Massachusetts Department of
Environmental Protection

DRAFT REPORT

The Occurrence and Sources of Perchlorate in Massachusetts

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Executive Summary

In recent years, the Massachusetts Department of Environmental Protection (MassDEP) has undertaken a series of initiatives and studies to ascertain the extent to which the perchlorate ion is present in the groundwater and surface waters of the state. While many questions remain, based upon the totality of information obtained to date, the agency has made a number of preliminary findings and conclusions:

Occurrence

The perchlorate ion is not pervasive in surface water or groundwater in Massachusetts, having been found in only 9 of 600 tested public water supply systems at or above an analytical Reporting Limit of 1 μg/L (ppb). Detections have in most cases been related to known or suspected uses or releases of perchlorate-containing materials.

Sources

The most prevalent sources of perchlorate contamination in environmental media in Massachusetts were found to be blasting agents, military munitions, fireworks, and, to a lesser extent, hypochlorite (bleach) solutions. Additionally, at one location, a perchloric acid user was identified as a significant source of perchlorate contamination to a river system.

Impacts

The order-of-magnitude impacts associated with observed sources to date include:

- *Blasting agents* - hundreds to thousands of μg/L (ppb) in groundwater and small streams
- *Military Munitions* - hundreds of μg/L (ppb) in groundwater
- *Fireworks* - single digit to double digit μg/L (ppb) in groundwater
- *Industrial Perchloric Acid Use* - hundreds of μg/L (ppb) in effluent from municipal sewage treatment plant; single to double digit μg/L (ppb) in receiving river systems

Based upon a limited sampling effort, hypochlorite solutions used at water and wastewater treatment plants were found to contain between 260 and 6750 μg/L (ppb) of perchlorate, with concentrations of perchlorate increasing with time of product storage. This could result in detectable levels of perchlorate (0.2 – 0.4 μg/L) in chlorinated drinking water distribution systems. Perchlorate was also found in household bleach, from 89 μg/L (ppb) to 8000 μg/L (ppb), with concentrations increasing with time of product storage. While the on-site discharge of household bleach via washing machine use could result in low-level impacts to groundwater, discharges of perchlorate to conventional (anaerobic) septic tanks were found to be treated to less than 1 μg/L (ppb).

Analytical

The use of a modified EPA Method 314.0 was shown to reliably detect and quantify 1 μg/L (ppb) or greater concentrations of the perchlorate ion in drinking water matrices common in Massachusetts (i.e., less than 500 μS/cm specific conductance).

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1.0 INTRODUCTION

Perchlorate is of concern because of its toxicity. It interferes with iodide transport into the thyroid gland, decreasing the availability of iodide needed for the synthesis of thyroid hormones, and thus has the potential to affect metabolism and normal growth and development, which could result in brain damage. The impacts of disrupting thyroid hormone synthesis are greatest on pregnant women and their developing fetuses, infants, children, and individuals who have low levels of thyroid hormones. More information in this regard is available from MassDEP at http://www.mass.gov/dep/brp/dws/percinfo.htm

Little is known about the prevalence of perchlorate in the environment, particularly at low concentrations. This is due in large part to the relatively recent introduction of mass-produced perchlorate-containing products to commercial and industrial marketplaces, combined with historical limitations in analytical testing technologies.

In an effort to shed some light on this subject, MassDEP has over the last 12 months initiated a series of investigatory efforts and programs. The purpose of this report is to explain and document these activities, and provide and discuss data and preliminary findings.

2.0 BACKGROUND

2.1. Production and Uses of Perchlorate

The unusual and desirable properties of Perchloric acid and perchlorate salts were first discovered in the early part of the 20th century. Both are powerful oxidizing agents that are also exceptionally stable and safe to use. (Schumacher, 1960)

The large-scale production of perchlorate salts began in the 1940s for military purposes, and in the following decades, for use as a solid oxidant in rockets and missiles. The two most common salts are ammonium and potassium perchlorate. To this day, the defense industry and NASA remain the largest users of perchlorate in the United States. According to the Department of Defense, perchlorate is currently used in over 250 types of munitions. (http://www.dodperchlorateinfo.net/facts/uses-benefits/)

Given this history and status, it is not surprising that concern over releases of perchlorate to the environment has focused on large perchlorate manufacturing and use facilities located in the western US, as well as military installations throughout the nation – including Massachusetts. However, in recent years it has become apparent

that the desirable properties of perchlorate and perchloric acid, combined with increased availability due to large scale production efforts, have led to uses in a wide variety of non-military applications and products. A partial list of these uses is provided in Table 1.

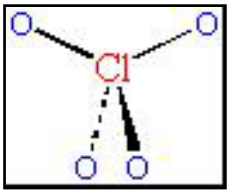
Table 1
Some Uses for Perchlorate Salts and Perchloric Acid (IME, 2004 & GFS, 2005)

Blasting agents	Brass and copper etching
Fireworks	Paints and enamels
Road flares	Leather tanning
Model rocket engines	Textile bleaching agent
Safety matches	Photographic flash powder
Automotive air bag initiators	Oxygen generators
Analytical testing agents	Ejection seats
Electroplating operations	Additive in polyvinyl chloride (PVC)
Electropolishing operations	Specialty industrial uses

This broadened industrial and commercial usage suggests the possibility that perchlorate contamination could be more widespread within Massachusetts than might be assumed.

2.2. Fate and Transport of the Perchlorate Ion

It is not only the expanded uses of perchlorate products that drive concern over accidental or incidental releases to the environment, but also its physical properties and mobility in environmental media, especially groundwater.



Specifically, perchloric acid and most perchlorate salts will readily dissolve in water, generating the perchlorate anion (ClO_4), a tetrahedral array of 4 oxygen atoms around a central chlorine atom. Although a strong oxidizing agent, the perchlorate anion is persistent in the environment, due to the high activation energy associated with its (abiotic) reduction to Chlorate (ClO_3). Moreover, given its relatively low charge density, perchlorate does not form complexes with metals in the same manner as other anions, and, in its ionic state, does not readily sorb to environmental media. [Urbansky, 2002] This combination of solubility, stability, and mobility creates the potential for both localized and area-wide impacts of toxicological interest.

2.3. Initial Detections of Perchlorate in Massachusetts

Perchlorate contamination of groundwater was first documented in Massachusetts in 2000 at the Massachusetts Military Reservation (MMR) on Cape Cod, as part of site assessment activities. A number of discrete plumes of perchlorate contamination have since been identified and characterized within the 15,000-acre Camp Edwards Impact Area and Training Ranges, emanating from a groundwater mound in the Northern portion of the base. Historical use of military munitions and flares are the suspected sources of contamination, which range from hundreds of μg/L in release areas, to single digit μg/L levels in the outlying edges of groundwater plumes. (http://www.mmr.org/)

In 2002, three municipal drinking water wells located just off the MMR boundary were found to be contaminated by low levels of perchlorate. The impacted community subsequently requested guidance from MassDEP on the health significance of this finding, which led to the issuance by the Department of a drinking water *Health Advisory* of 1 μg/L (see http://www.mass.gov/dep/brp/dws/percinfo.htm).

In the following two years, MassDEP continued to assess the toxicological significance of perchlorate, and began to obtain information that non-military releases of the contaminant were possible (e.g., via fireworks). In early 2004, the Department promulgated emergency regulations requiring public water supplies to test for perchlorate, as the first step in considering whether it was necessary and appropriate for the agency to promulgate a drinking water standard. As the data started to trickle in, discoveries of perchlorate in a drinking water source (groundwater or surface water) triggered field investigations designed to "back track" to the contaminant release area, and identify the source material(s). These efforts and experiences have led to an interim level of understanding of the nature and extent of perchlorate contamination across the state.

3.0 OCCURRENCE OF PERCHLORATE IN MASSACHUSETTS

The use, disposal, and/or accidental or incidental discharge of perchloric acid or perchlorate products could result in the contamination of environmental media, including surface water and groundwater. Recent reports have even suggested the possibility of the "natural" production of perchlorates in rain and in arid geological ecosystems. But how prevalent is perchlorate in Massachusetts, a region that is decidedly non-arid (44 inches of precipitation per year), and a state without a history of significant rocket propellant production or use?

Data from public water supply systems across the state provide a good starting point to begin answering this question.

There are approximately 450 community and 250 non-transient/non-community public water supply systems in Massachusetts, as plotted in Figure 1. The majority (89%) of these systems obtain water exclusively from groundwater aquifers. Collectively, this infrastructure constitutes a large, geographically and geologically diverse universe of water quality indicators.

Community public water supply wells in Massachusetts are comprised primarily of shallow overburden wells in water-table aquifers, providing a good vehicle to detect recent releases of soluble, mobile contaminants like perchlorate. Non-transient/non-community public water supplies in Massachusetts are comprised of extraction wells from both overburden and bedrock aquifers, servicing a variety of buildings and users (e.g., condominiums, schools).

In the last year, 85% (379) of the community and 86% (212) of the non-transient/non-community public water supplies in Massachusetts (groundwater and surface waters) have been tested for the presence of perchlorate, using analytical methodologies and laboratories capable of achieving a 1 μg/L Reporting Limit. *Of these 591 water supplies, only 12 sources in 9 water supply systems have detected perchlorate above 1 μg/L* (some systems have multiple groundwater production wells in close proximity). The communities where these 9 water supply systems are located are illustrated in Figure 2.

A summary of the relevant system parameters and findings for these 9 water supplies is provided in Table 2, including the range of perchlorate concentration values reported since the start of testing (early 2004).

As can be seen, perchlorate is not widely prevalent in public water supplies across the state, at least above 1 μg/L. Additional conclusions and observations of note in this regard are provided below:

- Although detections have been limited, they have occurred across the state, in a number of land-use and geologic settings, in both overburden and bedrock aquifers.

- The only impacted surface water supply was that for the Town of Tewksbury, which draws its drinking water from the Merrimack River, the state's second largest river, with a 5000 square mile watershed and average mean flowrate greater than 5000 cubic feet per second (CFS). In this case, the source of contamination in the river was eventually traced to an industrial user of Perchloric acid.

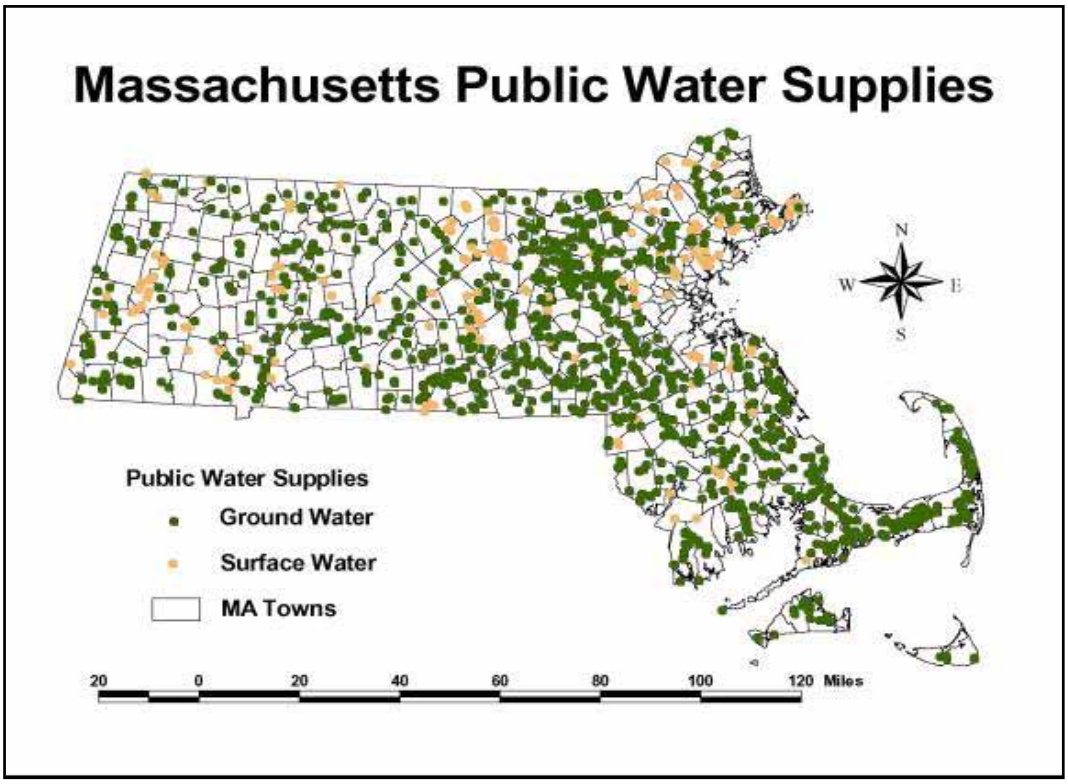


Figure 1 – Public Water Supplies in Massachusetts

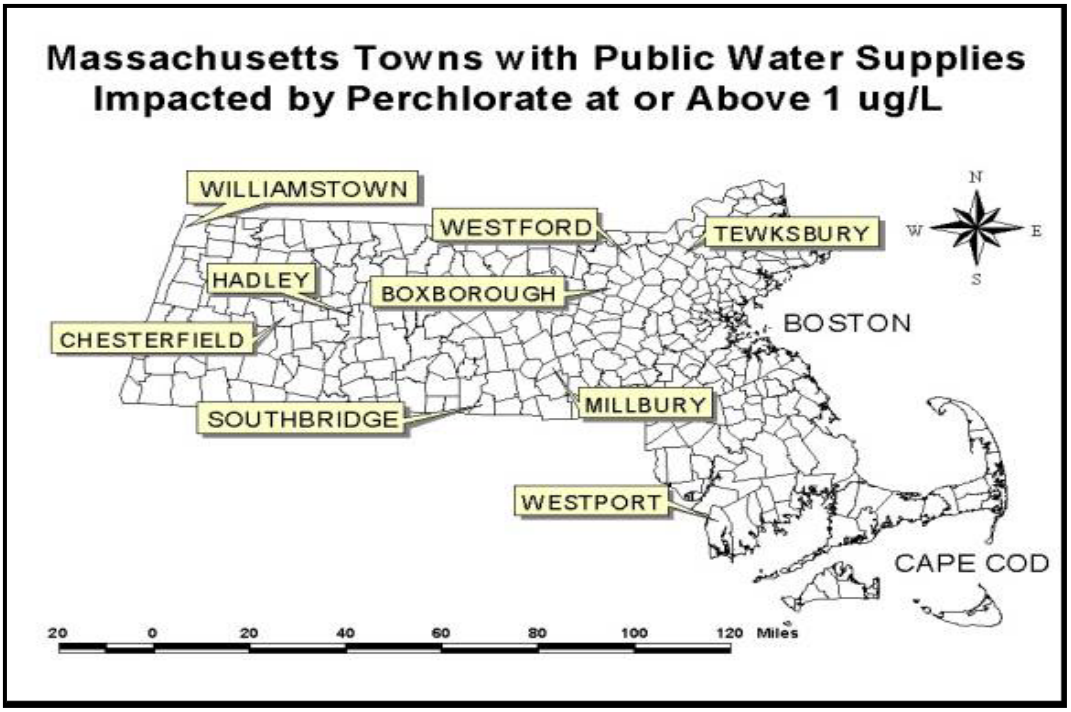


Figure 2 – Impacted Public Water Supplies in Massachusetts

Table 2
Massachusetts Public Water Supplies Impacted by at least 1 μg/L of Perchlorate
(Data current as of March 2005)

Town	System(s)	Description	Aquifer	Avg MGD	Sampling Rounds	Concentration Range μg/L	Likely Source(s)
Boxborough	Harvard Ridge	Condominium	bedrock	0.013	36	783 - 1300	Blasting
Chesterfield	Davenport Bldg	Town Office	bedrock	0.001	3	1-1.5	Fireworks
Hadley	Mt Warner Well #2	Municipal water supply	overburden	0.720	6	1.5 – 3.8	Unknown
Millbury	Aquarian – Wells Jacques 1 & 2	Municipal water supply	overburden	1.664	8	16.1 – 45.3	Blasting
Southbridge	Indust Company Well #1	Industrial Facility	bedrock	0.001	4	N.D. – 3.1	Unknown
Tewksbury	Merrimack River Intake	Municipal water supply	N/A	2.535	>50	N.D. – 3.26	Industrial Discharge
Westford	Nuttings Road	Municipal water supply	overburden	1.734	8	N.D. – 3.7	Blasting
Westport	High School 1 & 2	School	bedrock	0.001	13	1.06 – 3	Fireworks
Williamstown	Mt Greylock School 1 & 2	School	bedrock	0.005	14	1.03 - 10	Fireworks

- In 7 of the 9 cases, the source of contamination appears to have been identified, including: 3 situations where blasting activities occurred within one-half mile of the impacted water supply well(s), and have likely resulted in the observed perchlorate impacts; 3 sites where nearby fireworks displays appear to be the likely cause of contamination; and an industrial Perchloric acid user. The other 2 water supplies have shown low-level impacts up to 4 μg/L, without a clear source, although one system (Hadley) is located in an agricultural area where the use of perchlorate-containing fertilizers is possible.

One additional drinking water database is also available to provide some perspective in this matter: bottled water. Companies that sell bottled water in Massachusetts are regulated by the Massachusetts Department of Public Health (DPH), which establishes testing requirements for these products. Since early 2004, all bottled water purveyors have been required to test for the presence of perchlorate.

This testing information and data is available on the Massachusetts DPH web site at http://www.mass.gov/dph/fpp/pdf/perchlorate.pdf, and as of 12/7/04, contained test data for 50 bottled water products. These 50 products obtain their water from 7 locations in Massachusetts, 34 locations in 12 other states, 3 locations in Canada, and 6 locations in 4 other countries. *All of these products have reported perchlorate concentrations of Not Detected at a Reporting Limit of 1 μg/L.*

4.0 Sources of Perchlorate in Massachusetts

A number of reports exist documenting the nature and extent of perchlorate contamination at perchlorate production facilities, and at military installations, including the Massachusetts Military Reservation (MMR) on Cape Cod. However, despite our evolving knowledge on the use and/or presence of perchlorates in a wide variety of non-military products, little information exists on the "real world" impacts of these materials on surface and groundwater quality.

For this reason, the detection of the perchlorate ion in drinking water sources in Massachusetts triggered investigations by MassDEP to determine and examine the suspected source(s) of contamination. These investigations included site-specific assessment activities at and upgradient of the impacted water supplies, together with directed testing and evaluation programs of suspected source materials and activities.

On the basis of these efforts, in addition to military munitions, 3 other perchlorate-containing products in general commerce were identified as potential source materials of state-wide significance:

- Explosive Materials
- Fireworks
- Hypochlorite/Bleach Solutions

A fourth source of perchlorate contamination of a major water supply (Merrimack River) was found to be an industrial user of perchloric acid with a wastewater discharge to a Publicly-owned Treatment Works (POTW). While the prevalence of these types of users is unknown, it is clear that, on a mass-balance basis, such discharges can be a significant source of surface water and/or groundwater contamination.

4.1. Explosive Materials

Perchlorate salts (sodium, ammonium, and/or potassium) are used in some explosive materials, principally "water gels" and "emulsion" blasting agents, as well as some

blasting caps. Many questions remain, however, on where and how these products are used, and how they do or could impact environmental media, especially groundwater.

Water gels are explosive materials containing water, oxidizers, fuel, plus a cross-linking agent. Emulsions are explosive materials containing oxidizers that are dissolved in water droplets, surrounded by an immiscible fuel; or droplets of an immiscible fuel surrounded by water containing a dissolved oxidizer. Both types of products were first developed in the 1960s; presently, emulsions are more widely used than water gels. Both are sold and delivered in bulk form or as packaged products. (IME, 2004)

Most water gels and emulsions are classified as "blasting agents", as opposed to high explosives, because they are "insensitive" materials that are difficult to detonate. This is a beneficial attribute, for safety reasons. However, for certain difficult blasting applications, it is desirable to increase the sensitivity of these products; for example, at wet, water-saturated construction sites where the explosive is subjected to high static or dynamic pressures. Reportedly, perchlorate-sensitized blasting agents are among the best choices in these situations. (IME, 2004)

It is difficult to ascertain how much perchlorate is contained within a specific explosive material. This is because MSDS documentation provided for these products often specify a range, starting with zero percent, or a "less than" notation; for example:

- *Hydromite 400 Series* (Austin Powder Co)*:* 0-5% ammonium perchlorate and 0-5% sodium perchlorate (http://www.austinpowder.com/BlastersGuide
- *Dynosplit®E* (Dyno-Nobel): 0-15% sodium perchlorate http://www.dynonobel.com/dynonobelcom/en/global/
- *Slurran 915* (Slurry Explosive Corporation): <7% sodium perchlorate http://www.slurryexplosive.com/products.htm

During the course of MassDEP's investigation, the highest concentration of perchlorate encountered in an explosive material was "20% - 30%" for *Slurran XLS*, a watergel product manufactured by Slurry Explosive Corporation (SEC). While reportedly not added, small amounts of perchlorate (0.1%) could nevertheless be present in ANFO (Ammonium Nitrate/Fuel Oil), or other explosive products, given the use of Chilean nitrates by some manufacturers (e.g., see MSDS #1019 for *Unimax*® by Dyno Nobel, at http://www.dynonobel.com/NR/rdonlyres/23F3B92C-2FCD-4475-9896-24D401BF88CD/0/1019PackagedDynandBlastingGel012405.pdf)

While the exact percentage of perchlorate salts in an explosive material may be difficult to obtain, the overall amount of this added chemical sensitizer is generally not

sufficient to change the material's status as a "blasting agent". This means that the product is still relatively safe, and will not detonate without a "boost" from other explosive charges. This in turn leads to the use of a series of explosive materials in and among blast holes, including detonators, primers, and boosters, loaded and fired in a manner and sequence to ensure the intra and inter blast hole "chain reaction" needed to detonate all elements in the explosive train.

The effective propagation and magnification of this shock wave - a transient pressure pulse that travels at supersonic velocity – is an essential prerequisite for ensuring the detonation of the perchlorate-containing explosive materials. A number of factors, however, can lead to one or more "misfires" in this sequence, including: an excessive gap between a primer or booster charge and the blasting agent, timing problems, formation characteristics, and, in the case of water gels, low temperatures.

4.1.1. Potential Environmental Release Mechanisms and Pathways

Perchlorate-containing explosive materials could result in environmental contamination and/or lead to human health exposures via the following activities, uses, and/or scenarios:

- *Misfires*. While misfires are a major industry concern and high priority – necessitating immediate and rigorous remedial efforts – it is not unreasonable to assume that some un-detonated product may not be recovered at some sites; especially if bulk or even packaged materials are scattered throughout a blasting zone as a result of the partial detonation of a blast hole. This could leave pockets of un-reacted perchlorate salts within the blast fragments/rock pile, and lead to the solubilization and mobilization of the perchlorate ion.

- *Placement (e.g., pumping) of bulk materials into open boreholes*. Depending upon the rheology and density of the agent, and the presence, degree and connectiveness of formation fractures, it would seem reasonable to speculate that some product could migrate out of a blast hole and not be detonated. This may be more of an issue for emulsion products, given that the cross-linking agent used in water gels leads to a reportedly stable gelatinous consistency.

- *Placement of compromised and/or opened packaged products into blast holes*. Packaged materials are often slit upon being loaded into a blasting hole, to allow them to more completely fill the full cross-sectional area, and/or to release any air within the packages and ensure sinking when lowered into wet holes. (IME, 2005). This again could place bulk/uncontained product into the open environment, with the concerns articulated above.

- *Bad Housekeeping.* Spills of packaged or bulk material to or into the ground, or insufficient misfire recovery efforts, can place or leave bulk/uncontained product in the open environment.

- *Blast Rock Processing*. Crushing rock blasted by perchlorate containing agents can generate dust and particulates that may contain trace levels of perchlorate (especially in the case of misfires). Run-off or washing operations of this rock can also result in surface water and/or groundwater pollution.

- *Normal Residuals.* The detonation of explosive materials is a violent chemical reaction, in which component molecules are thought to be instantaneously destroyed or decomposed by a pressure pulse moving through the material at supersonic speed. While it seems reasonable to assume that the residue from such a reaction should be essentially free of perchlorate salts, MassDEP has not to date seen industry data in this regard. Given the parts-per-billion concern with perchlorate in the environment, even "negligible" residuals from a large blasting effort may be of significance in this regard.

4.1.2. Blasting near Public Water Supply Systems

To date, MassDEP has obtained data from 3 sites in Massachusetts where blasting operations have resulted in the contamination of surface and/or groundwater with perchlorate, and apparent impacts to nearby drinking water wells. These sites are located in the towns of Millbury, Westford, and Boxborough. Available data on explosive materials used at each of these sites is provided in Table 3. All 3 locations employed the same blasting contractor.

4.1.2.1. Millbury

Blasting operations occurred at the Millbury site from July 10, 2002 through January 6, 2004. Much of the blast rock was reused at the site to facilitate construction of a large shopping mall, which was essentially constructed on the side of a bedrock hill (see Figure 3). Importantly, runoff from the roof drains of the mall buildings are discharged to the subsurface; in some cases into areas where blast-rock has been deposited.

In May 2004, perchlorate was detected in two (overburden) public water supply wells - Jacques # 1 & Jacques #2 - at concentrations of 45.3 μg/L and 21.6 μg/L, respectively. Both wells were closed down, and MassDEP began an iterative search for the source(s) of perchlorate contamination, initially focusing on the

Table 3: Use of Explosive Products at 3 Construction Sites
(Per attestations of Blasting Company)

Town/ Dates	Explosives and Blasting Agents (Abridged List)				Perchlorate per MSDS?
	Product Name	Manufacturer	Type	Pounds	
Millbury 7/02 – 1/04	ANFO & ANFO WR	Dyno-Nobel	ANFO	621,252	Not Listed
	EZ-Det	Ensign-Bickford	Blast Cap	Not Avail	Not given
	Slurran 406	SEC	Watergel	74,257	Not Listed
	Detagel Presplit	SEC	Watergel	360	< 7% SP
	Emgel ≥ 4 inches	MSI	Emulsion	2,332	Not Listed
	Emgel 2" & 3"	MSI	Emulsion	82,722	Not Listed
	Optiprime Boosters	Ensign-Bickford	Booster	Not Avail	Not Listed
Westford 8/03 - 8/04	ANFO & ANFO WR	Not Avail	ANFO	94,740	Not Avail
	EMGEL 200 & 250	MSI	Emulsion	474	Not Listed
	Hydromite 860	Austin	Emulsion	3,254	Not Listed
	Slurran XLS	SEC	Watergel	9,563	20-30% AP
	Slurran XG	SEC	Watergel	1,029	Not Avail
	Unimax	Dyno Nobel	Dynamite	5,088	Not Listed
Boxborough 11/03	Information not currently available				

sampling and analysis of nearby private drinking water wells, the Blackstone River, and contributing tributaries. By June, these efforts had traced contamination back to a mall development site located 1000 feet west of the impacted wells. By the beginning of July, confirmation was obtained that perchlorate-containing blasting agents were used at the mall development site.

The mall owners retained an environmental consulting firm, who proceeded to conduct additional investigative activities to identify the nature and extent of contamination – and look for other potential sources of perchlorate releases.

To date, assessment efforts have disclosed tens to hundreds of μg/L of perchlorate in surface water runoff systems, overburden monitoring wells, and bedrock monitoring wells on the mall property. In total, 9 private drinking water wells have been tested, though none appear to be directly downgradient of the mall area. None of these wells were found to contain perchlorate above 1 μg/L.

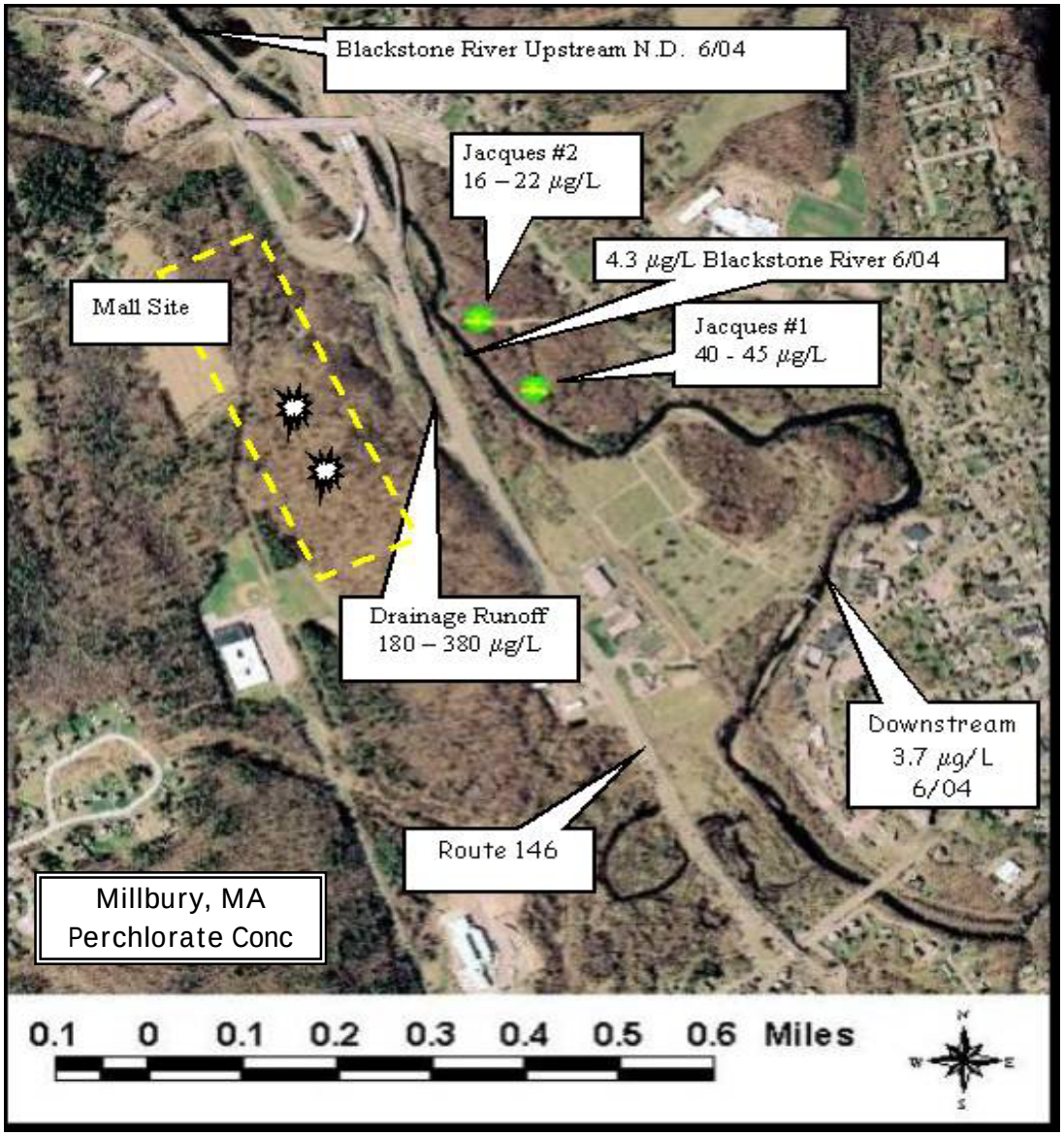


Figure 3: Millbury, MA Blasting Site

Monitoring wells upgradient of the mall site and upgradient of the presumed mall plume area have shown N.D. for perchlorate at a Reporting Limit of 1 µg/L. No other sources of perchlorate have been identified within the vicinity of this site.

4.1.2.2. Westford

Blasting operations occurred at the Westford site from August 26, 2003 to August 25, 2004, for the purpose of constructing a new municipal building (highway garage). The site is surrounded by a number of active and inactive

(rock) quarrying operations, which have presumably used a variety of explosive materials for decades.

In July 2004, 2 μg/L of perchlorate was detected in the Cote Well, a municipal water supply located approximately one-half mile northeast of the highway garage site (see Figure 4).

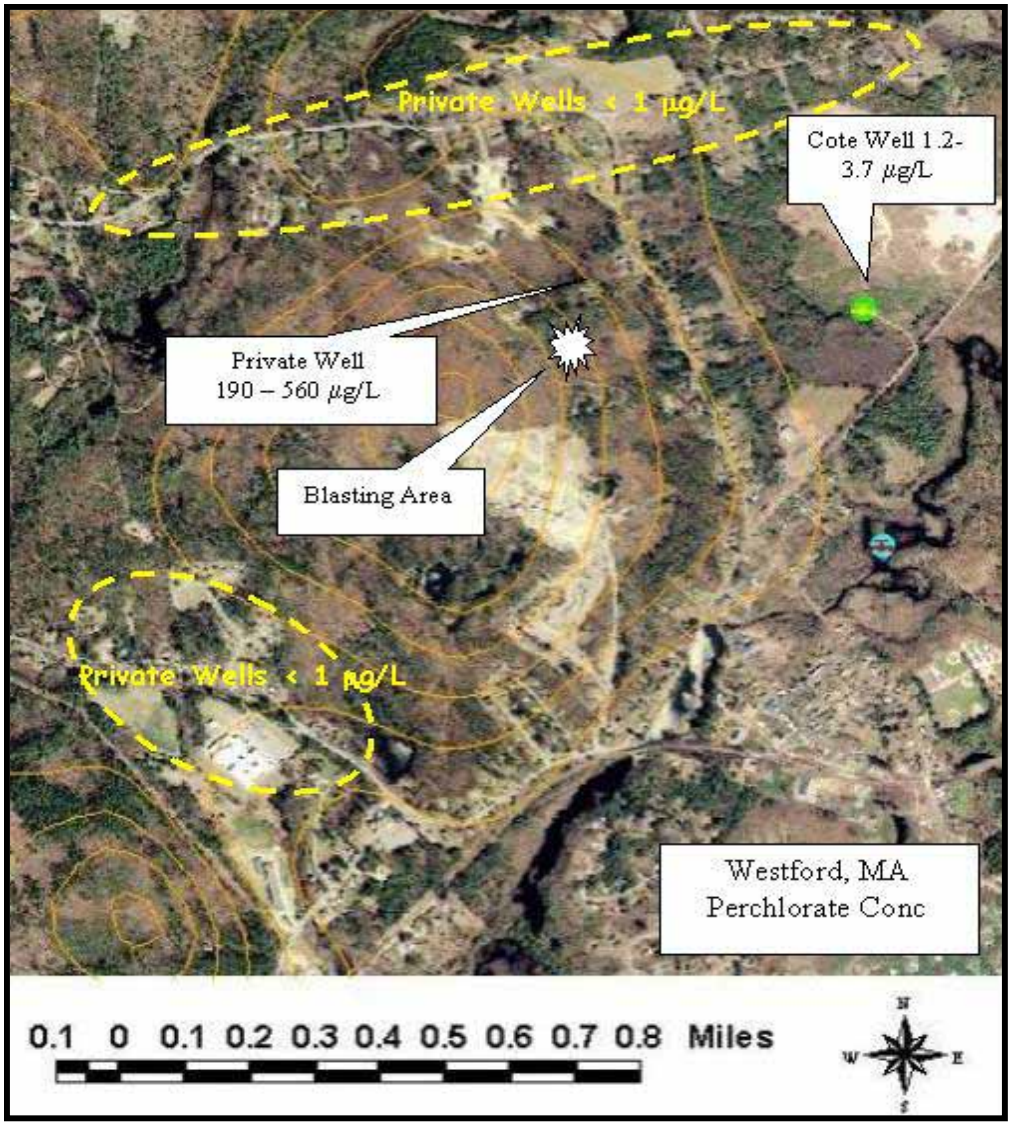


Figure 4: Westford, MA Blasting Site

This detection of perchlorate resulted in the shut down of the Cote well, and use of alternative water supply sources. It is interesting to note that two earlier rounds of sampling of this public water supply, in March and April 2004, reported N.D. for perchlorate at a Reporting Limit of 1 μg/L.

Following the shut down of the well, the Westford Water Department began to conduct additional testing of monitoring wells and surface waters. By early August, contamination was traced back to the highway garage location, via detections of tens to hundreds of μg/L of perchlorate in surface waters at and exiting the construction area. In mid-August, MassDEP began testing private water supply wells near the site. On August 23rd, data was received indicating the presence of 425 μg/L of perchlorate in a private drinking water well located within a few hundred feet of the construction site; the residents were immediately advised to cease using the water for drinking or cooking purposes. Over the next 4 months, 15 additional private drinking water wells within 4000 feet of the highway garage location were tested. Although these wells appeared to be hydraulically upgradient or cross-gradient from the suspected source area, some were drawing from the bedrock aquifer, and were sampled as a precautionary measure. All data from these wells were N.D. for perchlorate at a Reporting Limit of 1 μg/L.

Additional investigations were also conducted at an adjacent quarry, including sampling of on-site potable and process-water wells. Perchlorate was not identified, leading MassDEP to conclude that blasting at the Highway Garage site – using explosive materials that contained up to 30% ammonium perchlorate - appears to be the likely source of observed contamination.

4.1.2.3. Boxborough

Blasting was conducted at the Boxborough location during November of 2003, to facilitate the construction of a new wastewater treatment plant at a residential condominium complex.

In April 2004, 4.87 μg/L of perchlorate was detected in one of 5 on-site production wells. The other 4 wells reported N.D. In September, however, testing of a second well (Dunster House) identified 791 μg/L of perchlorate; a re-test two weeks later indicated 1080 μg/L. A peak concentration of 1300 μg/L was reported for this well in November 2004. (See Figure 5)

All five production wells are believed to be bedrock wells, spaced about 200 – 500 feet from each other. The most impacted well is located within several hundred feet of the blasting operations.

At the present time, MassDEP does not have information on the types and quantities of explosive materials used at this location, but suspects that perchlorate-containing blasting agents were among the inventory of products.

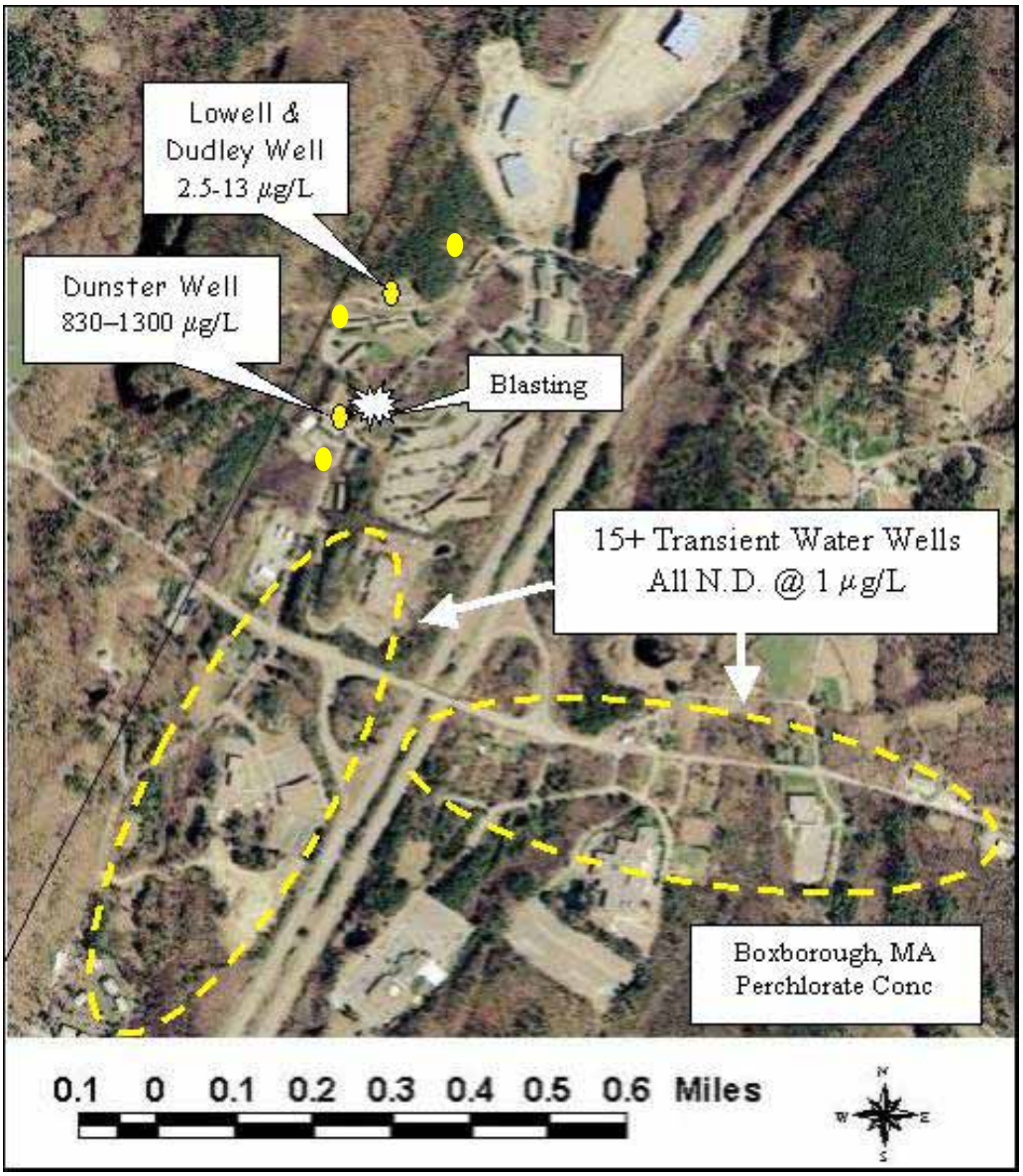


Figure 5: Boxborough, MA Blasting Site

In addition to the 5 condominium wells, approximately 20 other drinking water wells located within 1 mile of the site were sampled and analyzed for perchlorate, including 5 private wells and 15 "transient non community" public water supply wells. All results were N.D. at a Reporting Limit of 1 µg/L.

Because the condominium did not initially have an alternative water supply option, residents continued using the Dunster Well, until the end of 2004, though all were advised to use bottled water for drinking and cooking.

4.1.3. Discussion

The lines and weight of evidence appear sufficient to conclude that blasting activities at the 3 sites described above resulted in contamination of surface water and groundwater, and impacts to downgradient public drinking water supply wells:

- Perchlorate was present in blasting agents used at the Millbury and Westford sites, and is suspected at the Boxborough site;
- Environmental monitoring and assessment data are consistent with a source release within the area of blasting; and
- No other plausible sources or source areas of perchlorate contamination have been identified at any of these locations.

What is not clear is why contamination attributable to the use of explosive materials has only been observed at 3 public water supplies - out of a universe of almost 600 tested sources. Given the degree of construction (and blasting) activities in Massachusetts, and the environmental persistence and mobility of the perchlorate ion, why haven't more water supplies been impacted? Possible explanation include:

- Perchlorate-containing explosive products are relatively new formulations, and it would appear that their use has significantly increased in the last decade. It might take time for other impacts to be observed; and/or

- The specific practices and/or blasting agents used by the (same) blasting contractor at these 3 sites may have resulted in these (unintended and unanticipated) consequences.

Investigations and considerations in this matter continue.

4.1.4. Nitrate

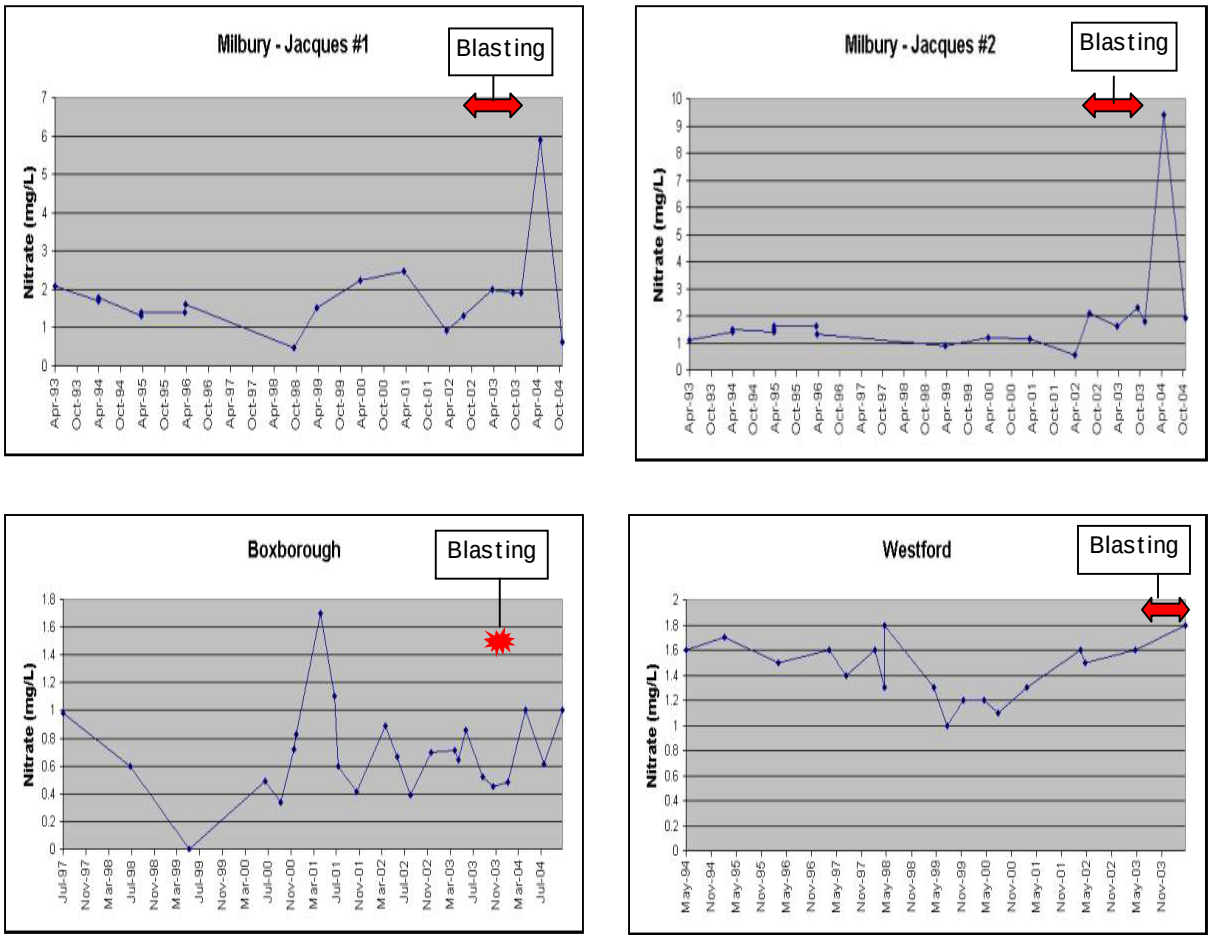
There is a blasting-related nexus between perchlorate and nitrate. Dissolved in an aqueous solution, both are anions, which result in significant groundwater mobility. Both are generally present in perchlorate-containing blasting agents. Moreover, perchlorate industry representatives have raised concerns over the potential environmental impacts from nitrates, which are by far the more predominant ingredient in explosives, including those products that would be used in lieu of perchlorate-containing blasting agents. For example, ANFO (ammonium nitrate + fuel oil) is commonly about 94% ammonium nitrate.

From a regulatory perspective, the 4-orders-of-magnitude disparity between the current nitrate drinking water standard of 10 mg/L and MassDEP perchlorate drinking water advisory of 1 μg/L suggests that an increased concern and emphasis on perchlorate is not unfounded. Moreover, MassDEP is not aware of any public water supply that became contaminated with more than 10 mg/L of nitrate as the likely result of nearby blasting activities.

However, there may be utility in establishing a perchlorate/nitrate link in blasting-related contaminated plumes, given that all water supplies routinely test for nitrates.

Figure 6 plots the last 10 years of routine nitrate monitoring data for the 3 blasting-related impacted water supplies.

Figure 6
Nitrate Levels in Wells Impacted by Perchlorate from Suspected Blasting Sources



The above data suggest the possibility of a relationship between nitrates and perchlorate at the Millbury site, given the 5-10 fold increase in nitrates in Jacques Wells #1 and #2, located 800 – 1000 feet to the east of the mall construction site, approximately 18 months after the start of blasting activities. This is also the site where large amounts of ANFO were used (621,000 pounds).

This relationship was further explored by the consulting firm overseeing work at the Millbury site, during a series of sampling events in February 2005, where split samples were analyzed for perchlorate and nitrates (NO_3-N). In total, 22 samples were synoptically analyzed in this manner, including 8 drainage/surface water samples, 8 overburden groundwater samples, and 6 bedrock groundwater samples. The results of all data are plotted in Figure 7. Once again, the possibility of a general correlation is suggested, though more evaluation of variables (e.g., site-wide explosive materials usage, precipitation events, groundwater elevations, etc.) would be needed to draw more definitive conclusions.

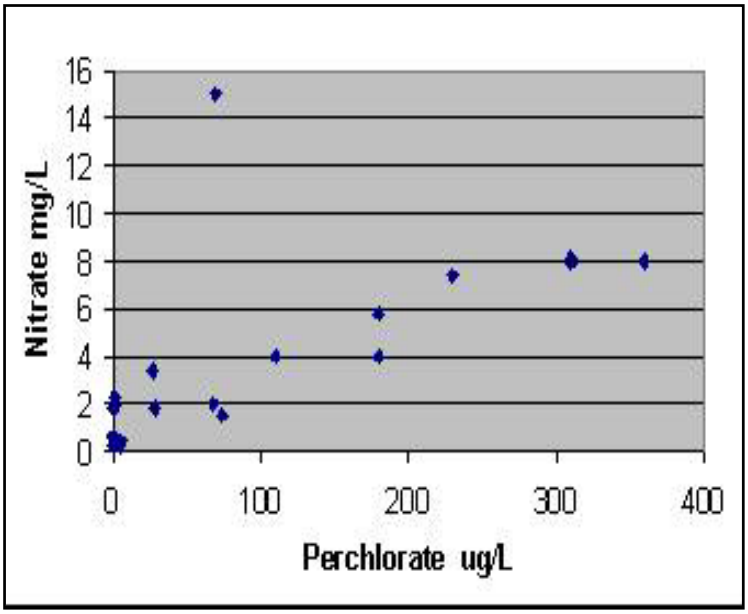


Figure 7
Millbury, MA Perchlorate vs Nitrate
(GeoSyntec, 2005)

A relationship between perchlorate and nitrate is not evident in the monitoring data for the Cote Well in Westford. This well is the most distant (2600 feet) and least impacted (3.7 μg/L) of the three blasting sites. Given these characteristics, and the fact that blasting did not begin until August 2003, it is possible that peak concentrations of both contaminants have not as yet been seen.

The lack of nitrate impacts to the Boxborough wells may be due to the formulation of the blasting agent(s) used for this construction project (not currently known). For example, Surran XLS, a perchlorate-containing watergel used in Westford, is comprised of (only) between 10 and 20% nitrates.

4.2. Fireworks

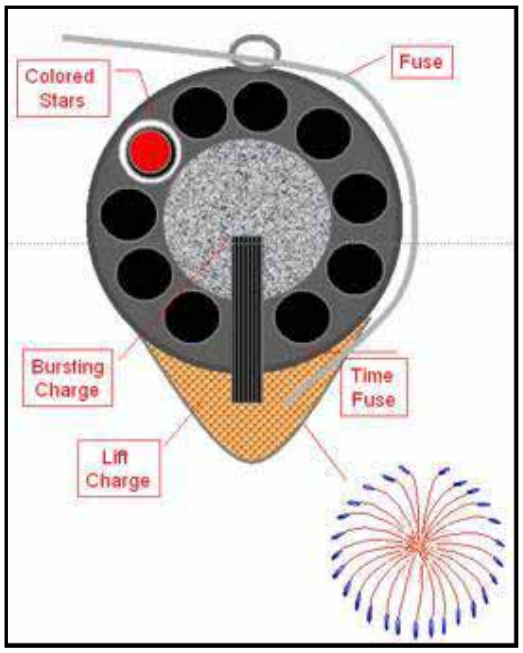
It has been difficult for MassDEP to obtain specific information on the chemical composition of fireworks.

By all accounts, most fireworks are manufactured in Asia (mainly China), using proprietary ingredients and formulations. Compositions are typically not listed on or provided for these products - just descriptive elements related to pyrotechnic colors, effects, and styles.

Industry sources have indicated two primary uses of perchlorates in fireworks:

- To produce color effects; and
- As flash powder in "Salute" shells (to produce a loud bang/flash).

Perchlorate use and content in fireworks has increased over the past two decades, in a (successful) effort to produce more vivid color effects (C&EN, 2001). Modern fireworks create these effects by the spectral emissions of excited gas-phase molecules, including barium chloride (green), strontium chloride (red), and copper chloride (blue). Potassium perchlorate is used as both an oxidizer as well as a chlorine donor in this process (bringing metal and chlorine together in a vapor state at high temperatures during the burning process). Perchlorate has replaced chlorate in this capacity for safety reasons; potassium salts are used (as opposed to sodium or potassium perchlorates) to limit interference with desired color emitters.



Fireworks color effects are most typically produced by the launching of aerial display shells, which contain numerous "stars" or small pellets containing a fuel/metal/oxidizer mixture. The frequency and extent of perchlorate use in these formulations – and whether those values are continuing to increase – is not clear.

In addition to color effects, potassium perchlorate is also used in a mixture with aluminum powder to create "flash powder". Containing up to 70% potassium

perchlorate, flash powder is used to create a loud noise and flash. Aerial shells containing flash powder are launched to provide "aerial salutes" during a display.

Aerial shells are packaged/wrapped in paper, and launched from a "mortar" (solid tube) using a black powder "lift charge". They range in size from 3 inches to 10 inches and more in diameter, and reportedly are launched 100 feet for every inch in diameter (http://pyrouniverse.com/professional.htm). There may be additional and expanding uses of perchlorate in the industry, given its availability, effectiveness, and relative stability and safety. Examples could include products available to the general public, including firecrackers and sparklers.

4.2.1. Potential Environmental Release Mechanisms and Pathways

Perchlorate-containing pyrotechnics could result in environmental contamination and/or lead to human health exposures via the following activities, uses, and/or scenarios:

- *Atmospheric Fallout*. Fine particles of burnt black powder, paper debris, and other chemical residues are the inevitable fallout from a fireworks event. The exact degree, nature, and extent of this fallout would seem to be highly site-specific, based upon the products used, weather conditions, and post-display cleanup (housekeeping) activities. This fallout could result in levels of perchlorate in soil, groundwater, and/or surface water. It could also result in inhalation exposures to perchlorate particulates during the display event.

- *Duds*. "Duds" are aerial shells that are launched from a mortar, fail to ignite in the atmosphere, and plummet back to the earth. Information available on the Internet suggests a common industry recommendation is to bury these shells for safety reasons. This could result in groundwater contamination from perchlorate salts within the shell.

- *Misfires*. Misfires are aerial shells that do not launch from the mortar. Information available on the Internet suggests a common industry recommendation is to apply water to/into the mortar for safety reasons. Uncontained run-off could result in soil and groundwater contamination from perchlorate salts within the shell.

While Massachusetts' regulations require collection and proper disposal of all debris, duds, and misfires, the degree of compliance is unknown.

4.2.2. Modeling of Potential Impacts from Fireworks Displays

MassDEP has conducted limited modeling efforts of hypothetical fireworks displays, in order to better define the scope and range of potential groundwater impacts and concerns. The details and results of this modeling effort are contained in Figure 8, which assumes a mid-sized "July 4th community display" of 1000 to 2000 aerial shells, with a total weight of 3000 pounds.

The average perchlorate content in all fireworks is assumed to be 40%, which is combusted in an aerial display, producing particulate/debris fallout that uniformly descends to the ground over a "football field" size area of 3600 square meters.

Beyond all of the normal areas of uncertainties in any generic analysis of site-specific events (e.g., wind speed and direction, atmospheric conditions and stability, hydrogeologic parameters), this analysis was further encumbered and limited by two key unknowns/variables:

- The amount of perchlorates used in fireworks, and
- The amount of perchlorates not consumed in the display (e.g., atmospheric fallout of un-combusted particulates and debris).

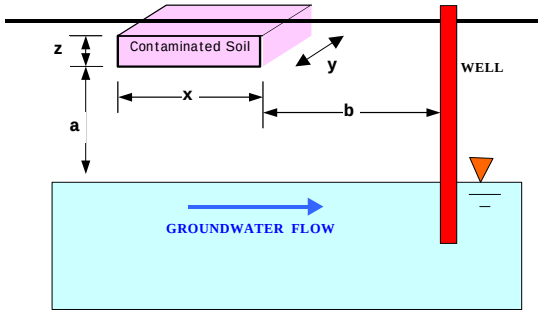
While the 40% perchlorate figure may be high, it is being used in the absence of anything more definitive from the pyrotechnics industry. On the basis of this analysis, even with 99.9% destruction of perchlorates, tens of μg/L of perchlorate could be expected immediately (100 meters) downgradient of the fallout area, with trace amounts (1 μg/L +/-) further downgradient. Higher concentrations could be expected with larger displays, use of pyrotechnics with higher amounts of perchlorates, less complete combustion, improper disposal of duds and misfires, excessive debris fallout and/or lack of post-display cleanup.

4.2.3. Fireworks Displays near Public Water Supplies in Massachusetts

Given the results of the generic modeling exercise discussed above, an effort was undertaken to geo-locate permitted fireworks displays with respect to proximate public water supplies.

In Massachusetts, the Office of the state Fire Marshall must permit all fireworks displays. In 2003, permits were issued for fireworks displays in 155 communities. Of these 155 displays, 47 were found to be located within the (calculated or assumed) groundwater recharge zones of public water supply wells (community and non-community water supplies). A total of 110 public drinking water supply wells

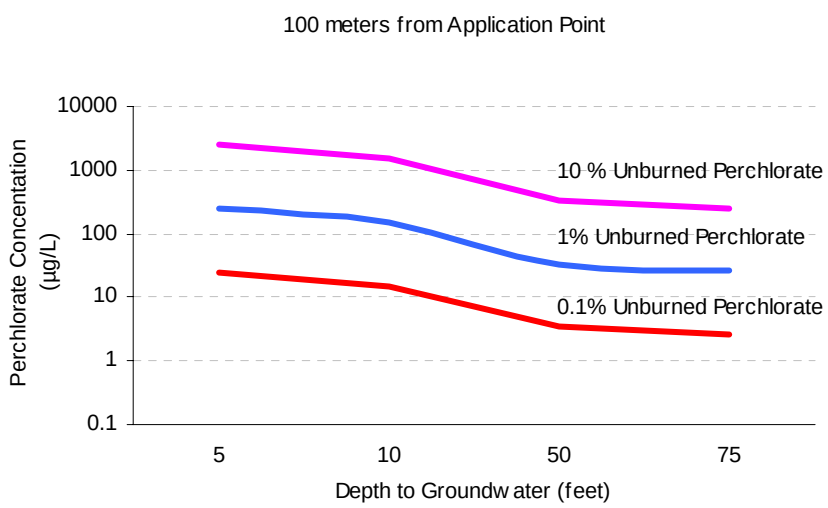
Figure 8: Modeled Perchlorate Impacts to Groundwater from Fireworks Display

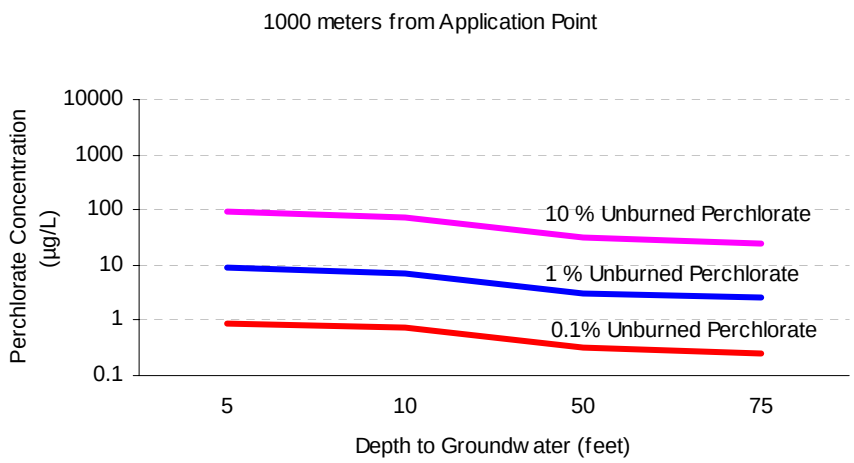


Model = SESOIL/AT123D

Assumptions:

- 3000 lbs fireworks (1000-2000 shells)
- Average perchlorate content = 40%
- x = 60 meters
- y = 60 meters
- z = 6 inches
- a = variable from 5 to 75 feet
- b = variable from 100 to 1000 meters





Additional Model Inputs:

- 44 inches of precipitation per year (Massachusetts)
- Solubility of Potassium Perchlorate = 1.5×10^7 µg/L
- Hydraulic Conductivity = 4.583 m/hr (sand)
- Hydraulic Gradient = 0.0031

are located within these 47 groundwater protection zones *(i.e., "Zone IIs"* or *"Interim Wellhead Protection Areas"*). Of these 110 wells, 97 have been tested to date; all but one have reported N.D. for perchlorate at a Reporting Limit of 1 μg/L. One well, at the Mount Greylock School in Williamstown, has detected up to 10 μg/L of perchlorate.

This finding provides some comfort that fireworks displays have not resulted in the widespread contamination of public water supplies. While MassDEP has not as yet researched past records for fireworks events, most contemporary displays of major significance are held at the same location each year, so the 2003 data is believed to represent the majority of concern in this area.

Smaller and/or historical events will be investigated as contaminated public water supplies are identified. So far, MassDEP has determined that historic fireworks displays are the likely source of contamination in 2 of the 9 public water supply systems showing perchlorate levels above 1 μg/L: Chesterfield and Westport. These two supplies, along with the Williamstown School, are small, non-community wells drawing from bedrock aquifers. All three have low (primarily single-digit) levels of perchlorate; consistent with model predictions, as further detailed in Table 4, and discussed below in more detail.

Table 4: Public Water Supplies near Fireworks Displays

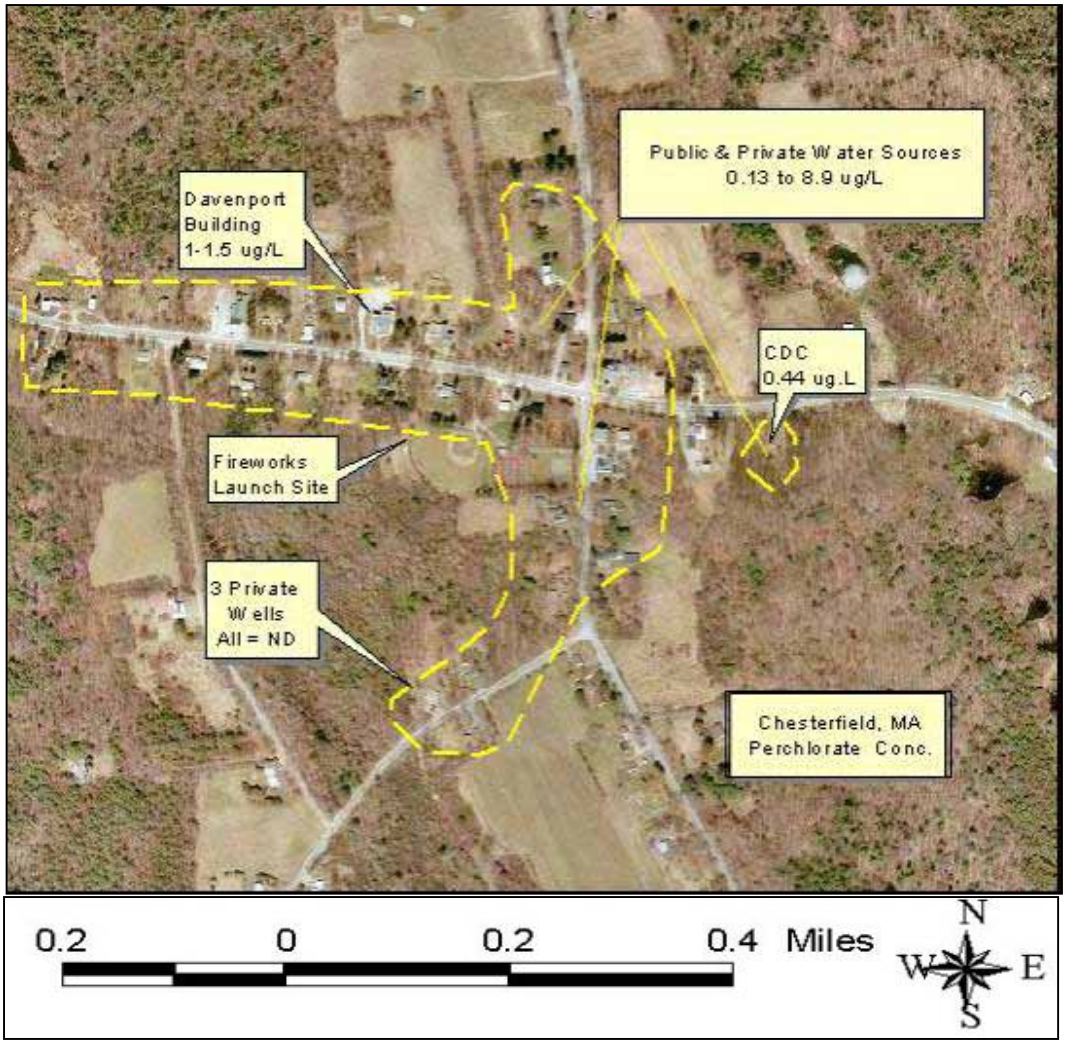
Town	Well(s)	Dist from Fireworks	Dates of Fireworks	Perchlorate Conc. (μg/L)
Chesterfield	Davenport Building	500 ft	Until 2002	1 – 1.51*
Westport	High School 1 & 2	600 ft	Mid 1990s	1.06 - 3
Williamstown	Regional School 1&2	800 ft	89-92; 99-03	1.03-10

* Nearby private well contamination up to 8.9 μg/L

4.2.3.1. Chesterfield

The Davenport Building is a small municipal facility in the Town of Chesterfield. On April 28, 2004, testing of the on-site well (considered a non-community/non transient public water supply) yielded 0.96 μg/L perchlorate. Follow-up testing in October and November 2004 reported 1.51 and 1.33 μg/L, respectively.

Although detailed records have not as yet been obtained, fireworks were reportedly launched from a municipal ball field located across the street from the Davenport Building, with the last event occurring on July 4, 2002 (see Figure 9).



Two residents from the area have recalled the existence of a significant amount of post-display debris; one resident stating that she had picked up five buckets of debris (5 gallons each) following one event. Recently, 29 private wells and two additional non-community public water supply wells within 1200 feet of the Davenport Building have been sampled and analyzed (via LC/MS/MS method). The data indicate detections of perchlorate in 17 of these wells, ranging from 0.13(J) to 8.9 μg/L, at a Reporting Limit of 0.20 μg/L. To date, no other confirmed or suspected sources of perchlorate containing materials have been identified at this location.

4.2.3.2. Westport

Fireworks were reportedly launched from the Westport High School for several years during the mid 1990s. On April 30, 2004, 3 μg/L of perchlorate was detected in the combined output from two bedrock production wells servicing

the High School, and located about 600 feet northeast of the former fireworks launch area (see Figure 10). Shortly thereafter, one well was taken out of service, and the remaining well has consistently reported perchlorate in the range of 1 to 2 μg/L.

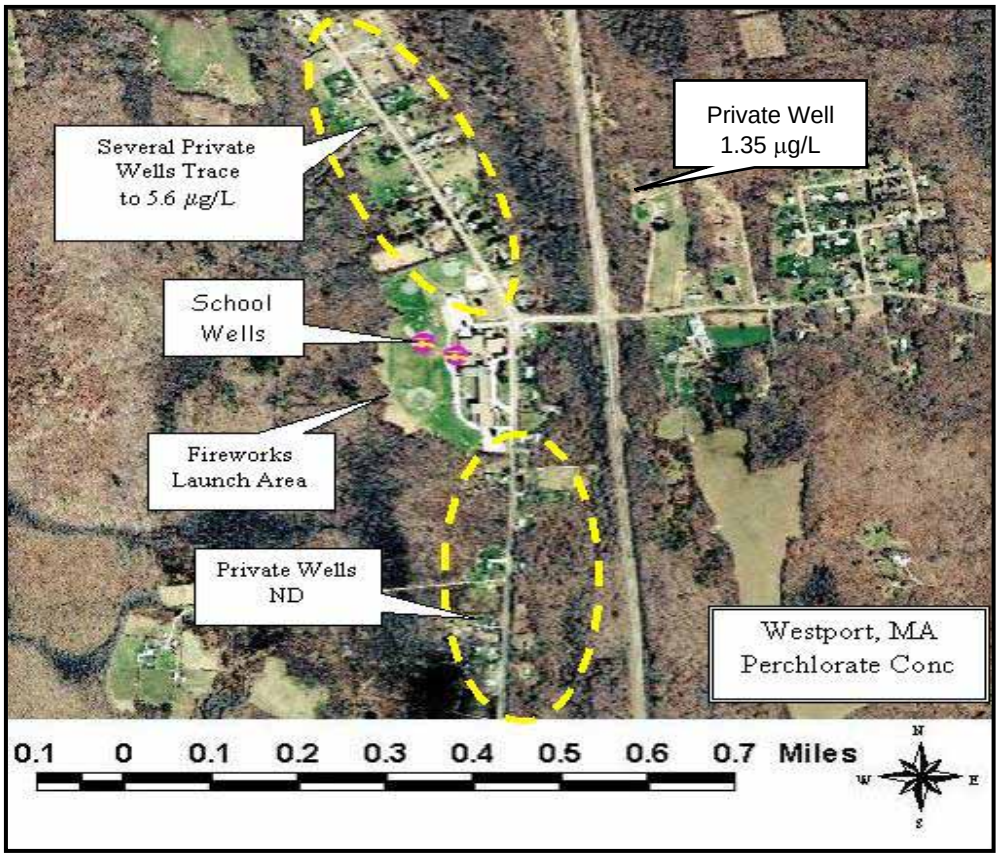


Figure 10: Westport, MA Fireworks Site

Groundwater movement in the area of the school is not known, but, based upon topography, is believed to be towards the south/southeast. Depth to groundwater is relatively shallow throughout the area (i.e., 10-15 feet below grade). The geology is expected to consist of glacial till overlying bedrock, with bedrock likely present 30 to 40 feet below grade. Importantly, the direction of wind during fireworks launching events is not known, though prevailing winds in this area are from the southwest.

This area of Westport is not serviced by a municipal water supply system, and homes surrounding the school obtain their potable water from on-property private water supply wells. In light of the detections at the school, MassDEP undertook a program to sample all wells within about a one-half mile radius of the fireworks launch area. In total, 30 private drinking water wells were sampled and analyzed via modified EPA Method 314; most homes were sampled

at least twice. Detections of perchlorates were reported in 8 of these homes, with 4 above the Reporting Limit of 1 μg/L. The maximum concentration was a value of 5.62 μg/L perchlorate in a home located about 1200 feet northeast from the fireworks launch area, and about 600 feet northeast of the impacted school wells. It is possible that other sources of perchlorate may be contributing to the low-level concentrations seen in these areas (e.g., hypochlorites).

One home with a point-of-use Reverse Osmosis filter system was sampled before and after treatment. In 3 rounds of synoptic sampling, the influent level of perchlorate fluctuated between 1.22 and 2.38 μg/L; the treated effluent was N.D. in all cases at a Reporting Limit of 1 μg/L.

4.2.3.3. Williamstown

Fireworks were launched from the Mount Greylock School in Williamstown between 1989 and 1992, and from 1999 to 2003. In April of 2004, two (bedrock) wells servicing the school were found to contain concentrations of perchlorate at 1.0 and 5.1 μg/L (see Figure 11).

Two private wells located to the east of the school and within 1000 feet of the school and fireworks were ND at a Reporting Limit of 1 μg/L. The depths of these wells are not known.

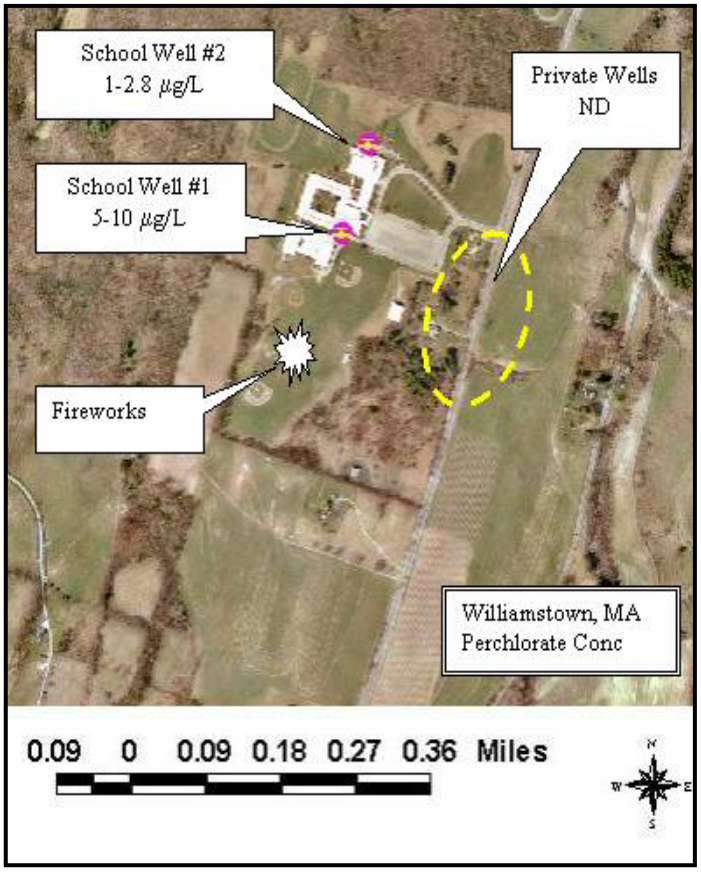


Figure 11: Williamstown, MA Fireworks Site

Bedrock is believed to be present within 10 to 15 feet of the ground surface, and the groundwater table is believed to be in the bedrock. Investigations are continuing.

4.2.4. Bourne Fireworks Display

Between 1997 and 2004, fireworks were launched during July 4th celebrations at the Upper Cape Cod Regional Technical School in Bourne. This launch area is located approximately 700 feet westerly of the Massachusetts Military Reservation, and 400 feet southwest of a groundwater contaminant plume containing explosive constituents, including perchlorate. One of 4 major perchlorate contamination areas under study at the 15,000-acre military installation, this 4500-foot, 318 acre plume contains predominantly single-digit concentrations of perchlorate, flowing in a northwest direction towards the Cape Cod Canal. The highest concentration of perchlorate in the plume is approximately 19 μg/L (see Figure 12), as opposed to higher perchlorate levels (several hundred μg/L) in other areas of the base.

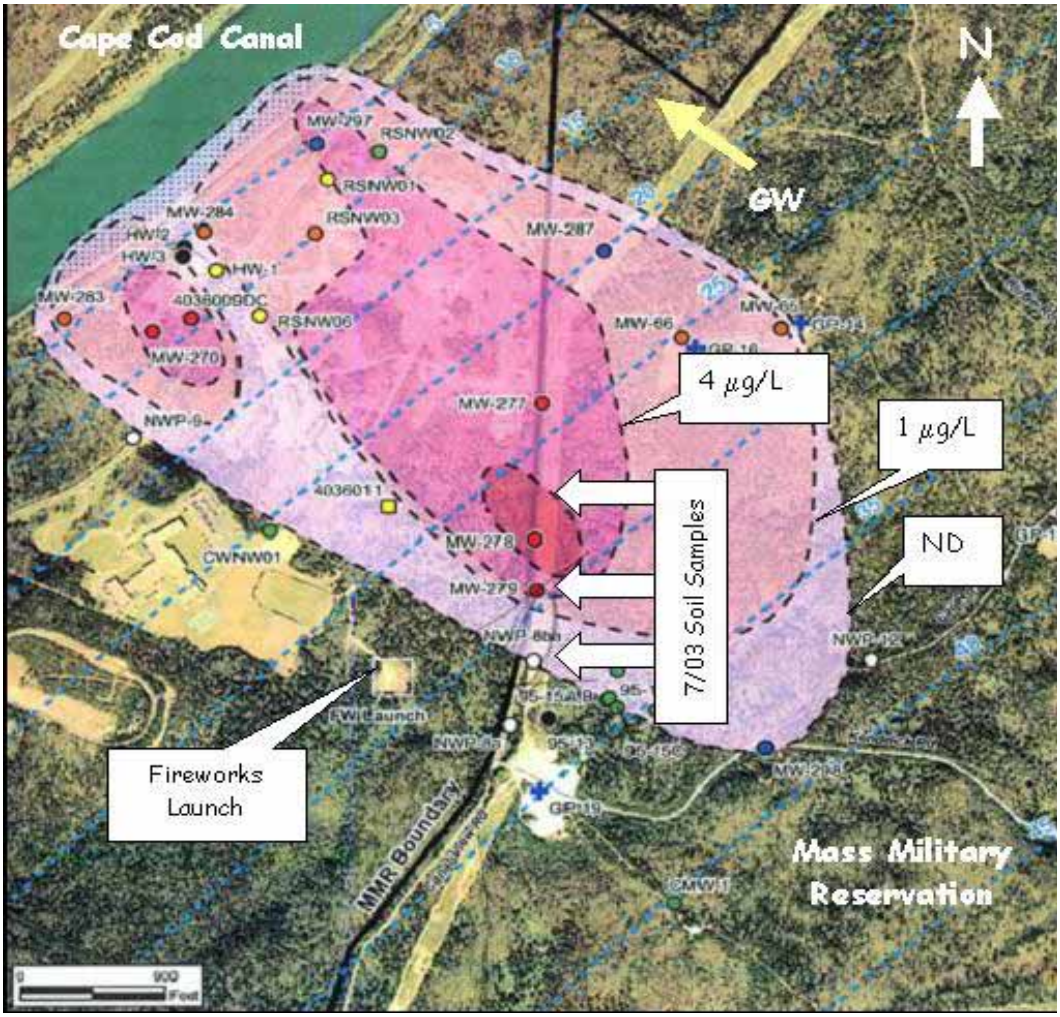


Figure 12: Bourne, MA Fireworks Site

In July 2003, a military contractor collected soil samples along the western border of the base before and after the annual July 4th fireworks display at the Technical School. At 3 locations 1000 – 2000 feet northwest and downwind from the launch site, in an area containing fireworks paper debris, post-event surficial soil samples were found to contain 1330, 1260, and 7560 μg/kg of perchlorate, compared to a pre-fireworks level of N.D. Two of these locations were re-sampled 2 months later, on 9/18/03 and 9/23/03, and were found to have gone from 1330 μg/kg to 5.3 μg/kg, and from 7560 μg/kg to 15 μg/kg perchlorate. The fireworks paper debris was also analyzed, and found to contain between 302 and 34,200 μg/kg of perchlorate. (AMEC, 2004)

It should be noted that to date MassDEP has not concluded that fireworks launched from the Technical School are the primary source of perchlorate identified in this "Northwest Plume". Contrary considerations in this regard are the known use of perchlorate-containing materials on the military base, and the presence of perchlorate 30 to 40 feet into the surficial water table in the downwind/ deposition area of concern (i.e., not clear why perchlorate ion would flow in a downward vertical direction to this depth in this presumed source area). Nevertheless, this investigation and data indicate that (a) measurable concentrations of perchlorate can be found in surficial soil thousands of feet downwind of a fireworks launch area, (b) perchlorate is not "completely combusted" in aerial display shells, and (c) debris fallout may be the most significant fireworks-to-surficial-soil mass-transfer mechanism.

4.2.5. Easthampton Fireworks Display

For a number of years, a July 4th, community-type fireworks display event has occurred at Galbraith Field in Easthampton. Located off Taft Avenue, Galbraith Field is a multi-acre athletic facility owned by the Williston Northampton School. It is underlain by an extensive system of sub-drains, presumably installed some years ago to dewater the fields by depressing the groundwater table and/or intercepting infiltrating rainwater and snowmelt. These sub-drains connect to a network of catch basins and outfalls which discharge into a wetland area adjacent to White Brook, which then flows in an easterly direction into Nashawannuck Pond.

A limited sampling effort was undertaken in November 2005, involving the collection and analysis of 8 soil samples, 2 sediment samples, and 8 water samples for perchlorate. As a result of this effort, perchlorate was not identified in any soil or sediment sample, at an analytical reporting limit of approximately 50 μg/kg. However, perchlorate was detected in 5 water samples, with the highest value of 6.62 μg/L identified in an outfall of the sub-drain system that discharges to a

wetland southeast of the field. This finding is consistent with modeling projections and data from other sites, with respect to "None Detect" concentrations of perchlorate in both soil and sediment samples, and 10 μg/L to 100 μg/L concentrations of perchlorate within the groundwater underlying the launch and fallout areas (given the expected dilution within the sub-drain system from non-impacted areas).

Of additional interest in the Easthampton study is a finding of low-levels of perchlorate (approximately 0.2 μg/L) in White Brook upstream of areas likely impacted by the Galbraith Field fireworks events. This suggests an area-wide "background" level of perchlorate due to unknown sources in higher reaches of the watershed.

4.2.6. Dartmouth Fireworks Study Area

The University of Massachusetts at Dartmouth has hosted one or more community fireworks displays in 9 of the last 10 years. In this time period, 11 events have occurred. Weather data obtained by MassDEP from 1996 to the present documents the prevailing wind direction on the date and at the time of fireworks launching to be predominantly to the north/northeast (70% of events). This is consistent with observations and statements made by campus officials.

In the Spring of 2004, MassDEP was granted permission by the University to install groundwater monitoring wells in and around the fireworks launch area, in an attempt to better understand groundwater impacts from suspected perchlorate-containing pyrotechnics. In total, 8 groundwater-monitoring wells were installed by MassDEP in June and August of 2004, including 4 small-diameter "direct push" wellpoints, and 4 additional 2-inch diameter wells installed via hollow-stem auger techniques. All wells were screened at the water table interface, which was about 5 feet below grade across the study area. Soil conditions in the area consisted of glacial till with large cobbles and small boulders. Bedrock is believed to be 20 to 30 feet below grade within the study area.

A fireworks event occurred on the campus on September 6, 2004, under calm wind conditions. According to records provided to the local fire department, the fireworks program consisted of a total of 1,750 aerial shells.

Prior to the September 6th event, surficial (0-1 inch) soil samples had been obtained and analyzed from the launch area, along with groundwater samples from the 8 monitoring wells. On the morning of September 7th, following a clear night without rainfall, soil samples were again collected from the same pre-event locations. One week after the fireworks display, following the first significant rainfall event,

groundwater samples were obtained from all 8 monitoring wells. Additional rounds of groundwater samples were obtained in October and December of 2004, and February of 2005. The location of key site features and monitoring points, along with all groundwater data, is provided in Figure 13.

As can be seen, fireworks were launched in a 500 foot by 300 foot field southwest of the campus center. Surficial soil samples obtained in this area prior to the launch (June 2004) were all N.D. for perchlorate. Surficial soil samples obtained in this area on September 7th ranged from N.D. to 560 μg/kg perchlorate.

Groundwater data for the 8 monitoring wells over all sampling rounds ranged from N.D. to a high of 62.2 μg/L of perchlorate. Concentrations have slowly declined over time in the 5 wells nearest the launch area. However, there has been no discernable "spike" in groundwater concentrations post September 6th; in fact, the high concentration of 62.2 μg/L perchlorate was recorded in August 2004 - prior to the latest display. Moreover, some of the highest levels of perchlorate are seen in wells UMD-7, 3, and 2, which are hydrologically cross and/or up gradient from the primary launching (mortar) sites.

Further analysis of site information and data suggest possible explanations for these observations:

- A likely (and perhaps most significant) pathway for perchlorate introduction to the groundwater from fireworks events is via fallout of aerial debris (e.g., pieces of un-combusted aerial shells). The predominant wind direction at this site is to the north/northeast, counter to the direction of groundwater flow. This could explain the elevated perchlorate concentration in the upgradient wells: the remnants of 10 years of fallout and surficial deposition.

- Based upon slug testing of wells UMD-5, 6, and 7, and consistent with the observed and expected geologic conditions, the hydraulic conductivity of site soils (at the water table interface) was calculated to be in the range of 10^{-3} to 10^{-4} cm/sec. Given the average hydraulic gradient across the site of 0.0167 ft/ft, groundwater velocity is expected to be in the range of 0.04 to 0.4 ft/day, or about 15 to 150 feet per year. This means that groundwater is moving relatively slowly, and would explain why the heart of the perchlorate plume has not yet moved beyond the launch area (i.e., still moving downgradient from the up-wind deposition areas).

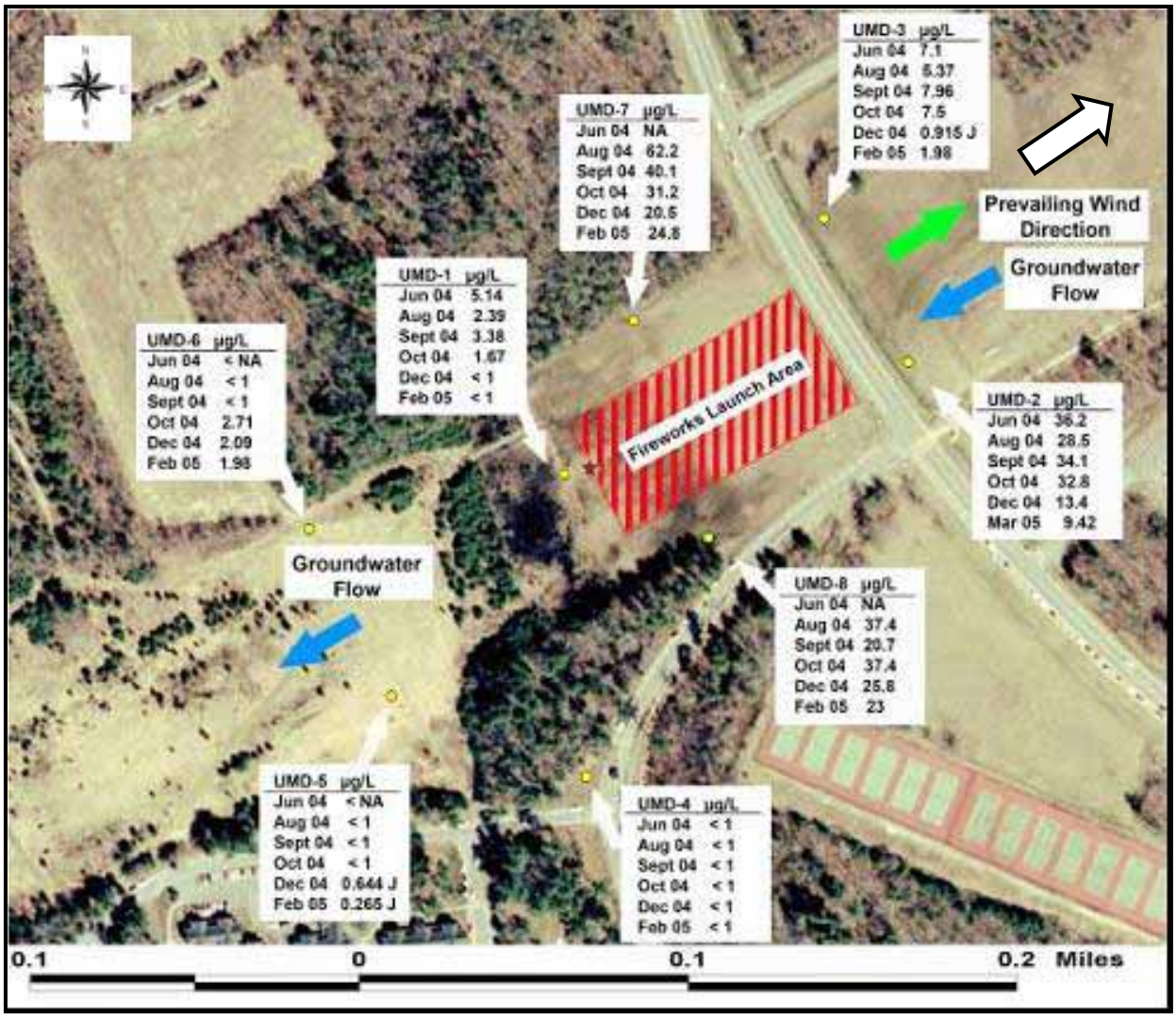


Figure 13
Fireworks Study Area, University of Massachusetts at Dartmouth

Other potential sources of perchlorate were investigated at this location, and are not likely to be a factor in this evaluation:

- While blasting activities have occurred at and proximate to the University, the nearest location is more than 2000 feet from the fireworks study area, in a likely cross-gradient groundwater direction. Moreover, available records do not indicate the use of perchlorate-containing explosive materials, or even water gels or emulsion explosive materials, which are the most likely to contain perchlorate salts.

- According to campus officials, herbicide use is limited in this area, and there is no reason to believe that chlorate-containing products have or would have been used (since these may contain perchlorate salts as impurities).
- While the use of Chilean fertilizers is always a (remote) possibility, it does not seem likely.
- Finally, the fireworks study area is located on the side of a small hill. If the groundwater table mirrors the surface topography, which is the expectation in geologic settings of this nature, the area of upgradient groundwater recharge is limited to only about 20 – 25 acres, in the predominant down-wind direction, on land containing (30 year old) university buildings and open spaces.

Additional information and data is available on the investigations at the Dartmouth campus at http://www.mass.gov/dep/brp/dws/percinfo.htm

4.3. Hypochlorite/Bleach Products

In the course of investigating the source of perchlorate contamination to the Tewksbury public water supply, data was obtained indicating the presence of perchlorate in hypochlorite disinfecting solutions. This has led MassDEP to conduct additional research in this area, to better define the scale of potential impacts from these materials.

4.3.1. Chemistry of Hypochlorite Products

The most common type of hypochlorite/bleach solution is sodium hypochlorite, NaOCl, a greenish-yellow liquid solution. A lesser-used salt is calcium hypochlorite, a white powder that is often used for swimming pool chlorination.

The primary method of manufacturing sodium hypochlorite is by reacting a dilute solution of caustic soda (NaOH) with liquid or gaseous chlorine. The end product is then processed and mixed to user specification. Typically, the concentration of sodium hypochlorite in commercial products range from about 6% (by weight) in household bleach, to up to about 16% (by weight) in products delivered and used at water and wastewater treatment facilities. (Powell, 2002)

Sodium Hypochlorite solutions are not stable, and “decomposition” is a well-known industry problem and concern. The most prominent degradation pathway results in the production of chlorate:

$$3OCl^- \longrightarrow ClO_3^- + 2Cl^-$$

In a basic solution, decomposition has been shown to be a second order process, i.e., Rate = k_2 $[OCl^-]^2$. (Gordon, 1996) Manufacturing specification typically set a limit of 1500 mg/L (ppm) of chlorate in delivered products. (Powell, 2002)

Steps can be taken in the manufacturing and post-production phases to minimize breakdown of the hypochlorite ion, by adding excess caustic soda to maintain a high (>11) pH condition. In addition, filtering is typically undertaken by manufacturers to remove transition metals (e.g., nickel, copper) that might have been present in the caustic soda feed stock. (Powell, 2002) These metals are known to catalyze a reaction that converts the NaOCl to O_2 (oxygen), lessening the (disinfecting) strength of the product, and potentially creating operational and safety problems:

$$2NaOCl \longrightarrow 2NaCl + O_2$$

Ionic strength and temperature are also key factors in controlling product breakdown during storage. Diluted product will degrade at a slower rate. Cooler storage temperatures also helps: one equipment manufacturer has indicated that for every 10°C increase in storage temperature, degradation of hypochlorite to chlorate will occur at a 3.5 times faster rate. (Powell, 2002)

Differences in manufacturing processes, quality control, and storage conditions will lead to differences in product chemistry. According to industry literature, it is clear that sodium hypochlorite solutions can become "enriched" in chlorate over time. *Moreover, based upon limited data obtained by MassDEP during this study, it appears that the chlorate may in turn break down over time into end products that include perchlorate.*

The chlorate-to-perchlorate pathway is well established. At present, the commercial production of perchlorates relies almost exclusively on the electrochemical conversion of chlorates. Other (less efficient) pathways are also known to exist, including 2 mechanisms of potential relevance to hypochlorite solutions:

- *Thermal Decomposition of Chlorates* – Through a "self-oxidation" process, chlorate salts have been shown to decompose to perchlorates (Schumacher, 1960). For example, in the case of sodium chlorate:

$$4NaClO_3 \longrightarrow 3NaClO_4 + NaCl$$

This approach is not considered commercially viable, however, because of energy and material requirements, as well as inherent difficulties in maintaining optimum production conditions, including production irregularities due to the "catalytic effect of impurities". (Schumacher, 1960) While significant production of perchlorates in this manner can only occur at high temperatures, it seems reasonable to speculate that "parts per billion" levels of perchlorate production could occur at room temperature over an extended period of time.

- *Chemical Oxidation of Chlorates* – The reaction of strong oxidizing agents with chlorates, including ozone, is known to result in the generation of perchlorates. (Schumacher, 1960). This leads to speculation over possible interactions between the (major) hypochlorite decomposition pathway that produces chlorate and the (minor) hypochlorite decomposition process that produces O_2; are intermediate by-products and/or related reactions oxidizing (a small percentage) of chlorate to perchlorate?

4.3.2. Perchlorate in Commercial Hypochlorite Products

During the agency's investigation of wastewater discharges to the Merrimack River – the source of the Tewksbury water supply – samples of sodium hypochlorite solutions were taken from the City of Lowell and Town of Billerica Wastewater Treatment plants, for analysis for perchlorate by EPA Method 314. When this data indicated positive detections, MassDEP sampled hypochlorite solutions at the Lowell and Billerica wastewater plants – together with a sample of the hypochlorite solution used at the Tewksbury water treatment plant, for analysis for perchlorate by both EPA Method 314 and an LC/MS/MS technique (EPA Method 331.0, available at http://www.epa.gov/safewater/methods/met331_0.pdf).

This data is provided in Table 5.

These data provide (a) empirical proof of the presence of perchlorates in the hypochlorite solutions; (b) evidence of potential differences in product chemistry among suppliers/manufacturers, and (c) indications of a relatively good correlation between the EPA 314 method and LC/MS/MS technique.

On the basis of the above findings, the Town of Tewksbury conducted an additional evaluation of a newly received shipment of product, as detailed in Table 6.

Table 5: Sampling of Commercial Hypochlorite solutions
October 8, 2004

Plant	Percent Hypochlorite	Manufacturer	Perchlorate Conc (µg/L)	
			EPA 314	LC/MS/MS
Lowell WWTP	NaOCl - 15 %	Univar	1500J	3400
	NaOCL - 15%	Jones Chemical	< 900	260
Billerica WWTP	NaOCl - 15%	Univar	4100J	4600
Tewksbury WTP	NaOCL - 15 %	Univar	3000J	4100

Table 6: Hypochlorite Study by Town of Tewksbury Water Treatment Plant
(Ladderbush, Zediana, 2004)

Hypochlorite Solution (Univar15% NaOCl)		Perchlorate µg/L (LC/MS/MS)
Bottom of tank before delivery		4380
New Delivery		< 0.2
Aged 26 days	Stored in Dark @5 C, capped	995
	Stored in Dark @5 C, capped	1020
	Filtered (DE), Stored in Dark @ 5 C, capped	490
	Stored in Dark @ Room Temperature, capped	6750
	Stored exposed to air & light, Room Temperature	3050

Data from the Tewksbury study are consistent with the expectations on the breakdown of NaOCl to chlorate, in that perchlorate concentrations are “enriched” with increasing storage times. Similar to chlorate, lowered temperatures significantly lessened perchlorate production. Although chlorate concentrations

were not obtained during this study, these findings do suggest a possible correlation between chlorate and perchlorate production in hypochlorite solutions.

The filtering of the newly delivered hypochlorite solution by DE (diatomaceous earth) is interesting, with respect to the substantially reduced levels of perchlorate at day 26; is something being removed that is facilitating or catalyzing a reaction? Diatomaceous earth is used to filter freshly manufactured hypochlorite solutions, to remove metal impurities that are known to catalyze reactions that convert NaOCl to O_2. (Powell, 2002) The DE used by the Town of Tewksbury in this experiment was EaglePicher Celatom® FW-14, a product used in their water filtration plant. Did this filtering operation remove transition metals, lessening decompositional generation of oxygen, which lessened the conversion of chlorates to perchlorates; and/or perhaps removed other "impurities" that were mentioned by Schumacher in his discussion of the "self oxidation" reactions involving chlorate?

4.3.3. Perchlorate in Household Bleach

Given the occurrence of perchlorate in commercial hypochlorite solutions, MassDEP conducted a limited investigation of household bleach products in December of 2004. Specifically, 4 bottles of products were obtained from local supermarkets. An attempt was (successfully) made to find an old product, to investigate the "aging" concern. All samples were promptly analyzed for perchlorate content by LC/MS/MS techniques. The data is provided in Table 7.

Table 7: Perchlorate Content of 4 Household Bleach Products

Brand	Brand Info	Perchlorate µg/L
Clorox Ultra Regular 1.5 pint size	6% NaOCl Made in USA	370/320 (blind duplicate samples)
Shaws Ultra Bleach 1.5 qt size	No NaOCl content given Made in Canada	8000
Market Basket Ultra 1.5 qt size	6% NaOCl (no info on where made)	390
Wal-Mart Ultra Bleach 3 qt size	6% NaOCl by wt Made in Canada	89

Of note is the 8000 µg/L value listed for the Shaws Ultra Bleach. According to the markings on the bottle (which were specifically sought out), this product was

manufactured 2.5 years prior to analysis; the other products appear to have been manufactured in the preceding year. Thus, this finding is consistent with data from the Tewksbury hypochlorite study, providing additional evidence of product "enrichment" with perchlorate over time.

4.3.4. Potential Impacts

Data obtained during this limited investigatory effort suggests that perchlorates are present in hypochlorite solutions used in water and wastewater treatment plants in the range of hundreds to thousands of μg/L, depending upon length and condition of product storage. Similarly, upon purchase in the supermarket, most household bleaches are likely to contain perchlorate in the low to moderate hundreds of μg/Ls - with levels rising into the thousands of μg/L with prolonged storage in the store and/or at a residence.

What are the implications of such a finding?

Drinking Water - There is a large dilution factor in the chlorination processes at water treatment plants. For example, at the Tewksbury plant, 50 gallons of (15%) sodium hypochlorite solution is used to disinfect one million gallons of drinking water, leading to a 20,000 to 1 ratio. Even at the highest perchlorate level of 6750 μg/L, the distributed water would have only 0.34 μg/L perchlorate. However, even this low concentration is now routinely detectable using an LC/MS/MS testing method. Accordingly, absent additional efforts to minimize breakdown of hypochlorite solutions, it would appear that low levels of the perchlorate ion (0.2 to 0.4 μg/L) detected in a drinking water supply disinfected with sodium hypochlorite solutions could be attributable to the chlorination process.

Drinking water impacts may be most pronounced, however, at smaller (non-community) public water supplies. In such cases, solutions of hypochlorite are often purchased in bulk, to keep costs low. Given the relatively low system flowrates and disinfectant usage, this can lead to protracted storage times between product purchase and application, which in turn can lead to increased generation of perchlorate. This phenomenon was recently observed at a small water supply at a school in Boxford, where post-disinfection concentrations of perchlorate exceeded 1 μg/L (ppb).

Of most concern is the potential presence of perchlorate in public water supply systems from the disinfection of raw water that may already have low levels of this contaminant, due to area-wide uses of blasting agents,

fireworks, and other commercial products that contain perchlorates. In such cases, the contribution of perchlorate from the use of the hypochlorite disinfectant is added to an existing "base" level in the raw water, which could result in detectable levels "at the tap" in excess of 1 μg/L (ppb)

Wastewater Plants – Similar to drinking water plants, low levels of perchlorate may be present in treated sewage effluent due to the use of hypochlorite disinfection processes. However, dilution in the receiving water body will in most cases reduce concentrations to less than detectable levels at downstream monitoring or use locations.

Household Bleach – Most household washing machines use between 40 – 45 gallons of water per large load of laundry; newer energy efficient models use between 15 and 20 gallons per large load. Even with the newer models, the dilution of 1 cup of (relatively fresh) bleach into 15 gallons of water will result in a perchlorate concentration of less than 5 μg/L. Dilution in a municipal sewer system would likely reduce these levels well below 1 μg/L. For homes with an on-site sewage disposal system, discharge to and dilution in a conventional (1000 to 2000 gallon) septic tank would likely reduce perchlorate levels to less than 1-2 μg/L. Moreover, beyond dilution effects, limited data obtained by MassDEP suggest nearly complete destruction of perchlorate in an (anaerobic) septic tank (see Section 5.2).

While this would indicate that normal household discharge of bleaches into municipal sewerage or conventional septic systems should not be an environmental issue, there are several scenarios where discharges and/or usage may be of concern, including:

- Homes where washing machine discharge is piped directly to a dry well, and is not diluted/treated via a septic tank/system;
- Laundromats with subsurface wastewater discharges; and
- Homes and businesses that use household bleach to disinfect (private) on-site drinking water wells.

4.4. Perchloric Acid

Perchloric acid has the same unique and desirable properties as perchlorate salts: a powerful oxidizing agent that is at the same time safe to use. While the extent of its use in Massachusetts is not at present known, it is clear that industrial-scale discharges of process wastewaters containing this material has the potential to create significant impacts to groundwater and surface water.

4.4.1. Chemistry of Perchloric Acid

Perchloric Acid is marketed principally as a 72% aqueous solution. At room temperature, this solution is not an oxidizing agent, and can be safely transported and stored. It is only when it is hot and concentrated does it become a powerful oxidizing agent – allowing for chemical engineering reactions and production processes that can be carefully designed and controlled. This property makes it unique among the strong acids. (GFS Chemicals, 2005)

4.4.2. Perchloric Acid Discharger in Northeastern Massachusetts

In August 2004, low levels (1 – 3 μg/L) of the perchlorate ion were first detected in the Town of Tewksbury, MA public water supply system, which draws its water from the Merrimack River, the second largest river in the state. It is noteworthy that this detection coincided with the low-flow conditions of August, in which average daily flow in the Merrimack is 3000 cubic feet per second (CFS), compared to almost 20,000 CFS in April.

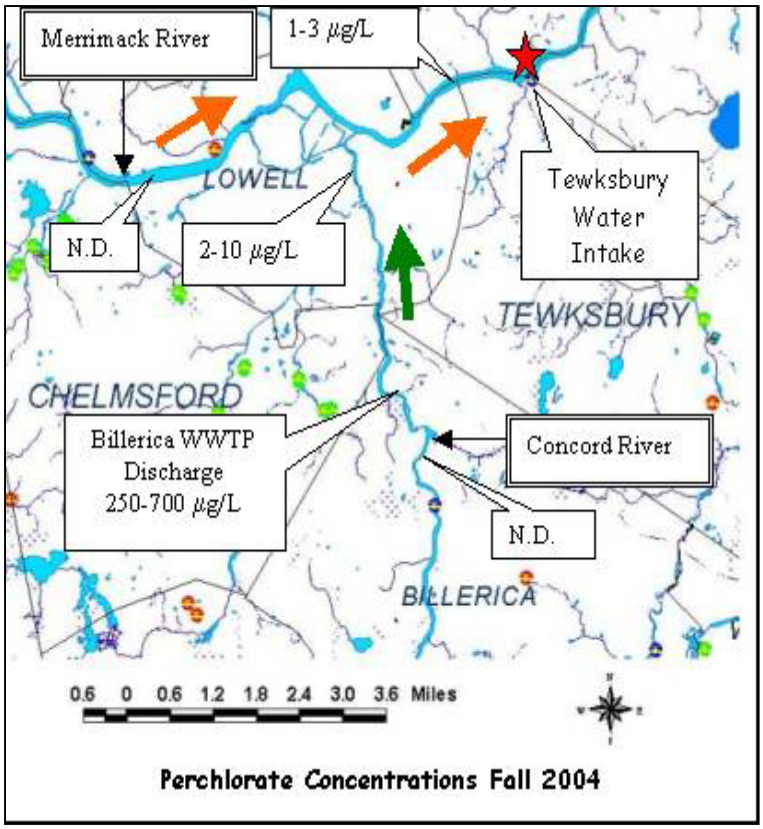


Figure 14: Perchloric Acid Discharge Concord and Merrimack Rivers, MA

This finding precipitated an effort by MassDEP to locate the source of perchlorate discharge to the river, involving a systematic and iterative sampling program tracking the contaminant upstream of the Tewksbury water intake. Eventually, the source was traced to the discharge from the Town of Billerica Wastewater Treatment Plant, which discharged into the Concord River, a tributary of the Merrimack, over 5 miles upstream of the Tewksbury intake (see Figure 14).

Monitoring of the effluent from the Billerica wastewater plant during September and October 2004 showed consistent levels of perchlorate in the range of 250 to 700 μg/L. The Billerica plant is a secondary treatment system servicing a community of 50,000, with an average daily flow of 3.1 million gallons/day (MGD), including 0.40 MGD of industrial wastewaters. At this average flowrate, approximately 6-10 pounds per day of perchlorates were being discharged from the plant. This was consistent with the 2-4 μg/L concentrations of perchlorate that were being detected in the Concord River downstream of the discharge, where river flowrates varied in the range of 250 to 600 CFS. The highest level detected was 10.3 μg/L of perchlorate on September 7, 2004, when the Concord River flowrate was at its lowest at 142 CFS.

In contrast to the data from the Concord River, mass-flux rates for perchlorate in the Merrimack River "did not add up", leading to speculation that there may have been additional sources of contamination impacting the Tewksbury water intake. Specifically, concentrations of between 1 and 3 μg/L of perchlorate in the Merrimack River at the Tewksbury intake equate to mass flowrates of 20 to 40 pounds/day of perchlorates, given the 2000 to 7000 CFS flowrate in the Merrimack during this time period. Ultimately, this discrepancy was attributed to complex flow patterns in this reach of the Merrimack River that tended to limit the mixing of inflow from the Concord River.

Investigations undertaken by the Town of Billerica eventually identified the (apparent sole) source of perchlorate discharge to the municipal sewerage system: a processor of surgical and medical materials, which was using approximately 220 gallons/month of perchloric acid. Although only a small portion of this acid was discharged (as rinsewater) to the sewer system, it equated to an average of 10 pounds/day of perchlorate. Moreover, perchloric acid use at this facility was via a "batch" operation process, which explained the variability (and spikes) in perchlorate data into and exiting the Billerica wastewater plant. It is noted that this industrial wastewater discharge was not in violation of the facility's permit, as perchloric acid and perchlorate were not (at that time) regulated contaminants in the wastestream.

Currently, this company is treating its wastewater prior to discharge into the Billerica sewerage system, utilizing ion-exchange technology that reduces influent perchlorate concentrations of 2000 mg/L to less than 0.050 mg/L in the company's effluent discharge.

5.0 ANCILLARY FINDINGS

In undertaking the investigations described in this report, MassDEP has made two ancillary findings of relevance to source and occurrence concerns.

5.1. Analytical Testing Procedures

The primary method used to date to test public water supplies for perchlorate in Massachusetts has been EPA Method 314.0, *Determination of Perchlorate in Drinking Water Using Ion Chromatography,* Revision 1.0, November 1999. In using this method, however, MassDEP has specified that laboratories achieve a Reporting Limit of 1 μg/L. This is accomplished by the use of lower concentration spiking solutions and standards, and a series of initial and ongoing quality control requirements and limits. (http://www.mass.gov/dep/brp/dws/files/perchlor.pdf)

MassDEP has conducted 2 rounds of "single blind" Proficiency Test (PT) studies to determine if laboratories are able to comply with method modifications, and achieve a 1 μg/L Reporting Limit. In total, 17 laboratories participated in one or both of these testing efforts, including 7 labs that had demonstrated an initial capability to conduct this procedure ("MassDEP approved labs"). Each study involved a blank sample, and a sample spiked at 1.04 μg/L (first study) and 1.25 μg/L (second study) of perchlorate, at conductivity levels on the high end of Massachusetts' drinking water supplies (approx 500 μS/cm @ 25°C). (http://www.mass.gov/dep/ors/files/perchpt.pdf)

In the first study, 13 of 15 laboratories – including all 7 MassDEP approved labs - successfully analyzed the spiked samples, reporting a perchlorate concentration within +/- 2 standard deviations of the study mean, with a mean recovery of 83% (i.e., biased slightly low). One of the 17 laboratories reported a "false positive" detection of perchlorate in the blank sample, but at a concentration below the 1 μg/L Reporting Limit. The results were similar in the second study, with 13 of 16 laboratories - including all 7 MassDEP approved labs - reporting acceptable results. In the second study, the mean recovery of the (1.25 μg/L) spike was 83.9%, with a standard deviation of 0.116 μg/L.

A subsequent "double blind" study was also conducted by the American Water Works Association of the 7 MassDEP approved laboratories, this time using samples with higher concentrations of dissolved salts (i.e., 1200 μS/cm) more typical of other areas of the country. Despite this challenge, 6 of the 7 MassDEP approved laboratories performed acceptably; the exception being a laboratory located in Arizona that did

little work within Massachusetts, and that reported < 0.3 μg/L perchlorate in all samples not prepared in Reagent Water.

Overall, these data and results enabled the agency to conclude that the use of the MassDEP-modified Method 314.0 is sufficient to achieve a 1 μg/L Reporting Limit on drinking water matrices common in Massachusetts, with a low probability of a false-positive detection above the Reporting Limit.

Field experiences have further supported the validity of this finding. Specifically, in reviewing over 600 analyses of drinking water samples, MassDEP is not aware of a single case of a "false positive" detection above the 1 μg/L Reporting Limit, provided all specified steps and methodological modifications are followed.[1] Split samples conducted on approximately 30 drinking water samples have demonstrated good correlation between the MassDEP-modified EPA Method 314.0 and an LC/MS/MS procedure (draft EPA Method 331.0). In a few cases, matrix interference in a drinking water sample (e.g., raw water sample from the Merrimack River) precluded quantitation by EPA 314.0; however, QC requirements in the modified method (i.e., retesting/spiking samples with detects above 0.8 μg/L) clearly revealed the condition of concern, leading to further retesting by LC/MS/MS.

Although MassDEP-modified EPA Method 314.0 has performed well for its intended application in Massachusetts (i.e., analysis of drinking water with relatively low dissolved salts), it cannot provide definitive identification and quantification of the perchlorate ion, and cannot be relied upon to quantitate levels of perchlorate less than 1 μg/L. It is for this reason that MassDEP has used an LC/MS/MS technique to verify positive results from a Method 314.0 analysis, as well as conduct testing/verification testing of wastewater, hypochlorite, and other non-drinking water matrices.

5.2. Perchlorate Treatment in Septic Tanks

In investigating sources and impacts of perchlorate contamination, MassDEP began to consider the degree of treatment that might occur in conventional septic systems. This interest was catalyzed by two specific issues and concerns:

- The fact that low-levels of perchlorate were likely being discharged into numerous residential septic systems (via use and discharge of household bleach) which could lead to pervasive low-level groundwater contamination in areas without central sewerage systems; and

[1] A suspected false positive report for an un-named reservoir in Springfield was later found by MassDEP to be a laboratory error

- The likely treatment of perchlorate-contaminated residential (private) drinking water wells by a Reverse Osmosis system, which would lead to a concentrated wastestream discharge to on-site septic systems (i.e., would this just be transferring the problem back to the groundwater?)

A number of researchers (e.g., Urbansky) have published materials on the anaerobic degradation/treatment of perchlorates. With this in mind, MassDEP had the opportunity to obtain septic tank effluent samples at two locations where the potable water source was contaminated with high concentrations of the perchlorate ion. Details and data in this regard are provided in Table 8.

Table 8: Treatment of Perchlorate in a Septic Tank

Town	Description	Date	Perchlorate Concentration by LC/MS/MS (μg/L)	
			Tap Water	Septic Tank Effluent
Boxboro	Condominiums	10/19/04	Approx 850*	0.23
Westford	Private Home	12/02/04	190	N.D. @ 0.2 μg/L RL

* 783 μg/L on 10/7; 943 μg/L on 10/22

As can be seen, the influent perchlorate ion is being almost completely degraded by the highly reducing conditions present within the septic tank environments. What is particularly noteworthy is the situation in Boxboro, where the septic tank in question was in the process of being decommissioned because of overload. Specifically, this 5000-gallon tank was receiving on average 3000 gallons/day of sewage from a block of buildings within a condominium complex – resulting in less than 48 hours of residence time.

6.0 CONCLUSIONS

On the basis of information and data obtained during the last 12 months, MassDEP has reached the following conclusions and tentative findings:

Occurrence – The perchlorate ion is not pervasive in surface waters or groundwater in Massachusetts, at a Reporting Limit of 1 μg/L (ppb). However, localized impacts exist at certain sites, creating conditions that can pose significant health risks to impacted populations.

Sources – Military products and operations have caused significant and extensive groundwater impacts in Massachusetts, creating long plumes containing hundreds of μg/L (ppb) of perchlorate. The most significant non-military sources of perchlorate contamination encountered to date in Massachusetts have been an industrial user of perchloric acid, and blasting operations that had used (or likely used) perchlorate-containing explosive materials. Lesser (though still locally problematic) sources have included fireworks displays and hypochlorite/bleach solutions.

Blasting Operations – Certain Emulsion and Water Gel Blasting Agents contain perchlorate salts, typically in the range of 5% – 15% by weight, but sometimes higher. It is theorized that misfires and/or "bad housekeeping" associated with the use of these products are the primary mechanisms that result in groundwater impacts, which can be in the hundreds or even thousands of μg/L (ppb) of perchlorate.

Fireworks – It would appear that potassium perchlorate salts have been increasingly used in pyrotechnic products in the last 10-15 years, because of their superior ability to produce vivid colors in aerial display shells. Atmospheric fallout of combustion particulates and, perhaps more importantly, un-combusted debris, result in localized groundwater impacts. These impacts range from tens of μg/L (ppb) of perchlorate locally for larger and more recent displays, to single digit concentrations in downgradient areas and/or for smaller or more historical launchings.

Hypochlorite/Bleach Solutions – Hundreds to thousands of μg/L (ppb) of perchlorate has been documented in commercial and household hypochlorite (bleach) solutions, with perchlorate concentrations increasing as a function of storage time, temperature, and ionic strength. It is theorized that perchlorate formation in these solutions is related to the formation of chlorates, a well-known hypochlorite decomposition by-product. The use of perchlorate-containing hypochlorite solutions at water treatment plants could lead to concentrations of perchlorate in the water supply distribution systems in the range of 0.2 to 0.4 μg/L.

7.0 RECOMMENDATIONS

It is recommended that regulators and industry further study and better understand the conditions and mechanisms that lead to the perchlorate releases and/or impacts discussed in this report, with the overall goal of preventing, minimizing, and/or mitigating impacts to human health and the environment.

Blasting Operations

1. Manufacturers of explosive materials should clearly indicate the percentage of perchlorate salts in their products.
2. Contractors and regulators should be mindful of the environmental sensitivity of blasting sites when using perchlorate-containing explosive materials, particularly if drinking water supply wells are located nearby. Additional guidance in this regard is available at http://www.mass.gov/dep/bwsc/files/blasting.htm.
3. Blasting contractors should make every reasonable effort to prevent misfires from occurring when using perchlorate-containing materials, and, in the event of a misfire, should ensure that all reasonable steps are taken to recover un-detonated materials.

Fireworks

1. Manufacturers and/or distributors should clearly indicate the percentage of perchlorate salts in their products.
2. Contractors, regulators, and display organizers should be mindful of the environmental sensitivity of launch areas, particularly if drinking water supply wells are nearby. All areas at and downwind of the launch area should be thoroughly surveyed following a display (and/or at first light) to identify and remove debris and fallout.

Hypochlorite/Bleach Solutions

Industry should further test and characterize hypochlorite solutions and, based on the results, consider taking necessary and practical steps to prevent the formation of perchlorates in stored materials. Based upon our limited data, improved or enhanced filtering of hypochlorite products may be beneficial to remove the impurities that may be catalyzing the production of chlorates and perchlorates.

8.0 RESEARCH NEEDS

Additional research is needed to further characterize sources, occurrences, and exposures to perchlorate. On the basis of the findings of this document, and other research efforts in this area, the following investigatory projects are suggested:

- *Swimming pools* – Investigate concentrations of perchlorate in swimming pools treated with hypochlorite products.

- *Private Drinking Water Wells* – Determine perchlorate residuals in wells that have been "shocked" and/or are systematically disinfected by hypochlorite products, with a goal toward developing Best Management Practices to minimize concerns in this regard.

- *Fireworks* – Investigate impacts of fireworks displays on ambient air, with respect to particulate fallout to soil, groundwater, and surface waters, as well as inhalation exposures to the viewing and general public.

- *Municipal Landfills* – Test leachate to determine perchlorate content, given the increasing use of perchlorate salts in common household and commercial products.

- *Roadway Flares* –Test monitoring wells and/or surface water runoff near major highways, to ascertain contribution of perchlorate to the environment from use (and discarding) of roadway flares.

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History of Revisions

Date	Section	Change
April 2006	4.2	Added new Section 4.2.5, "Easthampton Fireworks Display". New data is provided for a "community event" fireworks launch site. These data are consistent with modeled expectations and empirical data from other similar sites. Moreover, upstream samples in a receiving waterway suggest watershed "background" value of perchlorate of approximately 0.2 μg/L.
	4.3.4	New information and data provided on a small water supply system servicing a school in Boxford. Of significance is the observation that small water supplies may be most at risk for perchlorate impacts, given (a) low-level concentrations of perchlorate in (localized) sources waters, (b) the prevalent use of hypochlorite solutions as a disinfectant, (c) the low-usage rate of the hypochlorite solution (that can lead to long storage times with a concomitant build-up of perchlorate in the hypochlorite solution), and (d) infrequent cleanouts of the hypochlorite tanks.