells. This type of anion selective resin was designed to selectively remove perchlorate and nitrate ions. Other anions in the influent stream are not removed and thus extend the life of the resin. This type of ion exchange resin forms very strong bonds with the perchlorate ions and is difficult to regenerate. Due to the difficulty in removing the perchlorate from the resin, the resin needs to be disposed of once it is exhausted and replaced with fresh resin. The benefits with this type of resin over a conventional ion exchange resin is the maintenance is reduced and there are no issues with discharging a brine solution contaminated with perchlorate back into the groundwater. Information provided by the manufacturer indicates that the ion selective resin could operate for over a year in an average household with perchlorate levels of about 20 parts per billion.

If a homeowner selects to treat only the water at one faucet instead of using whole house treatment a Point of Use (POU) unit could be used. Possible treatment techniques for POU treatment may included ion exchange resins or reverse osmosis. If an ion exchange resin were used, only a perchlorate selective anion resin would be feasible. Currently there are no known suppliers of POU cartridges that are packed with this type of resin. Another POU unit that may be effective would be a reverse osmosis unit. These units are commercially available and would produce small quantities of treated water sufficient for drinking water purposes only.

New Jersey Water Treatment Data

Community Supplies

The Engineer’s Report submitted with the application for the Park Ridge Water System did a brief evaluation of four treatment technologies: Reverse Osmosis, Tailored Granular Activated Carbon, Biodegradation and Ion Exchange Resins. Within the Ion Exchange Resin group the options of Type I or II Strong Base Anionic, Nitrate Selective and Perchlorate Selective Resins were examined. It was determined that the project would be bid with the option of either Nitrate or Perchlorate Selective Resins. Selection will be made by Park Ridge based on the number of bed volumes which can be guaranteed by the contractors as compared to price.

It is proposed to utilize a GAC vessel which had previously been used at Well 15, with slight modifications, to house/contain the resin. The unit is owned by Park Ridge but is not currently in use. It is a U.S. Filter Model HP810. Its dimensions are 96” D x 84” H. The flux rate at 160 GPM is calculated to be 3.18 GPM/SF versus one supplier’s recommended minimum of 4.0 GPM/SF. The Engineer’s Report states that the manufacturer “…do(es) not foresee any problems using the existing 96” vessel at Well 10.”

Private Wells

The sampling of perchlorate in private wells was initiated as a response to finding perchlorate in the Park Ridge community water system (described above). Both the local health department and the DEP sampled residential wells in the surrounding area. Private wells were sampled in the Boroughs of Saddle River, Park Ridge and Woodcliff Lake. As of June 6, 2005 fifty-five (55) private wells were sampled with seventeen (17) wells showing levels over the detection level of 4 ppb. The highest concentration of perchlorate detected was 110 ppb. The extent of the perchlorate contamination has not been determined. DEP is planning additional sampling rounds of private wells.

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[i] Method 331.0, Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry, Revision 1.0, EPA Document #: 815-R-05-007, January 2005.

[ii] Method 332.0, Determination of Perchlorate in Drinking Water by Ion with Supressed Conductivity and Electrospray Ionization Mass Spectrometry, Revision 1.0, EPA Document #: EPA/600/R-05/049, March 2005.

Appendix A - Testing Subcommittee Members

Institute Members:

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