

INTERIM REPORT

Evaluation of Alternative Causes of Widespread, Low Concentration
Perchlorate Impacts to Groundwater

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EXECUTIVE SUMMARY

The frequency of detection of wide-spread, low concentration perchlorate impacts to groundwater has been increasing as regulators nationwide require perchlorate analysis as part of regional groundwater monitoring programs, even for areas not known for military activities involving propellants. While impacts from natural sources and mechanisms may explain some cases, other cases may result from long-term, non-military-based inputs, potentially including: explosives; road flares; environmental release of electrochemically-prepared chemicals (e.g., chlorate, hypochlorite) containing perchlorate as an impurity; and fireworks. Furthermore, EPA Method 314.0 is prone to a variety of false-positive detections and interferences related to common industrial chemicals such as sulfonates, raising the question of whether these low-level detections are perchlorate at all.

The objective of this Strategic Environmental Research and Development Program (SERDP) Project ER-1429 was to identify and ultimately quantify, to the extent possible, the potential impacts of the aforementioned wide-ranging, non-military perchlorate inputs to the environment. Few publications have estimated potential perchlorate impacts to the environment from these products based on their perchlorate content, production figures and common application/release rates. As an additional objective, the project team expanded on our previous research to understand the potential impact of sulfonates on perchlorate detections in groundwater.

This project combined literature reviews, laboratory studies, and controlled field experiments to generate data to estimate potential groundwater impacts from significant non-military perchlorate sources. A detailed White Paper (Geosyntec, 2005) that examined the potential historic and continuing contributions (production figures, use practices, application/release rates) of perchlorate to the environment from non-military inputs was completed in 2005 and is available on the SERDP website (www.serdp.org). The laboratory and field experiments were completed as five tasks under this SERDP project. Task 1 consisted of experiments to quantify the potential contribution of perchlorate to the environment from the use of explosives in rock blasting and/or mining. Task 2 involved laboratory experiments and field experiments in real and simulated highway environments to quantify the potential contribution of perchlorate to the environment from common road flare use. Task 3 consisted of laboratory testing to confirm and quantify the amount of perchlorate potentially present in electrochemically-prepared products, such as sodium chlorate and sodium hypochlorite. Task 4 involved laboratory research to confirm and assess the potential impacts interfering compounds, such as common sulfonate-containing compounds, on perchlorate analysis by EPA Method 314.0. Task 5 included the investigation of perchlorate impacts to soil and groundwater arising from firework use at two separate sites.

Explosives

Explosives used for mining, construction and blasting may contain perchlorate. While the main oxidizer employed is often ammonium nitrate (AN), ammonium perchlorate and other

perchlorates (sodium, potassium) are compatible with the AN mixtures and can be employed for special applications and to take advantage of large amounts of perchlorate available at low cost from military waste (i.e., demilitarization). Furthermore sodium nitrate used in commercial explosives, often of Chilean origin, may contain perchlorate as an impurity. Material Safety Data Sheets identify perchlorate as a common component (up to 10%) of many slurry gel explosives. The United States Geological Survey (USGS) estimates that 2.7 million tons of blasting agents are used annually (Kramer, 2003). The percent of blasting agents containing perchlorate is unknown but is estimated to be less than 0.5% (IME, 2005). At least three separate sites in Massachusetts (Dracut, Westford, and Millbury) have identified impacts to surface water and groundwater that appear to be the result of rock blasting using perchlorate-containing explosives. Impacts to the environment from blasting may therefore be more significant than currently known.

The objectives of this study were to determine the perchlorate content in a slurry gel explosive before detonation and the perchlorate content in the residue after detonation at the field scale. The experiments were conducted at ARES firing range in Ohio. The slurry gel explosive contained 5.6% perchlorate initially. When this emulsion explosive was detonated, only 0.035% of the initial perchlorate and 0.019 milligrams perchlorate per gram of total charge remained.

Given that the annual consumption of blasting agents is approximately 2.5×10^9 kg annually (Kramer, 2003) and if we assume that the percent of blasting agents containing perchlorate is approximately 0.5% (IME, 2005), then the maximum mass of perchlorate-containing explosive used annually is $\sim 10^7$ kg. If we multiply this estimated mass by 5.6% perchlorate assuming the tested explosive is representative, the total amount of perchlorate in explosives used annually is approximately 10^6 kg. If we consider only blasting residue, the minimum mass of perchlorate potentially impacting the environment is estimated to be 10^2 kg/year. Perhaps more significant is the perchlorate that could be released due to misfires or poor housekeeping. Consequently, it is important for unused and misfired explosives to be properly removed from the site to prevent environmental impacts.

Flares

Road flares used in highway accident applications may contain up to 10 % by weight perchlorate. Preliminary research by Silva (2003) of the Santa Clara Valley Water District (SCVWD) showed that 3.7 g of perchlorate could be potentially leached from an unburned, damaged (i.e., run over by a motor vehicle) 20-minute road flare. This amount of perchlorate could potentially contaminate 2.2 acre-feet of drinking water above the former California groundwater action limit of 4 μ g/L. An internet search identified that large cities may procure 100,000 - 200,000 road flares annually and that U.S. sales of flares are likely in the 20 – 40 million flares/year range (Geosyntec, 2005). Given these estimates, the potential for perchlorate leaching from road flares and subsequent surface runoff from highways and roads represents a

potentially significant, and largely uninvestigated, impact to surface water and groundwater quality.

In this work, laboratory experiments to determine the amount of perchlorate in flares before and after burning were conducted using Canadian, American and Chinese flares commonly used in North America. The Canadian, American, and Chinese flares contained an average perchlorate content of 5.4%, 6.2%, and 5.8%, respectively. The amount of perchlorate present in the residue after burning the Canadian and American flares was 0.2% and 0.03%, respectively.

If we assume that approximately 30,000,000 American flares are sold annually (Geosyntec, 2005) and we make the assumption that 15-minute American flares are representative, then a total of $\sim 10^5$ kg of perchlorate is used annually during flare deployment. The minimum amount of perchlorate potentially impacting the environment can be calculated assuming the flare is completely burned or 99.97% of the perchlorate is consumed. This would result in a minimum of 100 kg of perchlorate potentially finding its way into surface water or groundwater annually. The disposal of unburned or partially burned flares would result in much higher levels of perchlorate entering the environment.

Runoff was monitored for perchlorate following a road flare deployment by local police on the Interstate 95 (I-95) corridor at the scene of an accident near a USGS gauging station in Massachusetts. Using perchlorate concentration data and hind casted total flows, the total mass of perchlorate released to receiving waters (Cambridge Reservoir) was estimated to be 1,294 mg. The maximum load of perchlorate to the receiving waters was 31.8 mg/min and the peak concentration was 89 $\mu\text{g/L}$. This study demonstrated that a road flare can act as a substantial point source of perchlorate contamination.

Controlled road flare deployment experiments were also conducted to monitor the amount of perchlorate released from various flare deployment scenarios. The five scenarios included: (1) no flare (control); (2) a completely burned flare; (3) a partially burned flare; (4) a partially burned crushed flare; and (5) an unburned crushed flare. These scenarios were selected based on those typically encountered at accident scenes. Partially burned flares are often extinguished and left at accident scenes or discarded to the side of the highway in the storm gutter. The crushed scenarios were included as flares often get damaged by passing vehicles in the highway environment.

To permit a better comparison among the scenarios, simulated rainfall of constant intensity was employed. The experiments were conducted in a 2,000 square foot parking lot at the University of New Hampshire Storm Water Center. Under these controlled conditions, perchlorate concentrations for all scenarios ranged from 0.2 $\mu\text{g/L}$ to 2450 $\mu\text{g/L}$, with maximum concentrations generally observed with the initial runoff. The total mass of perchlorate released over the duration of the experiment was as high as 2.36 g and 2.32 g from the unburned crushed flare and partially burned crushed flare scenarios, respectively. These perchlorate masses represent enough perchlorate to contaminate 1.4 acre-feet of aquifer above an action limit of 6

µg/L. Road flares should be further investigated as a potential source where perchlorate contamination of surface and ground water is identified. Likewise, removal of unused or partially used flares from the highway environment should be considered to mitigate potential contamination of surface and ground waters.

Electrochemically Produced (ECP) Chemicals

During the electrochemical manufacture of chemicals such as chlorate and sodium hypochlorite, small amounts of perchlorate can be formed as an impurity. Approximately 1.2 million tons (1.1 trillion kilograms) of sodium chlorate are consumed annually in the United States (U.S. Department of Commerce, 2003). Historic and current uses for chlorate include pulp and paper bleaching, non-selective contact herbicide application, and plant defoliation (OMRI, 2000). Approximately 94% of the sodium chlorate is used for pulp and paper bleaching while the bulk of the remaining sodium chlorate is used in agricultural products (OMRI, 2000). Therefore, the potential exists for release of perchlorate to the environment through ECP manufacture, storage, handling and use.

In this work, twelve sodium chlorate samples from different suppliers were analyzed. All samples were “reagent-grade” and certified by the suppliers as greater than 99% pure sodium chlorate. Perchlorate levels ranged from 1.7 to 117 mg/kg, with a mean concentration of 41 mg/kg. If 1.1 trillion kilograms of sodium chlorate are produced annually, this equates to the annual use of at least $\sim 10^4$ kg of perchlorate, the fate of which is not well understood.

Two sodium chlorate-based herbicides, a commercial chlorate cotton defoliant, a non-chlorate defoliant, and two home-use non-chlorate herbicides were also analyzed for perchlorate. The chlorate defoliant, Defoliant 1, contained 16 ppm perchlorate. The perchlorate concentrations for the chlorate herbicides were 8.7 ppm and 164 ppm. Surprisingly, the non-chlorate defoliant and herbicides contained 100 to 400 ppb of perchlorate. The origin of the perchlorate could not be identified from the list of chemicals contained in these products. Areas with high chlorate product use, such as California, and agricultural lands used to grow crops such as cotton and rice may have low level perchlorate contamination due to the use of these products.

Sodium hypochlorite is widely used as a household bleach and industrial disinfectant and is also routinely used to disinfect groundwater monitoring and drinking wells. It also contains low levels of perchlorate. Bleach is used in high volume, with 818 million gallons (or 3 trillion liters) consumed in 2002 according to the Innovation Group (2003).

Several brands of bleach were analyzed for perchlorate. Each of the brands was analyzed on a weekly basis for six weeks to determine the effect of storage and sunlight on the perchlorate concentration. Perchlorate concentrations ranged from 2.9 to 56 µg/L upon initial opening. The perchlorate concentrations in the samples stored in the dark increased over the six week storage period, with a mean starting concentration of 19 µg/L increasing to a mean concentration of 154

µg/L by week 6. These results confirm that storage duration and exposure to oxygen significantly influences perchlorate concentrations in bleach.

The perchlorate concentrations in the samples exposed to sunlight dramatically increased over the six week storage period, from the mean starting concentration of 19 µg/L to a mean concentration of 3,500 µg/L at week 6. These results indicate that light exposure significantly influenced perchlorate formation in bleach. Thus, attention should be paid to the way in which bleach is handled, if it is to be used for environmental applications such as well disinfection.

EPA Method 314.0 Interferences

Previous groundwater investigations have shown that the compound p-chlorobenzenesulfonate (p-CBS) co-elutes with perchlorate during analysis using EPA Method 314.0 and that low level detections of perchlorate in groundwater have been shown to be false positives related to the presence of p-CBS. Sulfonate compounds are the most widely-used surfactants in detergents and related materials. Given the widespread use and environmental occurrence of sulfonate surfactants, the potential for spurious detections of perchlorate in groundwater at the µg/L level resulting from these compounds exists.

Groundwater and surface water samples were collected in locations where sulfonate or surfactant compounds were suspected to be present to evaluate whether these interferences were detectable in environmental media. A total of 29 water samples were collected from 14 sites throughout the United States and Canada. These sites included groundwater plumes (2 sites), a landfill, a carwash, surface waters (4 sites), groundwater near septic system discharge points (5 sites) and a wastewater treatment plant effluent (and surface water downstream).

False positive perchlorate concentrations in the septic samples ranged from 9.0 to 53 µg/L using EPA Method 314.0. Samples from two of the septic sites (5 samples) had high nitrate concentrations, ranging from 110 to 200 mg/L. The interfering compounds were not positively identified in any of these cases of false positives.

Groundwater known or suspected to be impacted by p-CBS had perchlorate concentrations, which ranged from 8,100 to 94,000 µg/L using EPA Method 314.0. However, the use of a modified Method 314.0 yielded perchlorate concentrations ranging from <4.0 ug/L to 159 ug/L. p-CBS was identified by IC-MS analyses in all four of these cases of over-reporting. The p-CBS concentrations ranged from approximately 13 to 3,200 mg/L.

The likelihood of a false positive or over-reporting increased when analyzing groundwater near septic systems or impacted by p-CBS. p-CBS is a by-product of DDT manufacturing and is used in the manufacture of phenol and aniline and as a solvent in some paints (Johnson et al., 2003). Mass spectrometry methods should be used to confirm perchlorate concentrations when sampling groundwater in the vicinity of septic systems or when p-CBS use is suspected.

Fireworks

Potassium perchlorate is known to be a significant component of fireworks, and as such, the manufacturing, storage, handling, use and disposal of these products have the potential to introduce perchlorate into the environment. Large quantities of fireworks (10^8 kg) are handled and discharged annually in the U.S. The impact of fireworks on soil and groundwater contamination was evaluated at two sites: Columbia Lake, Waterloo, Ontario and the University of Massachusetts at Dartmouth (UMD), Massachusetts.

Columbia Lake Study

Soil samples collected after the fireworks display appeared to have slightly elevated concentrations of perchlorate, especially in two samples collected from the launch area. The maximum perchlorate concentration measured was 308 $\mu\text{g}/\text{kg}$. Pore water samples from lysimeters located within and adjacent to the launch area, demonstrated a slight increase in perchlorate concentration over the first week following the fireworks display, with a maximum perchlorate concentration of 42 $\mu\text{g}/\text{L}$ measured. Groundwater collected from two monitoring wells showed increasing perchlorate concentration trends following the fireworks display; a maximum perchlorate concentration of 46 $\mu\text{g}/\text{L}$ was observed. Groundwater impacts were primarily limited to areas with higher soil and pore water concentrations, and areas down-gradient. Despite limited perchlorate concentration increases in groundwater, the concentrations were 1-2 orders of magnitude higher than perchlorate concentrations measured in groundwater in agricultural areas in Southern Ontario (Ptacek, 2007) and likely represent the long-term impact of multiple annual fireworks displays at Columbia Lake.

University of Massachusetts at Dartmouth Study

A second field experiment was conducted at the UMD campus to measure the concentration of perchlorate and metals in fireworks charges; to evaluate perchlorate impacts to soil from a commercial fireworks display; to evaluate metals impacts to soil from a commercial fireworks display; and to evaluate whether the isotopic signature for firework-derived perchlorate differs from other perchlorate sources.

The unspent fireworks charges contained high concentrations of perchlorate, aluminum, magnesium, and potassium while the fireworks debris sample contained high concentrations of perchlorate, calcium, potassium and sodium. The residual concentrations of perchlorate in the fireworks debris was 31.8 mg/kg versus 5 mg/kg detected in the most contaminated soil samples, suggesting that the incomplete combustion of fireworks has the potential to be the likeliest source of soil contamination.

Soil samples collected after the fireworks display had higher concentrations of perchlorate, aluminum, antimony, barium, magnesium, potassium and strontium than the samples collected from the same area before the fireworks display. These key constituents are reflective of the

fireworks charge composition and may serve as co-contaminants for fireworks source identification at other sites.

The concentration of perchlorate in groundwater samples collected from monitoring wells before and after the fireworks display did not exhibit a noticeable change in concentration other than a decrease over time, possibly due to in situ biodegradation and/or dilution.

Isotopic analyses showed that perchlorate from fireworks is sufficiently different from perchlorate of Chilean nitrate origin, but the isotopic signature may not be sufficiently unique to differentiate firework perchlorate from other anthropogenic sources.

Large quantities of fireworks ($\sim 10^8$ kg) are handled and discharged annually in the United States (APA, 2007). Fireworks charges may have very high perchlorate contents (e.g., 372 g/kg), which can represent point sources high in perchlorate if the fireworks are not fully combusted during the display. From the two studies reported herein, soil contamination is more likely than groundwater contamination, possibly due to in situ reduction of perchlorate in groundwater. Soil contamination tends to be focused near the launch area. Firework users should be cognizant of the potential for soil and groundwater contamination when storing and launching fireworks and should ensure that uncombusted charges or debris are removed from the area immediately after the display.

Overall Conclusions

There are several anthropogenic perchlorate-containing sources that are produced in high volume. In particular, fireworks are produced in high volume and also have very high perchlorate contents. Most of the perchlorate-containing sources are combusted or consumed during proper use, which greatly reduces the amount of perchlorate available to impact the environment. However, depending on the circumstance, even these lower levels of perchlorate may be sufficient to cause elevated concentrations of perchlorate in groundwater locally, given the low action levels for perchlorate in groundwater. Improper use (i.e., incomplete combustion or misfires) or poor housekeeping can create situations where much higher levels of perchlorate can impact the environment. Thus, it is critical that unused fireworks, flares and explosives be removed from the site following use. Sources such as Chilean nitrate fertilizers, sodium chlorate-based defoliant and herbicides, although potentially lower in perchlorate than the other sources, are directly applied to crops and soil and over large areas. Therefore, these sources have the potential to contaminate soil and groundwater, especially if they are used repeatedly over a number of years. When perchlorate is detected in the absence of military activity, anthropogenic or natural non-military sources should be suspected. Past practices, geographic regions, co-constituents and isotopic markers can provide evidence to identify the source of perchlorate.

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LIST OF ABBREVIATIONS

AMPAC	American Pacific Corporation
AN	Ammonium Nitrate
AWWA	American Water Works Association
CaCO ₃	calcium carbonate
Cl ₂	Chlorine
cm	centimeter
DDD	double-distilled deionized
DDT	dichloro-diphenyl-trichloroethane
DoD	Department of Defense
DI	deionized water
ECP	electrochemically-prepared chemicals
EDQW	Environmental Data Quality Workgroup
EPA	United States Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
ft	foot/feet
ft bgs	feet below ground surface
g	gram/grams
HMX	octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocane
IC	Ion chromatography
IC-MS	Ion chromatography/Mass spectrometry
IC-MS/MS	Ion chromatography/Mass spectrometry/Mass spectrometry
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectrometer
KClO ₄	potassium perchlorate
kg	kilogram
lb	pound
L	liter
MA	Massachusetts
MADEP	Massachusetts Department of Environmental Protection
mg	milligrams
mg/min	milligrams per minute
mL	milliliters
MSDS	Material Safety Data Sheet
MQ	Millipore Simplicity [®] Personal Ultrapure Water System
mV	millivolt
NaCl	sodium chloride
NaClO ₃	sodium chlorate
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
NASA	National Aeronautics and Space Administration

NWQL	National Water Quality Laboratory
OMRI	Organic Materials Review Institute
PAN	Pesticide Action Network
mg	milligram
p-CBS	para-chlorobenzenesulfonate
ppb	parts per billion
ppm	parts per million
PRGs	Preliminary Remediation Goals
RDX	hexahydro-1,3,5-trinitro-1,3,5 triazine
SCVWD	Santa Clara Valley Water District
SERDP	Strategic Environmental Research and Development Program
STL	Severn Trent Laboratory
TNT	2,4,6-trinitrotoluene
µg/L	micrograms per liter
UMD	University of Massachusetts, Dartmouth campus
URI	University of Rhode Island
USGS	United States Geological Survey

1. INTRODUCTION

1.1 Project Overview

The frequency of detection of wide-spread, low concentration perchlorate impacts to groundwater has been increasing as regulators nationwide require perchlorate analysis as part of regional groundwater monitoring programs, even for areas not known for military activities involving propellants. While impacts from natural sources and mechanisms may explain some cases, other cases may result from long-term, non-military-based inputs, potentially including: explosives; road flares; environmental release of electrochemically-prepared products (e.g., chlorate, hypochlorite) containing perchlorate as an impurity; and fireworks. Furthermore, EPA Method 314.0 is prone to a variety of false-positive detections and interferences related to common industrial chemicals such as sulfonates, raising the question of whether these low-level detections are perchlorate at all.

The objective of SERDP Project ER-1429 was to identify and ultimately quantify, to the extent possible, the potential impacts of the aforementioned wide-ranging, non-military perchlorate inputs to the environment. Few, if any, researchers/publications have estimated potential perchlorate impacts to the environment from these products based on their perchlorate content, production figures and common application/release rates. As an additional objective, the project team expanded on our previous research to understand the potential impact of sulfonates on perchlorate detection, and the role that these compounds may play in affecting the reliability of perchlorate detections in groundwater.

This project combined literature reviews, laboratory studies, and controlled field experiments to generate data to estimate potential environmental impacts from significant non-military perchlorate sources. A detailed White Paper that examined the potential historic and continuing contributions (production figures, use practices, application/release rates) of perchlorate to the environment from non-military inputs was completed in 2005 and is available on the SERDP website (www.serdp.org) (Geosyntec, 2005). The remaining laboratory and field experiments were completed as five tasks under this SERDP project. Task 1 consisted of experiments to quantify the potential contribution of perchlorate to the environment from the use of explosives in rock blasting and/or mining. Task 2 involved laboratory experiments and field experiments in real and simulated highway environments to quantify the potential contribution of perchlorate to the environment from common road flare use. Task 3 consisted of laboratory testing to confirm and quantify the amounts of perchlorate potentially present in electrochemically-prepared products, such as sodium chlorate and sodium hypochlorite. Task 4 involved laboratory research to confirm and assess the potential impacts of interfering compounds, such as sulfonate-containing compounds, on perchlorate analysis by EPA Method 314.0. Task 5, added later through a separate proposal and contract modification, included the investigation of perchlorate impacts to soil and groundwater arising from firework use at two separate sites.

1.2 Report Organization

In the following Sections 2.0 through 6.0, the experimental results of the laboratory and field studies are discussed. Section 2 presents the results of Task 1 (Blasting Explosives); Section 3 presents the results of Task 2 (Road Flares); Section 4 discusses the results of Task 3 (ECP chemicals); Section 5 presents the results of Task 4 (Method 314 Interferences); Section 6 discusses the results of Task 5 (Fireworks); and Section 7 summarizes the potential contribution of all the investigated sources to the environment and provides information that may be used to distinguish/identify the various sources.

2. TASK 1 – PERCHLORATE CONTENT IN BLASTING EXPLOSIVES

2.1 Background

Blasting agents are non-cap sensitive, intimate mixtures of inorganic oxidizers and fuels, rather than the organic explosives (e.g., RDX, TNT, HMX) commonly used in military applications. While the main oxidizer employed is ammonium nitrate (AN), ammonium perchlorate and other perchlorates (sodium, potassium) are compatible with the AN mixtures and can be employed for special applications and to take advantage of large amounts available at low cost from military waste (i.e., demilitarization). Furthermore sodium nitrate used in commercial explosives, often of Chilean origin, may contain perchlorate as an impurity. Material Safety Data Sheets identify perchlorate as a common component (up to 10%) of many slurry gel explosives. The USGS has estimated that 2.7 M tons (2.5×10^9 kg) of blasting agents are used annually (Kramer, 2003). The percent of blasting agents containing perchlorate is unknown but is estimated that to be less than 0.5% (IME, 2005).

At least three separate sites in Massachusetts (Dracut, Westford, Millbury) have identified impacts to surface water and groundwater that appear to be the result of rock blasting using perchlorate-containing explosives. Impacts to the environment from blasting may therefore be more significant than currently known.

2.2 Objectives

The objectives of this task were to determine the perchlorate content in a blasting explosive before detonation and the perchlorate content in the residue after detonation at the field scale.

2.3 Materials and Methods

2.3.1 Preparation of the Charge

An ammonium nitrate emulsion explosive was supplied to Dr. Jimmie Oxley and her team at the University of Rhode Island. It contained 7 wt% sodium perchlorate (5.6 wt% perchlorate), 67% ammonium nitrate and 5% sodium nitrate. Charges of about 500 g were placed in polystyrene foam containers; the top of each container was covered with duct tape and wire was laced through the sides to hang the container in the center of the test chamber. A detonator was inserted in each container by puncturing a hole through its base.

2.3.2 Preparation of Test Chamber

The experiments were conducted at ARES firing range in Ohio. The test chamber was a free-standing 8 ft wide x 8 ft deep x 7 ft high, (2.44 m x 2.44 m x 2.13 m) steel-reinforced concrete lean-to with three walls. The floor, ceiling, and walls were covered with plywood panels.

Aluminum foil was stapled to the rear wall, one side wall, and the ceiling, and laid on the floor. The aluminum foil coverage was approximately 64% of the internal surface of the building. After the charge was hung in the center of the room, chain-link gates (latticed metal) were placed across the open side of the building; nevertheless, after the shots were fired, some foil escaped onto the grass outside the building, where it was collected using a rake. Additionally, the force of the blasts caused pieces of foil to become tightly wrapped around the wire of the gates; this foil was laboriously removed by hand. Percent foil recovered from each shot (93-94%) was calculated by weighing recovered foil and comparing that to the calculated amount used. Between shots, the building was swept, but not washed. The charges were shot in triplicate.

2.3.3 Recovery of Perchlorate and Analytical Methods

The recovered foil was subjected to a three-step rinse, piece by piece. Each piece of foil was unfolded, placed in 3L of doubly-distilled deionized (DDD) water, and agitated for about five seconds. After the excess water was shaken from the foil, it was placed in a second aliquot of 3L of DDD water where the washing process was repeated. This was followed by a third aliquot, after which the foil was shaken dry and set aside or discarded. A small net was used to hold and wash the smallest pieces of foil.

Once all the foil from a single shot was washed, the water from each of the three rinses was filtered using Whatman #41 filter paper and then weighed. The walls and lids of the containers were scrubbed and rinsed with DDD water to ensure that all residues were removed. The water from scrubbing and water from the three rinses were thoroughly mixed. The solutions (one for each charge) were placed in separate 125-mL Nalgene bottles and sent out for analysis via EPA Methods 314.0 (perchlorate) and 300.0 (nitrate).

2.4 Results and Discussion

Pre-blast and post-blast analyses of the charges are provided in Table 2.1. Analysis yielded the parts-per-billion perchlorate present, and this was converted into total mass of perchlorate remaining. Perchlorate remaining was reported both as percentage of original perchlorate and as milligrams (mg) remaining per gram (g) of energetic material (i.e., explosive). The total perchlorate and nitrate were determined by extrapolation from the actual percentage of the surface covered with foil (64%) and actual or estimated percentage of foil recovered (93% - 94%) to 100% coverage of the interior surface area of the detonation chamber and 100% foil recovery. The original explosive contained 5.6% perchlorate. When this emulsion explosive was detonated, only 0.035% of the initial perchlorate and 0.019 milligrams perchlorate per gram of total charge remained. Most of the nitrate was also consumed with only 0.043% of the original nitrate remaining. It is acknowledged that the experimental techniques used may allow trace amounts of perchlorate to escape detection. Therefore, the numbers reported represent the minimum amounts of perchlorate released.

Given that the annual consumption of blasting agents is approximately 2.5×10^9 kg annually (Kramer, 2003) and if we assume that the percent of blasting agents containing perchlorate is less than 0.5% (IME, 2005), then the maximum mass of perchlorate-containing explosive used annually is approximately 10^7 kg. If we multiply this estimated mass by 5.6% perchlorate assuming the tested explosive is representative, the total amount of perchlorate in explosives used annually is approximately 10^6 kg. If we consider only blasting residue, the minimum mass of perchlorate potentially impacting the environment is estimated to be 2×10^2 kg/year, which is quite small on a national basis but could be important on a site-specific basis with respect to groundwater or surface water impacts above action levels. Perhaps more significant is the mass of perchlorate that could be released due to misfires or poor housekeeping. Consequently, it is important for unused or misfired explosives to be properly removed from the site to prevent environmental impacts.

2.5 Conclusions

Blasting agents are used in high volumes annually in the United States. Although only a small fraction is estimated to contain perchlorate, they represent a point source high in perchlorate. If the oxidation of the perchlorate is “complete” when the explosive is detonated, then little perchlorate should be left behind. To mitigate soil and groundwater contamination, misfired blasting agents should be removed from the site, and spills should be cleaned up immediately.

3. TASK 2 - PERCHLORATE IN ROAD FLARES

3.1 Background

Preliminary research by Silva (2003) of the Santa Clara Valley Water District (SCVWD) indicates that 3.7 g of perchlorate can potentially leach from an unburned, damaged (i.e., run over by a motor vehicle) 20-minute road flare. This amount of perchlorate can potentially contaminate 2.2 acre-feet of drinking water above the former California action limit of 4 µg/L. More than 40 metric tons of flares were reported to be used/burned in 2002 in Santa Clara County, California alone (Silva, 2003). An internet search identified that large cities may procure 100,000 -200,000 road flares annually and that U.S. sales of flares are likely in the 20 – 40 million flares/year range (Geosyntec, 2005). Given these estimates, the potential for perchlorate leaching from road flares and subsequent surface runoff from highways and roads represents a potentially significant, and largely uninvestigated, impact to surface water and groundwater quality.

In the following sections, laboratory and field experiments to determine the amount of perchlorate in flares before and after burning are discussed. The composition and uniformity of unburned flares is presented in Section 3.2, perchlorate content in burned flare residue is discussed in Section 3.3; results of highway runoff monitoring are presented in Section 3.4; results from a sampling event where road flares were deployed by Massachusetts State Police in the vicinity of a United States Geological Survey (USGS) sampling station are discussed in Section 3.5; and the results of a controlled field flare deployment are summarized in Section 3.6.

3.2 Composition and Uniformity of Unburned Flares

3.2.1 Objective

Experiments were conducted to determine the amount of perchlorate in road flares produced by several different manufacturers to assess the potential range of perchlorate content in flares available for purchase within North America. For this testing, flares produced in Canada, the United States and China were procured. For each flare type, tests were performed to determine perchlorate concentrations in different sections along the length of the flare (to assess in-flare variability), among (3) flares in the same lot (to assess between flare variability), and between different years of manufacture of the same flare type (2003 vs. 2005) for one of the flare types. These data provide some understanding of the perchlorate and nitrate content and uniformity in road flares, composition changes between flares, and the consistency of the flare production process over different years.

3.2.2 Methodology

Given the issues related to shipping of flares between Canada and the United States, analysis of the flares produced in Canada was conducted by Geosyntec/SiREM, whereas analysis of the American and Chinese flares was conducted under the direction of Dr. Jimmie Oxley at the University of Rhode Island (URI). The flares from both North American manufacturers were 15-minute red emergency flares. The flares manufactured in China had a variety of burn times: 5, 10, 15, 20 and 30 minutes (Figure 3.1).

Similar preparation methods were employed by both laboratories, although the analytical techniques differed due to differences in analytical instrumentation at the two laboratories. The sample preparation and analysis procedures employed by the two laboratories are summarized below.

For the flares produced in Canada, the following protocol was employed to extract and analyze perchlorate from road flares:

1. The mass of the flare was determined, and the ignition tip of the flare was removed.
2. The remainder of the flare was cut into three equal pieces, and the casing was removed.
3. Four grams of flare powder were measured from each section of the flare and dissolved in separate 500 mL volumetric flasks using water purified through a Millipore Simplicity[®] Personal Ultrapure Water System (MQ).
4. Each sample was stirred with a Teflon[®]-coated magnetic stir bar at 1200 rpm for ten minutes while heating to an approximate temperature of 70-80°C.
5. The sample was filtered using a 0.45 µm syringe filter, and the perchlorate and nitrate concentrations in each sample (mg/kg flare powder) were determined using ion chromatography (IC) following a modified USEPA Method 314.0.
6. To ensure that all of the perchlorate had been removed from the flare powder, another set of four gram samples was taken from the ignition tips of each flare.
7. These samples were extracted following steps 3-5. However, rather than discarding the material remaining on the filter, the filter and this material were once again stirred in water following steps 3-5 to remove any remaining traces of perchlorate, and the perchlorate contained in the water was quantified.
8. A separate analysis was conducted on the black ignition 'button' and wick. After all of the flare powder surrounding the ignition powder and wick had been removed, the ignition button, wick and small portion of remaining cardboard casing were weighed.

9. The button, casing and wick were then soaked in 200 mL MQ purified water for two days.
10. Following soaking, the wick and button were crushed while submerged in the 200 mL water sample and stirred at 600 rpm to a temperature of 70-80°C for a period of ten minutes.
11. The samples were then analyzed to determine the total perchlorate concentrations.

For the American and Chinese flares, the following protocol was employed to extract and analyze perchlorate from road flares:

1. The overall flare weight and length were measured.
2. A radial cut was made at two points, dividing the flare into three equal lengths. Each section was sliced longitudinally, and the core of filler was removed and placed onto a fresh piece of printer paper. The paper was folded in half, and the filler was crushed manually. A portion (20 g of the section) was poured into a sampling vial and sealed until use.
3. From the 20 g, a 4.00 g portion of flare filler was weighed into a flask. About 400 mL of doubly de-ionized water was added, and the solution was warmed in a water bath (70-80°C) and stirred about 10 minutes.
4. After stirring and heating, the solution was cooled to room temperature and diluted to exactly 500 mL. Aliquots were removed, filtered through a syringe filter, and placed in 2 mL, amber, wide-mouth, screw-cap, auto-sampler vials.
5. Samples of 10 µL were injected (via an auto-sampler) into a Hewlett Packard 1100 liquid chromatograph equipped with a Vydac 302IC4.6 anion column (250mm x 4.6mm) and a photodiode array detector using wavelengths of 280 nm and 360 nm.
6. De-ionized water blanks were analyzed periodically to check for contamination. The chromatographs of all the blanks were found to contain no anion peaks.

3.2.3 Results and Discussion

(i) Perchlorate Content in Canadian Flares

The perchlorate content in the flares produced in Canada averaged approximately 52,490 mg/kg of flare powder, based on an overall average of the 2003 and 2005 flares (Table 3.1), while the nitrate content was significantly higher at an average of 101,283 mg/kg of flare powder (data not shown). As indicated in Table 3.1, the black substance comprising the ignition button and the wick contained more than twice the concentration of perchlorate (i.e., 111,971 mg/kg) than the powder filling the remainder of the flare. The average mass of an unburned flare was ~178 g, while the average mass of perchlorate in an unburned flare was 9.734 g. Based on these results, the flare powder was calculated to be approximately 5.4% perchlorate.

The effectiveness of the laboratory protocol was measured through a second extraction of perchlorate from the insoluble fraction of the flare powder. The second extraction of flare powder filtrate showed very low levels of perchlorate – approximately 2% of the first extraction levels still remained in the particulate matter following filtration. This indicated that the laboratory protocol was reasonably successful in extracting perchlorate from the flare powder.

A series of flare tests were previously performed by the Santa Clara Valley Water District in California to measure the leachability of perchlorate from highway/emergency safety flares in water (Silva, 2003). Based on Silva's solids analysis, the composition of the flare was 6.6% (calculated) potassium perchlorate [KClO₄] by dry weight, or approximately 50,000 mg/kg measured perchlorate. The flares analyzed by Geosyntec contained a similar (calculated) percent perchlorate of approximately 5.4 wt%.

(ii) Uniformity of Perchlorate Content in Canadian Flares

The perchlorate concentration remained relatively constant over the length of the flare as shown in Figure 3.2 for six different flares in two separate lots. Error bars represent the 95% confidence interval. There were no significant differences in perchlorate content between flares in the same package (Figure 3.2), indicating flare production was consistent. There was also minimal variation in perchlorate between road flares manufactured in different years (Figure 3.2). The 2005 flares did, however, contain slightly higher levels of both nitrate-N and perchlorate when compared to the 2003 flares (106,298 ± 5,837 vs. 96,493 ± 4,058 mg nitrate-N/kg flare powder, and 57,939 ± 5,732 vs. 49,723 ± 1,787 mg perchlorate/kg flare powder, respectively) as shown in Figure 3.3.

(iii) Perchlorate Content in American and Chinese Flares

There is also little variation among replicate American or Chinese flares (Table 3.3). The American flares contained an average perchlorate content of 6.2%, while the Chinese flares had a lower perchlorate content of 5.8%. By comparison, the Canadian flares contained less perchlorate (5.4%) than either the American or Chinese flares.

3.3 Perchlorate Content in Burned Flare Residue

3.3.1 Objective

The objective of these experiments was to determine the amount of perchlorate remaining in the residue (ash) of flares when a complete burn had been attempted. These data allow us to predict the minimum amount of perchlorate that could leach from deployed road flares in a highway environment.

3.3.2 Methodology

Canadian Flares

The burn test for the flares produced in Canada was conducted by Geosyntec/SiREM. The following protocol was used to burn the flares, and to extract and analyze perchlorate in the residue:

1. The initial mass of the flare was determined.
2. The flare was placed into a retort stand with the flare suspended horizontally about 6 inches from the bottom of the stand.
3. The flare was lit while suspended in the retort stand, and the ashes were collected on a Teflon[®] baking sheet as they fell from the lit flare. Much of the residue was a hard whitish solid.
4. The ashes were scraped from the baking sheet using a wooden spatula and weighed.
5. Each sample was added to 500mL of MQ-purified water in a beaker inside a fume hood.
6. The sample was then stirred with a Teflon[®]-coated magnetic stir bar at 1200 rpm for ten minutes while heating to an approximate temperature of 70-80°C.
7. The sample was cooled inside the fume hood and allowed to soak for a 24-hour period.
8. After a brief manual stirring, the sample was filtered using a 0.45 µm syringe filter, and the perchlorate and nitrate concentrations in each sample were determined using modified EPA Method 314.0.

America and Chinese Flares

The burn tests for American and Chinese flares were conducted under the direction of Dr. Jimmie Oxley at the University of Rhode Island (URI). The following protocol was used:

1. The initial mass of the flares was determined.
2. The flares were positioned horizontally in a clean aluminum pan, which was placed on top of and surrounded by fresh sheets of aluminum foil.
3. The flares were ignited using their strikers and allowed to burn undisturbed until they self-extinguished.
4. After burning ceased, the residue and remaining slag were collected.
5. The slag was weighed in order to approximate the extent to which the flare had burned.

6. In order to collect the remaining residue, both the pan and the aluminum sheets were washed thoroughly with triple distilled, deionized water.
7. The washings and slag from each flare were placed in separate round-bottom flasks and stirred for ten minutes at 70-80°C before being allowed to cool to room temperature.
8. In order to permit the insoluble, non-perchlorate residue to settle, the flasks were placed in a refrigerator, where they sat overnight at a temperature of 4°C.
9. An aliquot was subsequently taken, filtered through a syringe, and placed in a vial to be analyzed.
10. Perchlorate analyses were performed on a Hewlett-Packard 1100 liquid chromatography equipped with a photodiode array detector, with signal and reference wavelengths set as 280nm and 360nm, respectively. Separations were performed on a 250mm x 4.6mm Vydac 3021C4.6 anion column; the eluent was a 4mM solution of isophthalic acid buffered to an approximate pH of 4.9 using sodium tetraborate. A flow rate of 2 mL/min and injection volumes of both 10 µL and 100 µL were employed. Since the isophthalic acid buffer absorbed at 280 nm and the perchlorate anion did not, analytic peaks were negative. Standard curves were prepared using a standard containing both perchlorate (100-1000 mg/L for unburned flares and 5-100 mg/L for burnt residue) and nitrate (1000-10000 mg/L). Residue from burned American flares was sent to an outside laboratory for analysis using EPA Method 314.0.

3.3.3 Results and Discussion

The average amount of perchlorate in the Canadian flare residue was 16 mg perchlorate per flare, or approximately 0.2% of the unburned flare (Table 3.2). These results show there is a greater than 99.8% reduction in the perchlorate content following complete burning of the flare.

More perchlorate remained in the Chinese flare residue than the American flare residue after burning. Using the average starting perchlorate contents, the % perchlorate removed during combustion was calculated. At worst 1.5% of the original perchlorate remained. In other words, greater than 98.5% of the perchlorate was consumed during combustion. For the American flares, the perchlorate remaining was 0.027% on average or 99.97% of the original perchlorate was consumed (Table 3.3). Nevertheless, a slag containing elevated perchlorate concentrations remained in all cases.

If we assume that approximately 30,000,000 American flares are sold annually (Geosyntec, 2005) and we make the assumption that 15-minute American flares are representative, then a total of 3.3×10^5 kg of perchlorate is used annually during flare use. The minimum amount of perchlorate impacting the environment can be calculated assuming the flare is completely burned

or 99.97% of the perchlorate is consumed. This would result in a minimum of 100 kg of perchlorate potentially finding its way into the environment annually. The disposal of unburned or partially burned flares would result in much higher levels of perchlorate entering the environment.

3.4 Background Highway Runoff Monitoring for Perchlorate

3.4.1 Objective

The objective of the highway runoff monitoring program was to assess background levels of perchlorate and strontium for comparison to environmental impacts of discarded flares in a simulated highway environment.

3.4.2 Methodology

For this study, Geosyntec partnered with the USGS to gain access to their highly instrumented highway monitoring stations at 12 locations along Massachusetts highways. Table 3.4 lists the information for each highway monitoring site in this study.

Figure 3.4 shows a typical monitoring station, and one of the primary monitoring stations, where runoff is piped to a manhole where the water temperature, conductance, water level, and water velocity sensors are mounted. At each site, both perchlorate and strontium were analyzed in the flow-weighted composite samples that were collected during wet weather runoff events. Laboratory analysis of perchlorate was conducted by Severn Trent Laboratories (STL) using Method IC-MS/MS under contract with the National Water Quality Laboratory (NWQL) and laboratory analysis of strontium was conducted by the USGS NWQL using Method ICP-AES.

3.4.3 Results and Discussion

For the eight storms monitored, perchlorate concentrations ranged from 0.006 to 0.26 $\mu\text{g/L}$ (Figure 3.5), while strontium levels ranged from 2.2 to 2,140 $\mu\text{g/L}$ (Figure 3.6). Strontium was elevated in the winter and early spring months, possibly due to road salt application. The highest perchlorate concentration (0.26 $\mu\text{g/L}$) was found in a water sample collected at the highway monitoring station along Interstate I-95 on 3/13/06 in Lexington, MA. The highest strontium concentration (2,140 $\mu\text{g/L}$) was found in the same location for the same storm. Both of these values are significantly higher than nearly all other water samples collected. Because background levels of perchlorate are very low (and in most cases typical of perchlorate levels found in rainwater (Dasgupta *et al.*, 2005)), these data were deemed representative of “control” conditions relative to experiments with deployed flares.

3.5 Monitoring of a Flare Deployment in the Highway Environment

3.5.1 Objective

The objective of this study was to determine the potential perchlorate loading based on an actual flare deployment by Massachusetts State Police in the vicinity of a USGS sampling station.

3.5.2 Methodology

On June 7, 2006, a road flare was used by local police on the Interstate 95 (I-95) corridor at the scene of an accident near a USGS gauging station (Figure 3.7). The USGS took samples for perchlorate analysis at the Hobbs Creek outfall, and flow measurements were taken at the I-95 USGS gauging station (Figure 3.7). Laboratory analysis of perchlorate was conducted by Severn Trent Laboratories (STL) using Method IC-MS/MS under contract of the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL).

At the time of the sampling event, the USGS was unaware of flows contributing to Hobbs Creek outfall from an additional pipe downstream of the USGS gauging station (where flow measurements were collected), which also contributes runoff to Hobbs Creek (Figure 3.7). Therefore, to accurately determine the total event mean flow, the total flow discharging to Hobbs Creek needed to be hind casted based on the flow from the I-95 USGS gauging station for the event sampling period and data collected from new instrumentation installed at the Hobbs Creek outlet. Additional flow measurements were conducted at both gauging stations between August 20, 2006 and September 6, 2006. A regression equation was developed to predict the relationship between the total flow at Hobbs Creek during the rainfall event on June 7, 2006 and flows measured between August 20, 2006 and September 6, 2006. The development of this regression equation can be found in Appendix A.

3.5.3 Results and Discussion

The predicted total event flow hydrograph and time points where samples for perchlorate analysis were taken are shown in Figure 3.8. Figure 3.9 shows the perchlorate concentrations in the Hobbs Creek outfall between 9:36 am and 9:36 pm on June 7, 2006 and the total predicted Hobbs Creek flow rate. The maximum perchlorate concentration was 0.089 mg/L. Figure 3.10 shows the perchlorate load in mg/min and the total predicted Hobbs Creek discharge rates with the maximum load being 31.8 mg/minute. Using Figure 3.10, the total perchlorate mass entering receiving waters from the June 7 sampling event was estimated to be 1,294 mg.

To determine the load at the inlet to the I-95 pipe, the perchlorate load in the Hobb's Creek outfall was divided by the flow recorded at the I-95 USGS gauging station (Figure 3.11) to generate an estimate of the concentration of perchlorate in the I-95 pipe at various time points. This calculation assumes that there was no perchlorate entering in the other pipe from I-95. The

maximum concentration of perchlorate in runoff leaving the highway was estimated to be 314 µg/L (Table 3.5).

3.5.4 Conclusions

Using perchlorate concentration data and hind casted total flows, the total mass of perchlorate released to receiving waters (Cambridge Reservoir) on June 7, 2006 was estimated to be 1,294 mg. The maximum load of perchlorate to the receiving waters was 31.8 mg/min and the peak concentration was 89 µg/L. The maximum concentration leaving the highway was estimated to be 314 µg/L. This study demonstrates that a road flare can act as a point source of perchlorate contamination to surface receiving waters.

3.6 Controlled Flare Deployments

3.6.1 Objective and Rationale

The objective of the controlled road flare deployment experiments was to monitor the amount of perchlorate released from various flare deployment scenarios. The five scenarios included: (1) no flare (control); (2) a completely burned flare; (3) a partially burned flare; (4) a partially burned crushed flare; and (5) an unburned crushed flare. These scenarios were selected based on those typically encountered at accident scenes. Partially burned flares are usually extinguished and left at accident scenes or discarded to the side of the highway in the storm gutter. The crushed flare scenarios were included as flares often get damaged by passing vehicles in the highway environment. To permit a better comparison among the scenarios, a controlled setting using simulated rainfall of constant intensity was employed.

3.6.2 Methodology

The controlled road flare experiments were conducted in a 2,000 square foot parking lot at the University of New Hampshire Storm Water Center. In the parking lot, overland flow runoff was simulated via a header distribution system that consisted of a clean water source tank, a pump, and a distribution manifold with sprayer heads. The use of simulated overland flow eliminated variations in runoff contamination that might otherwise be attributable to natural variations in rainfall event characteristics (intensity, volume, duration, etc.). In this study, American safety flares, with a burn time of approximately 20 minutes were used because their perchlorate content had been evaluated in the laboratory previously (see Section 3.2). The flares were deployed along the gutter line, where leaching was expected to be greatest. Runoff from the parking lot drained to a catch basin and subsequently to an automated 6712SR ISCO sampler. A bubbler module was used to record depth at the primary device and measure flow. The ISCO sampler recorded both flow data and water quality sample information and was configured with 24-300 milliliter (mL) sample bottles. Runoff from all events was collected and treated. Between each

flare deployment, the area was decontaminated by flushing the area with clean water for approximately 10 minutes.

The following sections describe each of the scenarios in more detail:

Scenario #1: No Flare (control)

In the control scenario, runoff was simulated on the parking lot for approximately 60 minutes with no road flare present. During this time, the simulated runoff drained via overland flow along the gutter line and was used to determine background levels of perchlorate in the parking lot system. A 3.33 milliliter (mL) sample was collected every 3 minutes and composited into 10 mL sample bottles.

Scenario #2: Completely Burned Flare

A flare was completely burned at a location along the gutter line. Then, overland flow runoff was simulated for approximately 146 minutes. During this time, 10 mL flow-weighted samples were collected every 2 minutes, and three samples were composited into 30 mL bottles.

Scenario #3: Partially Burned Flare

For this scenario, roughly half the flare was burned, and the extinguished flare was left in the deployment area along the gutter line. Overland flow runoff was simulated for 146 minutes. During this time, 10 mL flow-weighted samples were collected every 2 minutes, and three samples were composited into 30 mL bottles.

Scenario #4: Partially Burned Crushed Flare

For this scenario, roughly half the flare was burned and then extinguished. The partially burned flare was then crushed by driving a vehicle over the flare at approximately 20 miles per hour (mph). Normal highway speeds could not be duplicated because of the small deployment area due to safety restrictions. With the crushed flare in the deployment area along the gutter line, overland flow runoff was simulated for approximately 190 minutes. During this time, 7.50 mL flow-weighted composite samples were collected every 2 minutes at the catch basin. Four samples were composited into 30 mL bottles.

Scenario #5: Unburned Crushed Flare

In this scenario, an unburned flare was crushed along the gutter line by a car traveling at approximately 20 mph. The crushed flare was left in the deployment area along the gutter line where overland flow runoff was simulated for approximately 190 minutes. During this time, 7.50 mL flow-weighted composite samples were collected every 2 minutes at the catch basin.

3.6.3 Analytical Methods

Runoff samples were filtered and submitted for perchlorate analysis by EPA Method 314.0.

3.6.4 Results and Discussion

Perchlorate concentrations in the runoff samples for each scenario (except the no flare control) are plotted in Figure 3.12. Both the unburned crushed and the partially burned crushed flare generated high perchlorate concentrations in the runoff at early times, because the flare powder was exposed to the runoff. For example, for the partially burned crushed flare, the initial perchlorate concentration was approximately 2450 ug/L, nearly 100 times the EPA's drinking water equivalent level of 24.5 ug/L. The completely burned flare yielded the lowest perchlorate concentrations in the runoff (~0.2 ug/L) as expected, with the partially burned flare yielding concentrations of about 25-40 ug/L in the runoff. Perchlorate in the runoff for the no flare control was less than 0.3 µg/L (data not shown).

The average perchlorate load and flow rate for each of the scenarios versus time is plotted in Figures 3.13 through 3.16. The trends in these figures mirror those in Figure 3.12 because the flow rate was constant for each of the scenarios. Maximum loads ranged from 137 mg/min for the partially burned crushed flare to 0.09 mg/min for the completely burned flare. After the initial spike of perchlorate, loads ranged from ~ 5 mg/min for the partially burned crushed flare and the partially burned flare scenarios to 0.015 mg/min for the completely burned flare scenario. The runoff flow rate was maintained between 60 - 70 L/min (16 -19 gpm) throughout the experiments.

Figure 3.17 shows that the unburned crushed flare leached the largest amount of total perchlorate over the length of the experiment (2358 mg), as expected, while the partially burned crushed flare released almost as much perchlorate (2321 mg). The other two scenarios, partially burned and completely burned, yielded much less perchlorate – 509 mg and 3 mg, respectively. Clearly, the degree of burning and flare damage influenced the amount of perchlorate released. It should be noted that these tests were of a short-term nature (~2 -3 hours) and longer tests would have resulted in the cumulative release of more perchlorate. Likewise, these experiments involved the deployment of only one flare. Three to ten flares may be deployed at an actual accident scene, increasing the potential mass of perchlorate released 3- to 10-fold.

3.6.5 Conclusions and Environmental Implications

Under controlled conditions at the UNH facility, perchlorate concentrations for all scenarios ranged from 0.2 µg/L to 2450 µg/L, with maximum concentrations generally observed with the initial runoff. The total mass of perchlorate released over the duration of the experiment was as high as 2.36 g and 2.32 g from the unburned crushed flare and partially burned crushed flare scenarios, respectively. These perchlorate masses from a single flare were approximately double

that observed in the uncontrolled release discussed in Section 3.5 and represent enough perchlorate to contaminate 1.4 acre- feet of aquifer above an action limit of 6 µg/L.

Based on observations of actual accident scenes visited by the authors, small numbers of road flares are frequently extinguished by emergency personnel and discarded in partially burned or unburned states into roadside ditches, in rights of way, or on highway shoulders. At major accident scenes, large numbers of flares are frequently deployed. The findings of the studies discussed here indicate that road flares are likely to introduce perchlorate into the environment and should be further investigated as a potential source where perchlorate contamination of surface and ground water is identified. Likewise, removal of unused or partially used flares from the highway environment should be considered to mitigate potential contamination of surface and ground waters.

4. TASK 3 – PERCHLORATE IMPACTS FROM ELECTROCHEMICALLY PRODUCED (ECP) CHEMICALS

4.1 Background

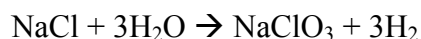
During the electrochemical manufacture of chemicals such as chlorate from chloride brine feedstocks, small amounts of perchlorate (e.g., 500 mg sodium perchlorate per kg sodium chlorate) can be formed as an impurity (Wanngard, 1991; Betts and Dluzniewski, 1997). Since perchlorate was not known to be a chemical of environmental concern until 1997, and since the impurity level was considered small relative to the primary chemical being produced (e.g., chlorate), little attention was paid to its presence, and thus, there is little publicly-available information regarding perchlorate content in ECP products. However, analysis of a sodium chlorate feedstock used for large-scale commercial perchlorate manufacturing showed that it contained 50 mg/kg perchlorate (unpublished AMPAC data), and therefore, the potential exists for release of perchlorate to the environment through ECP manufacture, storage, handling and use.

In this chapter, we discuss perchlorate in sodium chlorate (Section 4.2), in herbicides and defoliantes (Section 4.3) and in bleach (Section 4.4), all of which can be made electrochemically.

4.2 Sodium Chlorate

4.2.1 Background

Sodium chlorate is produced electrochemically by the electrolysis of aqueous sodium chloride (NaCl) according to the following overall equation (Betts and Dluzniewski, 1997):



The formation of perchlorate stems from anodic oxidation of chlorate during the electrochemical reaction in accordance with the following reaction (Betts and Dluzniewski, 1997):



Approximately 1.2 million tons (1.1 trillion kilograms) of sodium chlorate are consumed annually in the United States (US Dept. of Commerce, 2003). Historic and current uses for chlorate include pulp and paper bleaching, non-selective contact herbicide application, and plant defoliation (OMRI, 2000). Approximately 94% of the sodium chlorate is used for pulp and paper bleaching while the bulk of the remaining sodium chlorate is used in agricultural products (OMRI, 2000).

4.2.2 Equipment and Methods

The essential equipment, conditions and reagents are shown in Table 4.1. Sample preparation consisted of simple dissolution for solid samples and dilution of liquid samples in deionized water to obtain appropriate total conductance levels as dictated by EPA Method 314.0. In all sodium chlorate and herbicide samples, this required a sample dilution of about 1 gram of sample in 100 ml of deionized water. At this level of dilution, the perchlorate detection limit for all methods was on the order of 1 mg/kg (1 ppm or 0.0001%). Retention time for the perchlorate peak in all of the methods was about 12 minutes. Quality control procedures incorporated in these test methods included analyzing perchlorate-spiked DI water at known perchlorate concentrations (control samples), DI water (blank), duplicate samples, and perchlorate-spiked samples (spike samples). These analyses were conducted by American Pacific.

4.2.3 Results and Discussion

Twelve sodium chlorate samples, purchased from different suppliers, were analyzed. All samples purchased were “reagent-grade” and were certified by the suppliers as 99+% pure sodium chlorate. Figure 4.1 presents the perchlorate concentrations determined using EPA Method 314 (Modified). All of the samples were verified using the mass spectrometry (MS) method (mass peak at $m/e=99$). The results indicate that a wide variation is possible for different NaClO_3 manufacturers/suppliers. All samples tested showed a detectable level of perchlorate, with perchlorate levels ranging from 1.7 to 117 mg/kg, with a mean and median concentration of 41 mg/kg and 25.5 mg/kg, respectively. If 1.1 trillion kilograms of sodium chlorate are produced annually, this equates to at least 4.5×10^4 kg of perchlorate produced annually, the fate of which is not well understood.

4.3 Herbicides and Defoliant

4.3.1 Background

Sodium chlorate is used as a non-selective contact herbicide and as a defoliant for cotton, sunflowers, sungrass, safflower, rice, and chili peppers (OMRI, 2000). Sodium chlorate-based defoliants are used primarily on cotton to remove foliage before harvest, and on a wide range of produce crops (beans, pepper, corn, rice and various seeds) as a pre-harvest desiccant. As a defoliant, approximately 99% of sodium chlorate application is used on cotton plants (PAN, 2002). Use of sodium chlorate herbicides is primarily focused in California, Texas, Arkansas, Louisiana and Mississippi (USGS, 1997). California alone used 1,447,997 pounds of sodium chlorate pesticide in 2004 (PAN, 2006). The USGS estimates that 6.5 million pounds of sodium chlorate pesticide was used in the United States from 1995 to 1998 (USGS, 2006).

4.3.2 Materials and Methods

Sample Procurement

Four herbicides and two cotton defoliant were procured. Of these, three contained sodium chlorate. Chlorate-containing products proved more difficult to procure than anticipated at the outset of the project. An agriculture extension intended to send a chlorate-containing cotton defoliant but instead sent a non-chlorate defoliant, with a similar name. In another case, the specific product we attempted to obtain was not available and so instead we procured two non-chlorate containing products made by the same manufacturer.

Analytical Methods

All samples were analyzed in a similar manner using Ion Chromatography (IC) techniques of increasing sophistication. A screening step was performed first using EPA Method 314.0 on an appropriately diluted sample. For samples showing a definite perchlorate peak, a second step was performed using a modification of EPA Method 314.0 developed specifically to expose the presence of known interferences (see Section 5). Samples that gave a positive response for perchlorate in both of these steps were subjected to a final verification analysis using IC-MS. The equipment, conditions and reagents are shown in Table 4.1.

Sample preparation consisted of simple dissolution for solid samples and dilution of liquid samples in deionized (DI) water to obtain appropriate total conductance levels as dictated by EPA Method 314.0. For all samples, both solid sodium chlorate and solid and liquid defoliant, this required a sample dilution of about 1 gram of sample in 100 mL of deionized water. At this level of dilution, the perchlorate detection limit for all methods was on the order of 1 mg/kg (1 ppm or 0.0001%). Most liquid samples were analyzed without dilution. Some required dilution because of the high levels of common anions present in the matrix (which contribute to the level of total dissolved solids). Any sample matrix with high concentrations of common anions such as chloride, sulfate or carbonate can make the analysis problematic by destabilizing the baseline in the retention time window for perchlorate. The retention time for the perchlorate peak in EPA Method 314.0 is about 12 minutes. The retention time for the perchlorate peak in the laboratory-modified method, as well as the IC-MS method is about 15 to 18 minutes. Quality control procedures included running perchlorate-spiked DI water at known perchlorate concentrations (control samples), DI water (blank samples), duplicate samples, and perchlorate-spiked samples (spike samples).

4.3.3 Results and Discussion

Table 4.2 presents the perchlorate concentrations for two sodium chlorate-based herbicides, a commercial chlorate cotton defoliant, a non-chlorate defoliant, and two home-use non-chlorate herbicides. The chlorate defoliant, Defoliant 1, contained 16 ppm perchlorate. The perchlorate

concentrations for the chlorate herbicides were 8.7 and 164 ppm. Surprisingly, the non-chlorate defoliant and herbicides contained 100 to 400 ppb of perchlorate. The origin of the perchlorate could not be identified from the list of chemicals contained in these products. The presence of perchlorate raises concerns for use of these products, even if they are not labeled as containing sodium chlorate.

The manufacturer's label for Defoliant 1 indicated that 1 to 1.5 gallons (3.8 to 5.7 L) of the product should be added to 4 to 30 gallons (15 to 110 L) of water to treat 1 acre of land. This translates to the application of perchlorate at a concentration of 0.53 to 6 mg/L. The defoliant is intended to be sprayed on the crop itself. The fate of the perchlorate is unknown, although it is expected to reach the soil via rainfall.

For Herbicide 2, using the recommended application rate of 2 to 4 pounds of granules per 100 ft² of soil and assuming the top six inches of soil are impacted, an average soil concentration of 160 µg/kg could result. While this would be below USEPA Preliminary Remedial Goals (PRGs), these concentrations may be sufficient to impact groundwater at some sites. Site-specific cleanup levels as low as 20-50 µg/kg have been set as remedial goals to protect groundwater at sites in California. Distributing these quantities of perchlorate on an annual basis may inadvertently contribute to the wide-spread, low level perchlorate detections in some agricultural areas.

4.3.4 Conclusions

Perchlorate levels of 16 ppm were detected in the chlorate defoliant, levels up to 164 ppm in the chlorate herbicides, and concentrations up to 400 ppb were detected in the non-chlorate defoliant and non-chlorate herbicides. Areas with high chlorate product use, such as California, and agricultural lands used to grow crops such as cotton and rice may have low level perchlorate contamination due to the use of these products.

4.4 Bleach

4.4.1 Background

Hypochlorite is widely used as a household bleach and as an industrial disinfectant and is also routinely used to disinfect groundwater monitoring and drinking wells. Bleach is used in high volumes, with 818 million gallons (or 3 trillion liters) consumed in 2002 according to the Innovation Group (2003). The most common type of bleach solution is sodium hypochlorite, a greenish-yellow liquid solution. Calcium hypochlorite, a white powder, is often used for swimming pool chlorination.

Bleach is commonly generated through the electrolysis of a weak brine (i.e., NaCl) solution at a pH of 10-12 via the following overall reaction:



Sodium hypochlorite (NaOCl) 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:



This reaction is minimized during production by maintaining basic pH and keeping the temperature low.

It is not completely clear how perchlorate is generated from the sodium chlorate formed in bleach solutions. Schumacher (1960) discusses a number of mechanisms, including thermal decomposition and oxidation. However, efficient thermal decomposition requires high temperatures (e.g., 400-600 °C) and chemical oxidation requires strong oxidizing agents, such as ozone. Neither of these conditions exists in bleach at ambient temperature; however, temperatures above ambient and exposure to oxygen may result in low level production of perchlorate as discussed in Section 4.4.4.

4.4.2 Objectives

To determine the potential extent of environmental perchlorate contamination due to the use of sodium hypochlorite-based products, several brands of bleach were analyzed for their perchlorate content. Each of the brands was analyzed on a weekly basis for six weeks to determine the effect of storage and light on the perchlorate concentration. The following sections discuss the materials and methods used (Section 4.4.3); the results and discussion (Section 4.4.4) of this study; and the environmental implications of using bleach (Section 4.4.5).

4.4.3 Materials and Methods

Six different brands of bleach were used in this study. For the “initial opening” analyses, samples were immediately collected for IC-MS analysis upon opening the bottles. In addition, four vials of neat bleach were prepared from each brand, sealed to the atmosphere, wrapped in tin foil and stored to await analysis (“dark vials”). An additional four vials from each brand were prepared and sealed to the atmosphere, but left exposed to sunlight near a window (“light vials”). At weeks 1, 2, 3, and 6, a dark and a light vial of each bleach brand were opened and analyzed. A 1-mL sample of each bleach was diluted to 100 mL in deionized water, and samples were analyzed by IC-MS as described in Section 4.2.2.

4.4.4 Results and Discussion

The six brands of bleach analyzed in this study had dates of manufacture ranging from August 2005 through March 2006 (Table 4.3). Perchlorate concentrations ranged from 2.9 to 56 µg/L (with a mean concentration of 19 µg/L) upon initial opening (20 April 2006). Brand 4 had the highest concentration and had the earliest date of manufacture. The perchlorate concentrations in the samples stored in the dark increased over the six week storage period, with a mean starting concentration of 19 µg/L increasing by Week 6 to a mean concentration of 154 µg/L (Figure 4.2). These results confirm that storage duration and exposure to oxygen significantly influences perchlorate concentrations in bleach.

The perchlorate concentrations in the samples exposed to sunlight dramatically increased over the six week storage period, from the mean starting concentration of 19 µg/L to a mean concentration of 3,500 µg/L at Week 6 (Figure 4.3). The concentration detected at Week 6 was over 180 times the concentration found at initial opening. These results indicate that light exposure significantly influenced perchlorate formation in bleach.

4.4.5 Environmental Applications Employing Bleach

Use of a chlorine solution is the simplest and most effective way to disinfect or sterilize groundwater wells (Driscoll, 1995). Sodium hypochlorite is generally used as the chlorine solution. For sterilization, concentrations of 50 to 200 mg/L available chlorine in the well water are recommended (Driscoll, 1995). A milligram of active chlorine is equivalent to 0.73 mg of hypochlorite; therefore, the hypochlorite-equivalent concentrations recommended by Driscoll would be 36 to 145 mg/L. For a freshly opened bottle of bleach, this practice may introduce perchlorate concentrations of 0.019 to 0.076 µg/L in well water. For a bottle of bleach that had been previously opened and stored, these perchlorate concentrations could be as high as 0.62 µg/L (using the Week 6, dark sample concentration mean of 154 µg/L). If the bleach was exposed to sunlight these concentration could be an order of magnitude higher. Other references suggest injecting solutions of 500 to 2000 mg/L available chlorine (Smith 1995). This dose of hypochlorite in the injected solution may correspond to perchlorate concentrations up to 0.76 µg/L for a fresh bottle and 6.2 µg/L for a stored bottle. In summary, caution should be used when employing bleach for disinfection purposes. “Fresh” bleach is not likely to introduce environmentally significant levels of perchlorate into groundwater following the well disinfection guidelines above. However, bleach exposed to oxygen or sunlight should not be employed.

5. TASK 4 – EPA METHOD 314.0 INTERFERENCES

5.1 Background

Investigation of groundwater in the Henderson, Nevada area showed that the compound p-chlorobenzenesulfonate (p-CBS) co-elutes with perchlorate during analysis using EPA Method 314.0 and that, in at least one case, low level detections of perchlorate in groundwater in Nevada were determined to be false positives related to the presence of p-CBS. A simple adaptation of EPA Method 314.0 in which the column temperature was raised from the standard 30°C to 40°C resulted in sufficient separation of the perchlorate and p-CBS peaks to allow for quantification of both anions. This represents one of the few cases in which the compound responsible for producing a false positive for perchlorate following EPA Method 314.0 has been identified. Furthermore, the use of a simple change in column temperature to separate the peaks demonstrates that alternative analytical techniques (such as IC-MS) may not be required for screening suspect environmental samples for positive perchlorate interferences. Instead, simple modifications to EPA Method 314.0 may be sufficient to allow reliable separation of the interfering compounds and reliable identification of perchlorate.

The identification of p-CBS, which is a byproduct of pesticide (DDT) manufacturing (and is therefore likely to be restricted to pesticide manufacturing and waste disposal sites) led to the identification of a host of similar sulfonate-containing compounds that also interfere with perchlorate detection. Sulfonate compounds are the most widely-used surfactants in detergents and related materials. Given the widespread use and environmental occurrence of sulfonate surfactants, the potential for spurious detections of perchlorate in groundwater at the µg/L level resulting from these compounds exists. While surface water would be a key receiving body for these impacts, impacts to groundwater may also be significant in areas where septic systems are widely used.

5.2 Objective

The objective of this study was to assess the nature of interfering compounds on perchlorate detection using EPA Method 314.0 in environmental samples using IC-MS to confirm the presence of perchlorate.

5.3 Methods

Samples were collected from groundwater and surface water at locations where sulfonate or surfactant compounds were suspected to be present to evaluate whether these interferences were detectable in environmental media. A total of 29 water samples were collected from 14 sites throughout the United States and Canada. These sites included groundwater plumes (2 sites), a landfill, a carwash, surface waters (4 sites), groundwater near septic system discharge points (5

sites) and a wastewater treatment plant effluent (and surface water downstream). The landfill served as a positive control as it was known that p-CBS was present in groundwater at the site.

All equipment, conditions, and reagents are as described previously (see Section 4.2.2). Samples were analyzed by standard EPA Method 314.0, a laboratory-modified Method 314.0 and IC-MS by AMPAC's analytical laboratory. Method 314.0 uses ion chromatography with conductivity detection and therefore is not highly compound-specific. Retention times and standards are used to identify analytes but often analytes have similar or identical retention times. The modified Method 314.0 is a simple adaptation of the EPA Method 314.0, where the column temperature is raised from the standard ambient temperature to 40 °C, the eluent concentration is reduced from 50 to 35 mM (millimolar), and the pressure may be reduced by up to 30%. This method was developed by AMPAC to allow sufficient separation of the perchlorate and p-CBS peaks to allow for quantification of both anions. Simple modifications of EPA Method 314.0 are preferable to MS, as the costs of MS analytical equipment (plus staffing and maintenance) can be prohibitively expensive for smaller laboratories and research organizations that are already outfitted for EPA Method 314.0. Samples were analyzed by IC-MS to confirm if the detected compound was indeed perchlorate. MS identifies perchlorate by the mass peaks at 99 and 101 m/z (mass to charge), whereas p-CBS is identified by a mass peak at 191 m/z. The detection limit for perchlorate using IC-MS is 0.25 µg/L (micrograms per liter).

5.4 Results and Discussion

Results from six of the fourteen sites showed analytical interferences in the EPA Method 314.0 analyses, as presented in Table 5.1. In 10 of the 11 samples collected from these sites, the laboratory modified or IC-MS analyses determined that the EPA Method 314.0 results were false positives or falsely high detects ("over-reporting"). Analytical interferences were found in groundwater collected from a former DDT manufacturing facility (2 samples), a former naval base (1 sample), a landfill (1 sample), and near residential or public septic systems (6 samples). The remaining sites were either non-detect for perchlorate, or IC-MS confirmed the detections. These sites included a carwash, surface water (4 sites), groundwater near a residential septic system, groundwater near a public septic system and surface water near a waste water treatment plant.

False positive perchlorate concentrations in the septic samples ranged from 9.0 to 53 µg/L using EPA Method 314.0. Samples from two of the septic sites (5 samples) had high nitrate concentrations, ranging from 110 to 200 mg/L. The interfering compounds were not positively identified in any of these cases of false positives. However, one site had elevated levels of sulfate (a known Method 314.0 interferant) and one site had elevated alkalinity (270 mg/L as CaCO₃) and may have had surfactant present in the septic system discharge.

Groundwater known or suspected to be impacted by p-CBS had perchlorate concentrations, which ranged from 8,100 to 94,000 µg/L using EPA Method 314.0. p-CBS was identified by the

MS analyses in all four of these cases of over-reporting. The p-CBS concentrations ranged from approximately 13 to 3,200 mg/L.

5.5 Conclusions

The likelihood of a false positive or over-reporting increased when analyzing groundwater near septic systems or impacted by p-CBS. p-CBS is a by-product of DDT manufacturing and is used in the manufacture of phenol and aniline and as a solvent in some paints (Johnson et al., 2003). MS methods should be used to confirm perchlorate concentrations when sampling groundwater in the vicinity of septic systems or when p-CBS is suspected.

Although false positives using Method 314.0 were identified for 43% of the sites investigated, the remediation community has moved towards using MS methods for perchlorate detection since this task was proposed in 2003, and the DoD is now requiring all environmental restoration samples be analyzed by MS methods (DoD EDQW, 2006). Therefore, false positives from Method 314.0 will be less of an issue moving forward.

6. PERCHLORATE IMPACTS FROM FIREWORKS

6.1 Background

Large quantities of fireworks are handled and discharged annually in the U.S. For example, 221 million pounds (10^8 kg) of fireworks were consumed in 2003 (APA, 2007). Perchlorate is known to be a significant component of many pyrotechnics, and as such, the manufacturing, storage, handling, use and disposal of these products have the potential to introduce perchlorate into the environment. Potassium perchlorate can be used to produce colored flames, noise, and light as summarized in Table 6.1. Ammonium perchlorate is also used in some fireworks formulations. Another potential source of perchlorate is from the potassium nitrate in the black powder used in the lift charge. Potassium nitrate made from Chilean nitrate can contain perchlorate, as has been documented for sodium nitrate fertilizers.

Several recent studies have detected perchlorate in soils, groundwater and/or surface water following fireworks displays (Wilkin et al., 2007; MADEP, 2007). However, the number of case studies in the literature discussing the extent of soil and water contamination at firework discharge sites is very limited, and much of the information that is available is either anecdotal in nature or is not detailed enough to quantify impacts.

In the following sections, the results of two firework studies are discussed. Section 6.2 presents the results of a study conducted at Columbia Lake with the University of Waterloo in Waterloo, Ontario, Canada. Section 6.3 discusses a study conducted at the University of Massachusetts at Dartmouth (UMD) with the Massachusetts Department of Environmental Protection (MADEP).

6.2 Columbia Lake Site Study

6.2.1 Objectives

The objectives of the Columbia Lake study were to: 1) quantify perchlorate impacts to soil and groundwater from a commercial fireworks display; 2) evaluate the persistence and fate of perchlorate in soil, pore water and groundwater over a one year monitoring period and 3) evaluate whether metals related to fireworks displays can be used as indicators to differentiate perchlorate from fireworks versus other sources.

6.2.2 Site Description

The study site was located on a man-made island located on the east side of Columbia Lake (the "Site") in Waterloo, Ontario, north of the University of Waterloo (Figure 6.1). Columbia Lake has been the preferred launch area for commercial firework displays celebrating Canada Day (July 1) since 1984. The selected study area was known to have been the launch site for three displays from 2004 to 2006.

The Site is underlain by brown, silty clay with shallow discontinuous sand lenses. The depth to ground water in the overburden ranges from approximately 1 to 2 m below ground surface (m bgs) (3.3 to 6.6 ft bgs) across the site. The direction of groundwater flow is generally to the southeast.

6.2.3 Installation of Monitoring Wells and Lysimeters

A total of twelve shallow soil cores were collected for litho logic logging, and a network of eight monitoring wells (including two nested pairs) and ten shallow soil lysimeters were installed at the Site in May 2006 at locations shown in Figure 6.1. All boreholes for monitoring well installations were completed by a licensed Ontario well driller using 15 centimeter (cm) (6 inch) hollow stem augers. Drilling and instrument installation oversight was provided by Environment Canada. Split spoon soil samples were collected from select locations during drilling for classification of the aquifer matrix.

A monitoring well was installed in each of eight of the completed boreholes. Monitoring wells consisted of 2.54 cm (1 inch) inside diameter polyvinyl chloride (PVC) casing and a 0.254 millimeter (mm) (0.010-inch) slotted well screen wrapped in a Vylon™ mesh to prevent fine particles from entering the well. A silica sand pack was also poured around the well screen and a bentonite seal was placed above the sand pack and hydrated with distilled water before the remainder of the borehole was backfilled. To prevent surface water infiltration and to provide security, a locking well cap and steel protective casing was placed in the borehole over each well. Table 6.2 provides a summary of the well construction details. Dedicated tubing was used in each monitoring well for well development and sampling purposes.

Well development was completed by purging a minimum of three casing volumes from each monitoring well with a peristaltic pump where practicable. The pH, redox and temperature of the groundwater were recorded after each casing volume had been removed. Observations on the physical appearance and odor (if apparent) of the development water were also noted.

A soil lysimeters was installed in the unsaturated zone within each of ten hand-augered boreholes. Each lysimeters consisted of a pre-hydrated porous ceramic cup equipped with a sample and vacuum line. A silica powder was placed around the lysimeters and hydrated with deionized water in 5-cm (2 inch) lifts until the entire lysimeters was completely enveloped. Soil removed by the hand auger was used as backfill and the remainder of the open borehole was filled with bentonite pellets. To provide protection and security for the sample and vacuum lines, a polyethylene flush mount protective casing was placed in the borehole over the lysimeters. Table 6.2 provides a summary of the lysimeters construction details.

6.2.4 Monitoring and Sampling Methods

Each monitoring well and soil lysimeters was purged and sampled on at least one occasion to obtain a baseline condition at the site prior to the scheduled fireworks display. Samples were submitted for laboratory analysis of perchlorate, nitrate, nitrite, sulfate and metals. On June 29 and 30, 2006, surface soil samples were collected on a uniform sampling grid across the site, and stored at 4°C for later analysis. On July 1, 2006 the pyrotechnic display was completed as scheduled. Surface soil samples were collected on July 2, 2006 using the same grid system previously established, and selected grid samples from both sample dates were submitted for laboratory analysis of perchlorate, nitrate, nitrite, sulfate and metals. From July 3 to July 14, 2006 all monitoring wells and soil lysimeters were sampled, and samples were submitted for laboratory analysis. Additional soil, groundwater and pore water samples were collected during the week of August 7, 2006 for submittal to the laboratory. Groundwater and pore water samples were also collected October 19 and 20, 2006.

The following sections summarize the methods used to collect samples of soil, pore water and groundwater.

Shallow Soil Sample Collection

A grid system was developed to collect surface soil samples from locations across the site before and after the fireworks display. Samples from the top 5 to 10 cm (2 to 4 inches) of soil below the sod were collected using a 10.16 cm (4-inch) stainless steel flower bulb planter. The soil was divided between two pre-labeled sample containers, sealed and stored on ice in a cooler for shipment to the laboratory. Sampling equipment was manually cleaned using a phosphate-free soap solution and rinsed with distilled water after each sample had been collected.

Pore Water Sample Collection

Prior to sample collection, lysimeters purging was completed by exerting a vacuum on the ceramic cup and extracting the pore water present. Once purged of existing pore water, a vacuum of approximately 700 mm Hg was applied to each lysimeters to allow pore water to be pulled into the lysimeters overnight.

Pore water was collected into a 500 milliliter vacuum flask directly from the lysimeters and transferred into preserved sample vials supplied by the laboratory. Samples collected for analysis of dissolved metals were field-filtered with a 0.45-um filter prior to addition to the sample container. All samples were stored on ice in a cooler immediately after sample collection.

Groundwater Sample Collection

Prior to groundwater sample collection and monitoring well purging, water levels were measured to the nearest 0.001 m using a battery-operated, water level tape. The highest point of the PVC well casing was used as the reference point for all of the wells. Groundwater elevations were calculated by subtracting the depth-to-water from the reference geodetic elevation for each well.

Monitoring well purging was completed by pumping a minimum of three casing volumes from each monitoring well, where practicable, with a peristaltic pump through dedicated pump tubing. With the exception of well UW-2, the pH and redox potential (eH) was measured at each monitoring well during monitoring well purging on at least one occasion. Well UW-2 was unable to yield enough water to allow an accurate reading of the pH and eH.

Groundwater samples for analysis of perchlorate, nitrate, nitrite, sulfate and total metals were collected by pumping water directly from the well into sample vials provided by the laboratory. A 0.45 micrometer inline filter was connected to the effluent tubing to facilitate collection of groundwater for analysis of dissolved metals. After sample collection, the filled vials were stored on ice in a sample cooler. The dedicated pump tubing was decontaminated between sample events.

Sample Handling and Analysis

Groundwater, pore water, and surface soil samples were shipped on ice under chain of custody by courier to the selected laboratories. Samples for analysis of total metals, nitrate, nitrite and sulfate were performed by Maxxam Laboratory Services (Maxxam) of Mississauga, Ontario. Samples for analysis of perchlorate were performed by Environment Canada of Burlington, Ontario.

Groundwater and pore water samples were analyzed for total metals, nitrate/nitrite, sulfate and perchlorate by Environmental Protection Agency (EPA) Method 6020, SM 4500 and EPA extract method 375.4, and ion chromatography, double mass spectrometry (IC-MS/MS).

Soil samples were analyzed for total metals, nitrate/nitrite, sulfate and perchlorate by EPA Method 6010C/7010, SM 4500 and EPA extract method 375.4, and IC-MS/MS, respectively.

6.2.5 Results

Surface Soil Concentration Data

A total of 21 soil baseline samples were collected from the Site on June 29 and 30, 2006. A total of 22 soil samples and one debris sample were collected on July 2, 2006, the day after the fireworks display. The analytical results for these samples are summarized in Table 6.3. The

concentration of perchlorate in soil samples collected before the fireworks display ranged from 0.097 to 4.1 µg/kg while the concentration of perchlorate in soil collected the day after the fireworks display ranged from 0.41 to 308 µg/kg. Figure 6.2 shows the change in perchlorate concentration in soil samples collected before and after the pyrotechnic display. In addition to soil samples, one firework debris sample was collected and analyzed (see last column, Table 6.3). Perchlorate was present at 0.029 mg/kg. Nitrate, calcium, potassium and sulfur concentrations were also elevated.

A visual comparison of the pre and post perchlorate and metals concentrations were made by plotting the concentration of the pre-fireworks samples versus the concentration in the post-fireworks soil samples with a 1:1 ratio line and +/- 30% error lines. A summary of the visual comparisons for perchlorate and select metals (aluminum, antimony, barium, calcium, magnesium, potassium, sodium, and strontium) is presented in Figure 6.3, which shows the amount of scatter and general trend in the concentrations for each compound. The plots suggest that the concentration of perchlorate detected in the post fireworks samples were generally higher than those of the pre-fireworks samples; however, there was no discernable change in the metals concentrations in samples collected before and after the fireworks display.

Pore Water Concentration Data

Pore water samples were collected from each lysimeters on at least one occasion before and after the fireworks event. Due to difficulties in collecting pore water from some damaged lysimeters, a sample could not always be collected. Table 6.4 provides a summary of perchlorate concentrations in pore water. Figure 6.4 presents the perchlorate concentration trends at lysimeters installed at the Site. The lysimeters are divided into those installed upwind of the historical launch area (LY1 and LY6), those within the historical launch area (LY2, LY4 and LY8) and those downwind of the historical launch area (LY3, LY7 and LY9). The concentration of perchlorate in lysimeters installed upwind of the fireworks launch area ranged from 0.6 µg/L to 3.8 µg/L, with no obvious difference between the samples collected before or after the fireworks event. The concentration of perchlorate in lysimeters installed within the historical launch area ranged from 4.2 µg/L to 42 µg/L and those installed downwind of the historic launch area ranged from 13 µg/L to 29 µg/L. Lysimeters LY2, LY4 and LY9 demonstrated a slight increase in perchlorate concentration over the first week following the fireworks display.

Table 6.5 provides a summary of total metals concentrations in pore water at the Site. The concentration of total metals in pore water, especially those likely attributable to a fireworks event (i.e., aluminum, antimony, barium, calcium, magnesium, potassium, sodium, and strontium), did not show a consistent increasing trend after the fireworks event.

Groundwater Monitoring Data

Groundwater monitoring was conducted at each well during three events in June, and one event in July 2006, August 2006, October 2006, and March 2007.

The depth to the water table was measured prior to groundwater sampling and converted to elevation above a local datum. The water table beneath the Site ranged from near ground surface to 2 m bgs (6.6 ft bgs). Groundwater flow is from the northwest to southeast across the site. Figure 6.5 provides a representative potentiometric surface map, as measured on June 4, 2006. A summary of the groundwater elevations recorded at monitoring wells installed at the Site is presented in Table 6.6.

The pH and eH were measured in groundwater during at least one event for all but one of the monitoring wells (UW-2) (Table 6.7). The pH was approximately neutral and the eH ranged from 25 millivolts (mV) to 154 mV (nitrate-reducing to iron- and manganese-reducing conditions).

The monitoring wells completed at the Site are divided into those installed up-gradient or transgradient of the historical launch area (UW-1, UW-2 and UW-3), those within the historical launch area (UW-4, UW-5 and UW-6) and those down-gradient of the historical launch area (UW-7 and UW-8). Table 6.8 provides a summary of the perchlorate concentrations in groundwater samples. Figure 6.6 presents the perchlorate concentration trends in groundwater.

The concentration of perchlorate in up-gradient monitoring wells ranged from below the laboratory detection limit (0.011 µg/L) to 1.03 µg/L, with no substantial change after the fireworks event. The concentration of perchlorate in wells installed within the historical launch area ranged from below the detection limit (0.011 µg/L) to 45 µg/L and down-gradient monitoring wells ranged from below the detection limit (0.011 µg/L) to 15 µg/L. UW-4 installed within the launch area shows a wide range in perchlorate concentration over time (21 µg/L to 43 µg/L) with the peak concentration detected just prior to the fireworks display. UW-6 and UW-8 were the only wells with increasing perchlorate concentrations after the fireworks display.

The concentration of total metals in groundwater, especially those likely attributable to a fireworks event (aluminum, antimony, barium, calcium, magnesium, potassium, sodium, and strontium) did increase in many wells after the fireworks event (Table 6.9). However, most of these wells (UW-1, UW-2, and UW-3) were located up-gradient or away from the fireworks display; and therefore it is not clear why the metals concentrations increased. The increase may be the result of temporal or analytical variability.

6.2.6 Discussion

Soil samples collected after the fireworks display appeared to have slightly elevated concentrations of perchlorate, especially in two samples collected from the launch area (LA8 and

LA9). Pore water samples from lysimeters LY2, LY4 and LY9, located within and adjacent to the launch area, demonstrated a slight increase in perchlorate concentration over the first week following the fireworks display. The locations of LY2 and LY4 were in close proximity to the two soil samples collected within the launch area that exhibited elevated concentrations of perchlorate. The perchlorate trend observed for LY9 is limited to samples collected up to four days after the fireworks event. All other lysimeters did not demonstrate a noticeable trend in perchlorate concentrations over time.

Only groundwater collected from two monitoring wells showed increasing perchlorate concentration trends following the fireworks display. UW-6 exhibited an increase in perchlorate concentration after October 2006 when the perchlorate concentration increased substantially to 45 µg/L. The close proximity of lysimeters LY4, which had elevated perchlorate concentrations, suggests an infiltration pathway through soil to groundwater. Well UW-8, which is down-gradient from well UW-6, showed perchlorate concentrations up to 15 µg/L. Therefore, it appears that groundwater impacts were primarily limited to areas with higher soil and pore water concentrations, and areas down-gradient. Despite limited perchlorate concentration increases in groundwater, the concentrations are 1-2 orders of magnitude higher than perchlorate concentrations measured in groundwater in agricultural areas in Southern Ontario (Ptacek, 2007) and likely represent the long-term impact of multiple annual fireworks displays at Columbia Lake.

Because of the limited extent of perchlorate impacts to soil and the lack of increased metals concentrations in the soil, pore water and groundwater below and down-gradient of the launch area, metals such as aluminum, antimony, barium, calcium, magnesium, potassium, sodium, and strontium could not be used to identify perchlorate impacts from fireworks in this case.

6.3 University of Massachusetts Site Study

6.3.1 Past Activities

In order to better understand the magnitude of impacts to the environment from fireworks displays, MADEP conducted soil and groundwater sampling at UMD, the site of summertime fireworks for more than 10 years. Soil and groundwater samples were initially collected before a September 2004 fireworks display to assess pre-launch/event conditions in and near the Study Area. A limited number of soil and groundwater samples were collected shortly after the 2004 fireworks event to assess the immediate impact of perchlorate on soil and groundwater. A series of groundwater monitoring events were also conducted after September 2004 to evaluate perchlorate infiltration and to assess long-term impacts of perchlorate on soil and groundwater.

A report was posted to the MADEP website (MADEP, 2007) and the results suggest that the concentration of perchlorate in soil increased after the fireworks display while the highest concentration of perchlorate in groundwater was observed prior to the fireworks display.

6.3.2 Study Objectives

To supplement the data collected at the Columbia Lake Site, a second field experiment was conducted to: 1) measure the concentration of perchlorate and metals in fireworks charges, 2) evaluate perchlorate impacts to soil from a commercial fireworks display; 3) evaluate metals impacts to soil from a commercial fireworks display; and 4) evaluate whether the isotopic signature for firework-derived perchlorate differs from other perchlorate sources.

6.3.3 Site Description

The UMD site is located at the University of Massachusetts, Dartmouth campus in an open field with a forested area to the north, campus buildings to the east and south and a wetland to the west. The geology is described as a compact unsorted silty, bouldery, gravel till with a hydraulic conductivity ranging from 0.7 to 4.5 ft per day. The depth to water typically ranges from ground surface to approximately 5 ft bgs due to seasonal effects (MADEP, 2005). As part of the MADEP study conducted in 2004, eight shallow monitoring wells were installed.

In previous years, including the display in 2004, the fireworks have been staged from a launch area located to the west end of the open field adjacent to monitoring well UMD-1. The location of the launch area was changed for the 2006 fireworks display as shown in Figure 6.7.

6.3.4 Methods

Shallow Soil Sample Collection

On June 14, 2006, a grid system was developed to collect surface soil samples from locations across the UMD site before and after a fireworks display. A total of 17 soil sample pairs were collected on June 15, 2006 and then again on July 5, 2006, the day following the fireworks display. Each sample pair was collected from the top 2 inches of soil using a stainless steel trowel and placed in 250 mL wide mouth glass jars. Paired samples were collected from within 15 feet of each other in the same grid. Pre-fireworks display samples were labeled as “Grid Number – A”, and post fireworks display samples labeled as “Grid Number – B”. For those grids where a fireworks launch pad was staged, a post fireworks sample was collected from directly beneath the launch platform (sand pile) and a composite sample was collected from the four corners of the launch platform. All soil samples were stored on ice in a cooler for shipment to the laboratory. Sampling equipment was manually cleaned using a phosphate-free soap solution and rinsed with distilled water prior to each use.

Fireworks related debris and two unspent fireworks charges were discovered at the site during soil collection and submitted for laboratory analysis.

Groundwater Monitoring

The specific conductance, pH, temperature, oxidation reduction potential and dissolved oxygen content were recorded at each monitoring well during the purging process. Approximately three well volumes were purged from each well using a low flow peristaltic pump prior to groundwater sample collection. Monitoring wells were sampled by a representative of MADEP for analysis of perchlorate.

Laboratory Analysis

Soil and fireworks debris samples were submitted to Alpha Woods Hole Laboratory (Alpha) of Westborough, Massachusetts for analysis of perchlorate, sulfate, nitrate and select metals (aluminum, antimony, barium, calcium, magnesium, potassium, sodium and strontium) by EPA Methods 332.0, 9038, 4500 and 6010B, respectively. The fireworks charge samples were analyzed for perchlorate, sulfate and nitrate/nitrite (EPA Method 314.0 and 300, respectively) by the Shaw Environmental Research Laboratory and for select metals (EPA Method 6020A) by Alpha. The list of metals was limited to those likely associated to fireworks (i.e., aluminum, antimony, barium, calcium, magnesium, potassium, sodium, and strontium). The groundwater samples were submitted to Alpha for analysis of perchlorate by modified EPA Method 314.0.

Isotopic Analysis

As part of this study, firework charges and groundwater samples were collected for isotopic analysis to establish if there were isotopic markers indicative of perchlorate derived from fireworks. This work was conducted in conjunction with ESTCP project ER-0509 (led by P. Hatzinger, Shaw Environmental).

Groundwater was pumped from the well (either UMD-7 and UMD-8) and then passed through an ion exchange column until at least 10 mg of perchlorate was trapped on the resin (Sturchio et al., 2006; Böhlke et al., 2005). Once sufficient perchlorate had been collected (from groundwater or extracts in the case of the fireworks charges), an aqueous solution containing tetrachloroferrate was passed through the column. This ion preferentially binds and displaces the perchlorate ions from the resin (Gu et al., 2001). The perchlorate-bearing solution was subsequently subjected to a series of purification steps, which ultimately resulted in a pure precipitate of either KClO_4 or CsClO_4 , both of which are relatively insoluble. After verification of the purity of this material, the salts were analyzed by isotope ratio mass spectrometry (IRMS) for determination of $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and/or $\Delta^{17}\text{O}$. IRMS utilizes a mass spectrometer that is designed specifically to measure isotopic proportions of a given element, rather than to determine exact molecular quantities.

The stable isotope ratios of light elements gained from IRMS are generally reported relative to those of established reference materials as “delta” (δ) values and measured in parts-per-thousand

(denoted “‰” = per mil). As an example, the expression used to report relative abundances of Cl isotopes ($^{37}\text{Cl}/^{35}\text{Cl}$) is provided below (Eq. 6.1).

$$\delta \text{ (in ‰)} = \left[\frac{R_x - R_s}{R_s} \right] \times (1000) \quad \text{(Eq. 6.1)}$$

Where: R = ratio heavy/light isotope (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$)

R_x = sample (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$ in environmental sample)

R_s = standard (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$ in “standard mean ocean chloride”)

Thus for Cl isotopes:

$$\delta^{37}\text{Cl}_{\text{sample}} \text{ (in ‰)} = \left[\frac{\left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}} \right)_{\text{sample}} - \left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}} \right)_{\text{standard}}}{\left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}} \right)_{\text{standard}}} \right] \times (1000) \quad \text{(Eq. 6.2)}$$

The ratio of the heavy to the light isotope is used by convention, and for the case of Cl, the established international reference material is standard mean ocean chloride (SMOC). A positive delta value indicates that the sample is enriched in the heavy isotope relative to the standard, while a negative delta value shows that the sample contains less of the heavy isotope. For example, if $\delta^{37}\text{Cl}$ is reported as +15‰, this means that the ratio of $^{37}\text{Cl}/^{35}\text{Cl}$ is 15 parts-per-thousand (or 1.5%) higher in the sample of interest than in SMOC (for which $\delta^{37}\text{Cl}$ is 0.00 ‰).

6.3.5 Results

Debris and Fireworks Charges Concentrations

Results of the analysis of fireworks debris and two unspent fireworks charges are provided in Table 6.10. The compounds detected at high concentrations in the fireworks debris sample were perchlorate (31.8 mg/kg), calcium (22,000 mg/kg), potassium (4,600 mg/kg) and sodium (9,300 mg/kg). High concentrations of perchlorate (389,000 mg/kg), aluminum (120,000 mg/kg), magnesium (120,000 mg/kg), and potassium (160,000 mg/kg) were detected in the samples of the unspent fireworks charges.

Surface Soil Concentration Data

The concentration of perchlorate in soil samples collected before the fireworks display were typically below the laboratory reporting limit of 0.008 mg/kg, while the concentration of perchlorate in soil collected the day after the fireworks display ranged from below the laboratory reporting limit to 5.0 mg/kg. Figure 6.8 shows the change in perchlorate concentration in soil samples collected before and after the pyrotechnic display. An increase in the concentration of metals, such as potassium and magnesium, in the soil occurred as a result of the fireworks

display, as shown in Figures 6.9 and 6.10. The results of the pre and post soil sample analyses are summarized in Table 6.11.

A visual comparison of the pre and post soil sample results was made by plotting the concentration of the pre-fireworks samples versus that in the post fireworks soil samples with a 1:1 ratio line and +/- 30% error lines, as shown in Figure 6.11. The plots suggest that the concentration detected in the post fireworks samples were generally higher than those of the pre-fireworks samples, particularly for perchlorate, potassium, magnesium, strontium, and barium. A statistical analysis of the pre and post soil sample pairs was performed (at the 95% confidence level) to determine if the concentrations were indeed different between sample pairs. The statistical analysis indicated that the concentrations of all detected compounds in pre fireworks soil samples were significantly different than the concentration in post fireworks soil samples, with the exception of calcium and sodium.

Groundwater Concentration Data

Groundwater samples were collected from the monitoring wells installed at the UMD site by Geosyntec and MADEP on July 25, 2006, allowing some time for perchlorate from the July 3, 2006 fireworks display to infiltrate with approximately 2 inches of precipitation that fell during the intervening days (<http://www.wunderground.com>). The perchlorate concentrations in groundwater ranged from the laboratory detection limit of 1 µg/L to 22 µg/L. The groundwater redox at the site is generally reducing up-gradient of and below the launch area (UMD-2, -3 and -1) but oxidizing down-gradient and trans-gradient of the launch area (UMD-5, -6, -7 and -8). A comparison of the historical perchlorate concentrations in groundwater (Table 6.12) does not show any obvious spikes in perchlorate concentrations coinciding with fireworks displays at the UMD site. This may be due to the microbial degradation of perchlorate in reduced groundwater up-gradient and below the launch area.

Isotopic Data

The results of the isotopic analysis of groundwater from wells UMD-7 and UMD-8, along with the results from firework debris and a flare found on site, are presented in Table 6.13. The table presents $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ data. The perchlorate from the fireworks charges had $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values in the range of 0.1 to 0.7, -20.1 to -19.4 and 0.074 to 0.09, respectively. These values fall in or very near the range of 0.6 ± 0.9 for $\delta^{37}\text{Cl}$, -17.2 ± 2.8 for $\delta^{18}\text{O}$, and 0.01 ± 0.08 for $\Delta^{17}\text{O}$ previously measured for synthetic perchlorate as part of ESTCP project ER-0509. By comparison, Chilean nitrate fertilizer has $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ signatures of -12.8 ± 2.0 , -6.3 ± 2.5 , and 9.6 ± 0.7 , respectively (Sturchio *et al.*, 2006). The $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ data for the groundwater samples show that the perchlorate in groundwater is synthetic (i.e., not fertilizer derived). The ^{18}O signatures in groundwater from each well are very consistent and are much closer to the firework samples that we have analyzed than to the flares.

6.3.6 Discussion

The unspent fireworks charges contained high concentrations of perchlorate, aluminum, magnesium, and potassium while the fireworks debris sample contained high concentrations of perchlorate, calcium, potassium and sodium. The residual concentrations of perchlorate in the fireworks debris was 31.8 mg/kg versus 5 mg/kg detected in the most contaminated soil samples, suggesting that the incomplete combustion of fireworks has the potential to be the likeliest source of soil contamination.

Soil samples collected after the fireworks display had higher concentrations of perchlorate, aluminum, antimony, barium, magnesium, potassium and strontium than the samples collected from the same area before the fireworks display. These key constituents are reflective of the fireworks charge composition and may serve as co-contaminants for fireworks source identification at other sites.

The concentration of perchlorate in groundwater samples collected from monitoring wells before and after the fireworks display did not exhibit a noticeable change in concentration other than a decrease over time, possibly due to biodegradation and/or dilution.

Isotopic analyses showed that perchlorate from fireworks is sufficiently different from perchlorate of Chilean nitrate origin, but the isotopic signature may not be sufficiently unique to differentiate firework perchlorate from other anthropogenic sources.

6.4 Conclusions

Large quantities of fireworks ($\sim 10^8$ kg) are handled and discharged annually in the U.S. (APA, 2007). Fireworks charges can have very high perchlorate contents (e.g., 372 g/kg), which can represent point sources high in perchlorate if the fireworks are not fully combusted during the display. From the two studies reported herein, soil contamination is more likely than groundwater contamination, possibly due to in situ reduction of perchlorate in groundwater. Soil contamination tended to be focused near the launch area. Firework users should be cognizant of the potential for soil and groundwater contamination when storing and launching fireworks and should ensure that uncombusted charges or debris are removed from the area immediately after the display.

7. RELATIVE MAGNITUDE OF PERCHLORATE SOURCES AND SOURCE IDENTIFICATION

7.1 Relative Magnitude of Perchlorate Sources

One of the objectives of this work was to estimate the relative contribution of non-military anthropogenic sources of perchlorate to the environment using information from a literature survey (Geosyntec, 2005) and laboratory and field tests. Table 7.1 presents a summary of the perchlorate sources arising from work under this project. The first column presents the anthropogenic sources investigated along with rocket fuel, precipitation, and Chilean nitrate fertilizer for comparison. The second column presents the mass in kilograms of each source produced annually in the USA. References are provided for each of the production numbers. Most were reported as part of the literature survey (Geosyntec, 2005). The third column, % Product Containing Perchlorate, denotes the estimated percentage of the product that contains perchlorate. For example, although 10^8 kg of fireworks are produced annually, we estimate that only 50% of that mass contains perchlorate. The amount of perchlorate in the original uncombusted product represents the perchlorate concentrations measured in our laboratory studies, except for the perchlorate content in Chilean nitrate, which is a literature value (Urbansky et al., 2001). By multiplying the amount produced annually by the % of product containing perchlorate by the amount of perchlorate in the original (unaltered) product, we can estimate the mass of perchlorate contained in each source, as shown in the fifth column of Table 7.1. The sixth column presents the concentration or percentage of perchlorate remaining in the original product after combustion or reaction. Most of these values were determined during this project with the exception of the rocket fuel value, which was estimated by Dr. Jimmie Oxley as part of other ongoing experiments. By multiplying this perchlorate concentration, or % of original perchlorate remaining, times the mass of perchlorate in the original product, we can estimate the minimum mass of perchlorate potentially impacting the environment as shown in the last column. The word “minimum” is emphasized because these numbers assume only residue (largely from attempts to achieve complete combustion). They do not include spills, misfires or poor housekeeping when using these products, which would serve to significantly increase the amount of perchlorate impacting the environment. It should also be emphasized that the units are in kilograms. The way in which each of these sources is distributed/used will affect the ultimate concentrations observed in soil, groundwater or surface waters.

When comparing the mass of perchlorate in the original uncombusted source, fireworks and rocket fuel have similar levels of perchlorate (i.e., 10^7 kg/year are used). When the values in the column showing the minimum mass of perchlorate potentially impacting the environment are compared, it is clear that many of the non-military anthropogenic sources are of similar or greater magnitude than the rocket fuel. Note that these values represent the minimum mass of perchlorate potentially impacting the environment and do not include spills, misfires or poor-housekeeping. Sites that been identified with high concentrations of perchlorate contamination (in the thousands of part per billion or more) have typically involved manufacturing, testing or

disposal of solid rocket propellant (ITRC, 2005). Nevertheless, it is clear that there are several other anthropogenic sources of significance.

7.2 Source Identification

Another objective of this work was to identify tools to help identify anthropogenic non-military sources. Three techniques identified include: historic practices at the site (including geographic regions that point to historic practices), information on co-constituents and their concentrations, and isotopic signatures. These techniques are summarized in Table 7.2. Co-constituents and their respective concentrations may assist in distinguishing anthropogenic non-military sources from each other and from military sources. For example, the presence of high levels of strontium suggests road flares or possibly fireworks instead of rocket propellant. Geography and/or past practices may also shed light on the perchlorate source. For example, agricultural areas may have used Chilean nitrate fertilizer historically or may be using sodium chlorate or herbicides, containing perchlorate as impurities.

Isotopic markers may be useful for distinguishing natural or Chilean nitrate fertilizer from other perchlorate sources, as presented in Table 7.2. Only aged bleach and Chilean nitrate fertilizer have unique isotopic markers. For example, in aged bleach, the chlorine is much heavier and the oxygen is much lighter than in other anthropogenic sources. However, the other anthropogenic sources are not reliably distinguished from each other at this time. Further information on isotopic analyses can be obtained from ESTCP project ER-0509 (Validation of Chlorine and Oxygen Isotope Ratio Analysis to Differentiate Perchlorate Sources and to Document Perchlorate Biodegradation).

7.3 Conclusions

There are several anthropogenic perchlorate-containing sources that are produced in high volume. In particular, fireworks are produced in high volume and also have very high perchlorate contents. Most of the perchlorate-containing sources are combusted or consumed during proper use, which greatly reduces the amount of perchlorate available to impact the environment. However, depending on the circumstance, even lower levels of perchlorate in combustion residue may be significant enough to cause elevated concentrations of perchlorate in groundwater locally, given the low action levels for groundwater. Improper use (i.e., incomplete combustion or misfires) or poor housekeeping can create situations where much higher levels of perchlorate can impact the environment. Thus, it is critical that unused fireworks, flares and explosives be removed from sites following use. Sources such as Chilean nitrate fertilizers, sodium chlorate-based defoliant and herbicides, although potentially lower in perchlorate than the other sources, are directly applied to crops and soil and over large areas. Thus, these sources have the potential to contaminate soil and groundwater, especially if they are used repeatedly over a number of years. When perchlorate is detected in the absence of military activity, anthropogenic or natural

non-military sources should be suspected. Past practices, geographic regions, co-constituents and isotopic markers can provide evidence to identify the source of perchlorate.

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TABLES

TABLE 2.1
PRE- AND POST BLAST ANALYSIS OF SLURRY GEL EXPLOSIVE

	Shot	Pre-Blast Analysis				Post-Blast Analysis					
		Charge (g)	ClO ₄ ⁻ (g)	Initial % CO ₄ ⁻ in charge	Initial NO ₃ (g)	ClO ₄ ⁻ Residue* (g)	mg ClO ₄ ⁻ Residue/g charge	% of ClO ₄ ⁻ Residue/Initial ClO ₄ ⁻	NO ₃ ⁻ Residue* (g)	mg NO ₃ ⁻ Residue/g-charge	% NO ₃ ⁻ Residue/Initial
	a	516	28.67	5.56	288	0.0062	0.012	0.022	0.066	0.13	0.023
	b	522	29.00	5.56	291	0.0128	0.0245	0.044	0.158	0.30	0.054
	c	520	28.89	5.56	290	0.0116	0.022	0.040	0.153	0.29	0.053
Average:		519	28.85	5.56	290	0.0102	0.020	0.035	0.126	0.24	0.043

Notes:

* The perchlorate and nitrate residue amounts have been extrapolated to 100% room coverage and 100% foil recovery.

Rinse solutions were analyzed via EPA Method 314.0 for perchlorate and EPA Method 300.0 for nitrate

% - weight percent

g - gram

mg-milligrams

NO₃⁻-Nitrate

ClO₄⁻ -Perchlorate

NO₃⁻ -Nitrate

TABLE 3.1
PERCHLORATE CONTENT OF CANADIAN FLARES MANUFACTURED IN 2003 AND 2005

Year/Replicate	mg Perchlorate/ kg Flare Powder¹	mg Perchlorate/ kg Wick Material²	Total mg Perchlorate/ Flare	Total Percentage Perchlorate/ Flare
2003A ³	48,887	123,124	9,175	5.13%
2003B	50,563	113,361	9,410	5.26%
2003C	53,398	119,799	9,937	5.55%
Mean	50,949	118,761	9,507	5.31%
95% C.I.	2,580	5,617		
2005A	51,905	125,983	9,715	5.43%
2005B	56,764	94,097	10,372	5.80%
2005C	53,398	95,462	9,797	5.48%
Mean	54,022	105,181	9,961	5.57%
95% C.I.	2,300	16,657		

Notes:

1 - Flare powder refers to the yellow powder within the cardboard flare casing

2 - Wick material refers to the black substance of the ignition button and the short wick extending down into the main portion of the flare.

3 - Flares A,B,C from each year were taken from the same package

mg - milligrams

kg - kilograms

% - Percentage

C.I. - confidence interval

A,B,C - Flare Samples

TABLE 3.2
AMOUNT OF PERCHLORATE REMAINING IN BURNED CANADIAN FLARE MATERIAL

	Unburned Flare		Burned Flare		After Combustion	
	mg perchlorate/ kg flare powder	mass perchlorate per flare (mg)	mg perchlorate/ kg residue	mass perchlorate per flare (mg)	% perchlorate remaining	% perchlorate removed
2005A	51,905	9,288	305	28	0.30%	99.70%
2005B	56,764	10,157	166	16	0.16%	99.84%
2005C	53,398	9,555	61	6	0.06%	99.94%
Mean	54,022	9,667	177	16	0.17%	99.83%

Notes:

Samples A, B and C were taken from the same package

mg - milligrams

kg - kilograms

**TABLE 3.3
PRE-BURN AND POST-BURN ANALYSIS OF AMERICAN AND CHINESE FLARES**

Flare Origin	Mass of flare (g)	Pre-Burn Analysis		Post-Burn Analysis	
		Initial ClO ₄ ⁻ (g)	ClO ₄ ⁻ (%)	mg ClO ₄ ⁻ per g flare	ClO ₄ ⁻ remaining/initial (%)
Chinese					
10 min.	119	6.4	5.4	0.809	1.50
	121	6.5	5.4	0.079	0.15
	120	6.5	5.4	0.098	0.18
15 min.	163	10.6	6.5	0.041	0.063
	160	10.4	6.5	0.047	0.073
20 min.	203	11.5	5.7	0.05	0.088
	202	11.5	5.7	0.056	0.10
	200	11.4	5.7	0.047	0.082
	201	11.5	5.7	0.032	0.055
30 min.	282	16.3	5.8	0.062	0.11
	281	16.3	5.8	0.077	0.13
	284	16.5	5.8	0.045	0.077
Average			5.8	0.120	0.217
American					
15 min.	184	11.5	6.2	0.025	0.04
	176	11.0	6.2	0.003	0.005
	176	10.9	6.2	0.035	0.057
	174	10.8	6.2	0.003	0.005
Average	177.5	11.05	6.2	0.0165	0.027

Notes:

g - grams

mg - milligrams

min. - minute

% - Percentage

ClO₄⁻ - perchlorate

TABLE 3.4
USGS HIGHWAY SAMPLING SITE INFORMATION

Highway ¹	Number of Total Lanes Monitored	Highway Station Number	Latitude	Longitude
Primary Monitoring Sites				
RT-119 ASHBURHAM, MA	2 of 2	55	420420.155	710540.867
RT-2 (east bound) LITTLETON, MA (about 1.4 miles east of I-495)	2 of 4	UNKNOWN	42030.448	71029.223
I-495 (north bound) BOXBOROUGH, MA	3 of 6	N-2	42028.351	71033.333
I-95 (RT-128) LEXINGTON, MA (south of RT-2A)	8 of 8	LE-23 (CWD)	42026.337	71015.554
Primary Quality Assurance (QA) Monitoring Sites				
RT-119 (north bound) ASHBURHAM, MA	1 of 2	75	42 ⁰ 41.917'	71 ⁰ 54.527'
<i>RT-2 (west bound) LITTLETON, MA (about 1.4 miles east of I-495)</i>	<i>2 of 4</i>	<i>UNKNOWN</i>	<i>42030.448</i>	<i>71029.223</i>
I-495 (south bound) HARVARD, MA	2 of 4	S-26	42027.267	71034.645
<i>I-95 (RT-128) WALTHAM, MA (about 1/4 miles north of Winter Street)</i>	<i>2 of 8</i>	<i>WA-43 (CWD)</i>	<i>420240.341</i>	<i>710150.553</i>
Secondary Monitoring Sites				
RT-8 ADAMS, MA	4 of 4	63.5	42040.317	73006.433
<i>I-195 (west bound) MARION, MA</i>	<i>2 of 4</i>	<i>UNKNOWN</i>	<i>41043.65</i>	<i>70046.367</i>
I-190 (south bound) LEOMINSTER, MA	2 of 4	585	42030.275	71043.25
<i>I-93 (RT-128) QUINCY, MA (about 1/4 mile north of Granite Street)</i>	<i>8 of 8</i>	<i>739</i>	<i>42016.78</i>	<i>71002.75</i>

¹ Highway sites in *italics* were installed after 11/01/05.

TABLE 3.5
ESTIMATED PERCHLORATE CONCENTRATION IN RUNOFF LEAVING HIGHWAY

First sample collected	Estimated I-95 Perchlorate Concentration (µg/L)
7-Jun-06 10:29 AM	5.7
7-Jun-06 1:07 PM	25
7-Jun-06 1:25 PM	50
7-Jun-06 1:39 PM	314
7-Jun-06 1:52 PM	153
7-Jun-06 2:16 PM	31
7-Jun-06 2:50 PM	14
7-Jun-06 3:46 PM	17
7-Jun-06 3:54 PM	5.0
7-Jun-06 4:04 PM	5.1
7-Jun-06 4:26 PM	6.0
7-Jun-06 4:54 PM	4.6
7-Jun-06 6:30 PM	3.8
7-Jun-06 9:23 PM	26.2

Notes:

µg/L - micrograms per liter

TABLE 4.1
LIST OF EQUIPMENT, CONDITIONS AND REAGENTS
USED IN THE ANALYSIS OF ECP CHEMICALS

Equipment/Reagent	EPA Method 314.0	Modified 314.0	IC-MS
Pump	Dionex GP-50		
Autosampler	Dionex AS-40, 5mL		
Eluent Generator	None		Dionex EG-50
Detector	Dionex CD-25		Dionex AXP-MS
Column (Temperature)	Dionex AS-16, 4 mm (Ambient)	Dionex AS-16, 4 mm (40°C)	Dionex AS-16,2mm (Ambient)
Eluent	50 mM NaOH	35 mM NaOH	45 mM KOH
Eluent Flow Rate	1.2 mL/min		0.3 mL/min

Notes:

EPA - Environmental Protection Agency

IC-MS - Ion chromatography/Mass Spectrometry

mL/min - milliliter per minute

NaOH - Sodium Hydroxide

KOH - potassium hydroxide

mm - millimeters

mM - millimolar

°C - Celcius

TABLE 4.2
AGRICULTURAL PRODUCT SAMPLE SUMMARY

Agricultural Products	Perchlorate (ppm)	Sodium Chlorate (ppm)	Comments
Herbicide 1 ¹	8.7	224,226	Label indicates product is 30% NaClO ₃ by weight
Herbicide 2 ¹	164	254,528	Label indicates product is 30% NaClO ₃ by weight
Defoliant 1 ¹	16	490,000	Label indicates product is 45% NaClO ₃
Defoliant 2A ¹	0.4	<0.5	NaClO ₃ is not indicated on label
Defoliant 2B ¹	0.1	<0.5	NaClO ₃ is not indicated on label
Herbicide 3 ²	0.39	--	NaClO ₃ is not indicated on label
Herbicide 4 ²	0.21	--	NaClO ₃ is not indicated on label

Notes:

ppm - parts per million

1 - perchlorate analyzed by laboratory modified EPA Method 314.0 and verified the presence of perchlorate by IC-MS, chlorate analyzed by EPA Method 300

2 - analyzed by IC-MS

IC-MS - Ion Chromatography/Mass Spectrometry

TABLE 4.3
BLEACH MANUFACTURE DATES AND INITIAL CONCENTRATIONS

Bleach	Date Of Manufacture	Perchlorate Concentration ($\mu\text{g/L}$)
Brand 1	13-Jan-06	8.9
Brand 2	--	4.3
Brand 3	27-Mar-06	2.9
Brand 4	24-Aug-05	56
Brand 5	5-Feb-06	20
Brand 6	27-Mar-06	20

Notes:

All analyses were conducted by IC-MS

IC-MS - Ion chromatography/Mass Spectrometry

$\mu\text{g/L}$ - micrograms per liter

-- label smeared, unable to read date of manufacture

**TABLE 5.1
SUMMARY OF THE EVALUATION OF FALSE POSITIVES USING EPA METHOD 314.0**

Site Type	Site Description	EPA Method 314.0	Modified 314.0		IC-MS		EPA Method 300
		ClO ₄ ⁻ (µg/L)	ClO ₄ ⁻ (µg/L)	Interfering Compound	ClO ₄ ⁻ (µg/L)	Interfering Compound	NO ₃ ⁻ (mg/L)
Groundwater Plume	DDT Manufacturing Facility	16,461	<4.0	p-CBS - 2,767,472 ppb	Positive	p-CBS confirmed	-
		93,547	71	p-CBS - 3,190,448 ppb	Positive	p-CBS confirmed	-
		121,241	127,174	-	Positive	-	-
	Surfactant Use, Former Naval Base, California	8,137	53	p-CBS - 12,776 ppb	Positive	p-CBS confirmed	-
Groundwater Near Landfill	Stringfellow Landfill, California	31,640	159	p-CBS - 28,078 ppb	Positive	p-CBS confirmed	-
Carwash Runoff	Coin Operated, Massachusetts	<4.0	-	-	<0.250	-	-
	Coin Operated, Massachusetts	<4.0	-	-	<0.250	-	-
	Automated, Massachusetts	<4.0	-	-	0.90	-	-
	Automated, Massachusetts	<4.0	-	-	0.87	-	-
Surface Water	Burnt Bridge Creek, Vancouver, Washington	<4.0	<4.0	ND	0.6	-	-
		<4.0	<4.0	ND	1.6	-	-
	Willamette River, Portland, Oregon	<4.0	<4.0	ND	<0.250	-	-
		Eramosa and Speed River, Guelph, Ontario	<4.0	-	-	-	-
			<4.0	-	-	-	-
	Columbia River (downstream of Longview, Washington)	<4.0	<4.0	ND	<0.250	-	-
Groundwater near Septic System	Near Residential Septic System, Ontario	9.0	-	-	<0.250	-	7.6 ^a
	Near Septic System at Public Park, Ontario	53	<4.0	-	<0.25	-	110
		45	<4.0	-	<0.25	-	180
	Near Residential Septic System, California	<4.0	-	-	Positive	-	-
	Near Residential Septic System after Research Experiment to Determine Effect of Detergent-Use on Septic System, Ontario	20	15	-	0.7	-	200
		13	39	-	<0.25	-	200
		21	52	-	0.5	-	200
	Near Septic System at Public Park, Ontario	<4.0	<4.0	-	<0.250	-	39
<4.0		<4.0	-	<0.250	-	53	
<4.0		<4.0	-	<0.250	-	46	
Waste Water Treatment Plant	direct effluent of treatment plant (15 June06), Ontario	790	760	-	331	-	98
	about 25 feet downstream (15 June06), Ontario	700	640	-	1300	-	86
	direct effluent of treatment plant (1 Aug 06), Ontario	<4.0	-	-	-	-	16
	approx. 750 feet downstream (1 Aug 06), Ontario	<4.0	-	-	-	-	14

Notes:
 NO₃⁻ - nitrate
 ClO₄⁻ - perchlorate
 p-CBS - *p*-chlorobenzenesulfonate
 µg/L - micrograms per liter
 mg/L - milligrams per liter
 ND - not detected, quantitation limit not available
 < - not detected, associated value is quantitation limit
 Positive - confirmed positive for perchlorate, but concentration not available
 a - this sample also contained high sulfate (160 ppm)
 - - not analyzed

perchlorate over-reported
 false positive

TABLE 6.1
HISTORIC PERCHLORATE AND METALS CONTENT OF FIREWORKS

Purpose/Effect	Composition	(% by Wt)
White Light	Potassium Perchlorate	64
	Antimony, Sb	13
	Gum	10
	Potassium Nitrate	13
White Sparks	Potassium Perchlorate	42.1
	Titanium	42.1
	Dextrine	15.8
White Sparks "water fall"	Potassium Perchlorate	50
	"Bright" Aluminum Powder	25
	"Flitter" Aluminum, 30-80 mesh	12.5
	"Flitter" Aluminum, 5-30 mesh	12.5
Red Torch	Ammonium Perchlorate	70
	Strontium Carbonate	10
	Wood Meal (slow fuel)	20
Red Fireworks	Potassium perchlorate	67
	Strontium Carbonate	13.5
	Pine Root Pitch	13.5
	Rice Starch	6
Green Fireworks	Potassium Perchlorate	46
	Barium Nitrate	32
	Pine Root Pitch	16
	Rice Starch	6
Purple Flame	Potassium Perchlorate	70
	Polyvinyl Chloride	10
	Red Gum	5
	Copper Oxide	6
	Strontium Carbonate	9
	Rice Starch	5 (additional %)
Blue Flame	Ammonium Perchlorate	70
	Red Gum	10
	Copper Carbonate	10
	Charcol	10
	Dextrine	5 (additional %)
Yellow Flame	Potassium Perchlorate	70
	Sodium Oxalate	14
	Red Gum	6
	Shellac	6
	Dextrine	4
Black Smoke	Potassium Perchlorate	56
	Sulfur	11
	Anthracene	33
Flash and Sound	Potassium Chlorate	43
	Sulfur	26
	Aluminum	31
Whistle	Potassium Perchlorate	70
	Potassium Bensoate	30

Reference: J.A. Conkling. 1985 Chemistry of Pyrotechnics. Basic Principles and Theory.
Marcel Dekker, Inc. New York.

TABLE 6.2
SUMMARY OF WELL COMPLETIONS
Columbia Lake, Waterloo, Ontario

Location	Co-ordinates		Installed By	Date Installed	Ground Surface Elevation (m adatum)	Top of Casing (m adatum)	Stickup (m)	Well Diameter (cm)	Total Depth (m bgs)	Total Depth (m adatum)	Top of Sand Pack (m bgs)	Top of Well Screen (m bgs)	Bottom of Well Screen (m bgs)	Bottom of Sand Pack (m bgs)
	Easting	Northing												
Monitoring Wells														
UW 1	535,860.0	4,813,545.0	Env't CAN	18-May-06	101.357	102.056	0.699	2.5	3.75	97.607	2.30	2.50	3.10	3.75
UW 2	535,812.0	4,813,590.0	Env't CAN	18-May-06	101.582	102.449	0.867	2.5	3.40	98.182	2.44	2.80	3.40	3.40
UW 3	535,812.0	4,813,529.0	Env't CAN	18-May-06	102.467	102.363	-0.104	2.5	4.75	97.717	2.44	4.27	4.88	4.75
UW 4	535,828.0	4,813,525.0	Env't CAN	17-May-06	101.763	101.71	-0.053	2.5	4.03	97.733	3.00	3.35	3.96	4.03
UW 5	535,828.0	4,813,534.0	Env't CAN	17-May-06	101.926	101.878	-0.048	2.5	4.08	97.846	3.00	2.60	4.00	4.08
UW 6	535,828.0	4,813,533.0	Env't CAN	17-May-06	101.926	101.867	-0.059	2.5	1.90	100.026	1.00	1.20	1.80	1.90
UW 7	535,842.0	4,813,474.0	Env't CAN	18-May-06	100.982	101.654	0.672	2.5	3.82	97.162	2.70	3.00	3.66	3.82
UW 8	535,842.0	4,813,472.0	Env't CAN	18-May-06	100.982	101.613	0.631	2.5	1.96	99.022	1.00	1.20	1.80	1.96
Lysimeters														
LY1	535,820.3	4,813,493.7	Env't CAN	19-May-06	101.916	--	--	--	0.86	--	--	--	--	--
LY2	535,830.9	4,813,532.6	Env't CAN	19-May-06	NA	--	--	--	0.7	--	--	--	--	--
LY3	535,828.0	4,813,520.0	Env't CAN	24-May-06	NA	--	--	--	0.6	--	--	--	--	--
LY4	535,828.0	4,813,531.0	Env't CAN	24-May-06	NA	--	--	--	0.69	--	--	--	--	--
LY5	535,824.0	4,813,542.0	Env't CAN	24-May-06	101.922	--	--	--	0.81	--	--	--	--	--
LY6	535,818.0	4,813,538.0	Env't CAN	24-May-06	NA	--	--	--	0.61	--	--	--	--	--
LY7	535,828.0	4,813,523.5	Env't CAN	24-May-06	NA	--	--	--	0.66	--	--	--	--	--
LY8	535,824.0	4,813,527.0	Env't CAN	25-May-06	102.116	--	--	--	0.81	--	--	--	--	--
LY9	535,838.9	4,813,538.2	Env't CAN	25-May-06	NA	--	--	--	0.71	--	--	--	--	--
LY10	535,828.0	4,813,533.0	Env't CAN	7-Jun-06	NA	--	--	--	0.66	--	--	--	--	--

Notes:

m - metres

m adatum - metres above datum

m bgs - metres below ground surface

cm - centimetres

NA - lysimeter not surveyed prior to destruction

-- not applicable

Env't CAN - Environment Canada

TABLE 6.3
SUMMARY OF ANALYTICAL RESULTS FOR SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
Columbia Lake, Waterloo, Ontario

Sample ID	FO1A	FO1B	FO3A	FO3B	FO5A	FO5B	FO7A	FO7B	FO9A	FO9B
Date Sampled	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006
Date of Analysis	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,
<i>Parameters (mg/kg)</i>										
Perchlorate	0.00014	0.0016	0.0033	0.0012	0.00052	0.0012	0.000097	0.0016	0.00088	0.0010
Nitrate (N)	11	7	3	4	3	4	11	15	2 U	3
Nitrite (N)	1.1	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.9	0.5 U	0.5 U	0.5 U
Soluble (20:1) Sulphate	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U
Antimony	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Selenium	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Aluminum	6,100	7,600	6,600	7,700	7,800	9,700	4,900	5,200	6,900	7,700
Arsenic	3	3	2	3	3	4	2	2	3	3
Barium	41	54	47	54	52	70	33	39	47	57
Beryllium	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5	0.5 U	0.5 U	0.5 U	0.5 U
Bismuth	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Cadmium	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U
Calcium	9,100	11,000	5,100	5,100	4,600	5,000	2,900	3,700	8,600	7,200
Chromium	13	15	13	16	15	18	10	12	14	16
Cobalt	4.5	5.3	4.8	5.5	5.8	6.8	3.5	3.7	4.8	5.4
Copper	9.5	13	12	12	11	15	8.1	9.4	11	11
Iron	16,000	18,000	16,000	18,000	19,000	21,000	13,000	15,000	17,000	19,000
Lead	17	19	14	16	20	20	13	13	14	16
Magnesium	5,100	5,700	3,300	3,000	3,300	3,400	1,500	1,600	4,900	4,000
Manganese	570	670	470	530	620	660	550	620	500	580
Molybdenum	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Nickel	8.5	11	9.4	15	11	15	6.1	6.8	9.7	13
Phosphorus	840	880	690	740	720	790	750	790	790	820
Potassium	750	750	730	830	910	1000	770	560	790	770
Silver	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U
Sodium	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U
Strontium	14	18	12	12	12	13	9	11	13	13
Sulfur	450	480	370	420	380	440	430	480	360	380
Thallium	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Tin	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Titanium	270	280	260	310	300	340	230	250	280	300
Uranium	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U
Vanadium	29	31	26	30	31	34	23	27	30	33
Zinc	53	65	48	57	58	67	44	48	50	55
Zirconium	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U

TABLE 6.3
SUMMARY OF ANALYTICAL RESULTS FOR SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
Columbia Lake, Waterloo, Ontario

Sample ID	FO10A	FO10B	FO11A	FO11B	FO13A	FO13B	FO15A	FO15B	FO20A	FO20B
Date Sampled	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006
Date of Analysis	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,
<i>Parameters (mg/kg)</i>										
Perchlorate	0.045	0.0067	0.0019	0.00059	0.0012	0.0037	0.0017	0.00041	0.00017	0.0016
Nitrate (N)	7	10	7	7	17	13	8	3	2 U	6
Nitrite (N)	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Soluble (20:1) Sulphate	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U
Antimony	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Selenium	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Aluminum	5,000	6,100	7,400	8,200	5,000	5,200	8,500	8,000	7,600	8,100
Arsenic	2	3	3	3	2	3	4	4	3	3
Barium	32	40	47	54	29	32	53	50	49	51
Beryllium	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Bismuth	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Cadmium	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U
Calcium	2,800	3,900	7,300	10,000	4,200	3,800	9,900	12,000	5,700	6,400
Chromium	11	13	13	15	10	11	16	15	16	17
Cobalt	3.8	4.6	5.2	5.6	3.4	3.8	5.8	5.8	5.8	6.1
Copper	7.3	9.9	12	14	7.0	7.6	14	13	11	12
Iron	15,000	17,000	16,000	18,000	13,000	14,000	19,000	18,000	20,000	20,000
Lead	12	15	17	21	13	15	20	19	18	18
Magnesium	1,700	2,000	4,600	6,100	2,000	1,900	6,100	7,000	3,400	3,800
Manganese	420	550	700	760	390	400	720	660	550	600
Molybdenum	0.5 U	0.5 U	0.5 U	0.6	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Nickel	6.8	9.7	12	13	7.1	9.7	12	13	11	11
Phosphorus	630	750	740	830	680	650	790	720	710	850
Potassium	570	630	940	950	850	670	970	970	890	1,100
Silver	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U
Sodium	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U
Strontium	8	10	12	13	9	8	15	15	10	11
Sulfur	330	400	450	510	430	390	470	430	370	480
Thallium	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Tin	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1
Titanium	240	270	280	310	240	250	320	320	330	340
Uranium	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U
Vanadium	26	30	26	29	22	24	30	28	35	34
Zinc	42	53	60	73	43	45	67	62	59	65
Zirconium	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U

TABLE 6.3
SUMMARY OF ANALYTICAL RESULTS FOR SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
Columbia Lake, Waterloo, Ontario

Sample ID	FO20C	FO21A	FO23A	FO23B	FO24A	FO24B	FO25A	FO25B	FO26A	FO26B
Date Sampled	02 Jul 2006	29 Jun 2006	29 Jun 2006	02, 04 Jul 2006	29 Jun 2006	02, 04 Jul 2006	29 Jun 2006	02, 04 Jul 2006	30 Jun 2006	02 Jul 2006
Date of Analysis	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,
<i>Parameters (mg/kg)</i>										
Perchlorate	0.24	0.013	0.00039	0.00028	0.00044	0.00051	0.00032	0.00010	0.00013	0.0026
Nitrate (N)	5	5	6	2 U	4	2 U	6	4	2 U	4
Nitrite (N)	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Soluble (20:1) Sulphate	10 U	10 U	10 U	23	10 U	10 U	10 U	10 U	350	1,800
Antimony	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Selenium	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Aluminum	7,700	6,100	6,700	5,700	6,700	7,100	8,600	8,900	3,200	3,600
Arsenic	3	3	3	3	3	2	3	4	3	3
Barium	50	38	39	36	40	44	55	56	46	40
Beryllium	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Bismuth	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Cadmium	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U
Calcium	5,800	6,400	12,000	11,000	4,200	6,300	6,700	5,500	120,000	120,000
Chromium	16	14	12	11	11	12	15	16	8.2	8.9
Cobalt	5.7	4.3	4.5	3.9	4.5	5.0	6.3	6.5	3.5	4.3
Copper	12	9.0	8.9	8.8	8.6	9.7	12	13	7.9	12
Iron	19,000	17,000	13,000	12,000	13,000	14,000	16,000	17,000	9,700	11,000
Lead	14	16	12	11	14	15	14	14	6	6
Magnesium	3,500	3,300	6,900	6,100	2,500	3,300	4,300	3,700	32,000	28,000
Manganese	500	450	430	390	450	480	590	610	470	410
Molybdenum	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Nickel	12	8.6	16	8.0	10	8.9	13	12	9.0	8.5
Phosphorus	740	640	620	650	540	590	680	720	530	580
Potassium	960	600	970	880	830	880	930	990	810	800
Silver	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U
Sodium	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U	140	180
Strontium	12	10	11	10	9	11	11	12	120	120
Sulfur	350	370	260	310	320	390	350	380	710	1,300
Thallium	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Tin	1 U	1 U	1	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Titanium	350	290	270	250	290	310	320	340	250	260
Uranium	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	42	47
Vanadium	32	30	21	19	21	22	25	26	14	14
Zinc	51	54	51	46	48	53	49	52	38	41
Zirconium	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U

TABLE 6.3
SUMMARY OF ANALYTICAL RESULTS FOR SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
Columbia Lake, Waterloo, Ontario

Sample ID	LA1A	LA1B	LA2A	LA2B	LA3A	LA3B	LA3C	LA4A	LA4B	LA8A
Date Sampled	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	02 Jul 2006	29 Jun 2006	02 Jul 2006	29 Jun 2006
Date of Analysis	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,
<i>Parameters (mg/kg)</i>										
Perchlorate	0.00023	0.0025	0.00037	0.0052	0.0004	0.0083	0.0065	0.00063	0.0034	0.00048
Nitrate (N)	7	8	9	14	7	13	8	38	10	3
Nitrite (N)	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	1.5	0.5 U	0.5 U
Soluble (20:1) Sulphate	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U	10 U
Antimony	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Selenium	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Aluminum	6,400	5,400	5,300	5,700	6,000	6,000	5,500	5,500	5,700	6,200
Arsenic	3	3	2	2	3	3	3	3	3	2
Barium	39	34	34	36	35	33	33	37	46	37
Beryllium	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Bismuth	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U
Cadmium	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U
Calcium	4,500	9,900	4,600	4,000	3,100	2,700	3,600	3,500	6,100	2,900
Chromium	13	14	11	13	12	13	12	11	13	13
Cobalt	4.9	3.9	3.8	4.0	4.2	4.9	4.1	4.3	4.1	4.5
Copper	8.5	9.2	7.9	11	8.0	6.5	7.0	7.8	8.4	8.9
Iron	16,000	14,000	13,000	14,000	15,000	17,000	15,000	14,000	15,000	16,000
Lead	16	16	14	14	22	12	15	16	16	14
Magnesium	2,700	4,400	2,500	2,000	2,000	1,900	2,000	2,000	2,800	2,000
Manganese	500	450	480	470	460	480	430	520	500	450
Molybdenum	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Nickel	16	7.2	7.6	7.0	9.7	7.9	7.1	8.7	7.3	11
Phosphorus	700	750	680	730	650	700	700	640	710	650
Potassium	760	610	580	650	700	510	600	540	700	610
Silver	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U
Sodium	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U	100 U
Strontium	10	16	9	9	11	9	11	8	13	8
Sulfur	370	450	370	480	370	140	370	380	470	300
Thallium	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Tin	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U	1 U
Titanium	280	250	240	270	270	280	270	260	260	290
Uranium	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U	20 U
Vanadium	29	24	24	25	26	30	26	25	26	28
Zinc	52	47	48	47	49	39	43	47	49	49
Zirconium	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U	5 U

TABLE 6.3
SUMMARY OF ANALYTICAL RESULTS FOR SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
Columbia Lake, Waterloo, Ontario

Sample ID	LA8B	LA9A	LA9B	DEBRIS B
Date Sampled	02 Jul 2006	29 Jun 2006	02 Jul 2006	02 Jul 2006
Date of Analysis	14,17 Jul 2006,	14,17 Jul 2006,	14,17 Jul 2006,	
<i>Parameters (mg/kg)</i>				
Perchlorate	0.31	0.0041	0.013	0.029
Nitrate (N)	6	2 U	5	370
Nitrite (N)	0.5 U	0.5 U	1.3	48
Soluble (20:1) Sulphate	10 U	10 U	10 U	1,900
Antimony	1 U	1 U	1 U	4
Selenium	1 U	1 U	1 U	1 U
Aluminum	5,900	7,000	5,600	1,900
Arsenic	2	3	2	4
Barium	34	43	86	410
Beryllium	0.5 U	0.5 U	0.5 U	0.5 U
Bismuth	5 U	5 U	5 U	19
Cadmium	0.3 U	0.3 U	0.3 U	0.3 U
Calcium	3,000	7,900	6,400	39,000
Chromium	12	13	11	16
Cobalt	4.3	5.0	4.2	1.9
Copper	8.3	9.0	8.0	390
Iron	15,000	15,000	12,000	1,800
Lead	14	15	13	230
Magnesium	1,900	4,500	3,500	5,000
Manganese	450	440	360	320
Molybdenum	0.5 U	0.5 U	0.5 U	0.6
Nickel	9.4	12	7.6	2.2
Phosphorus	620	600	660	1,300
Potassium	770	910	890	22,000
Silver	0.3 U	0.3 U	0.3 U	0.3 U
Sodium	100 U	100 U	100 U	1,400
Strontium	8	15	10	54
Sulfur	320	320	410	5,700
Thallium	1 U	1 U	1 U	1 U
Tin	1 U	1 U	1 U	79
Titanium	260	280	240	49
Uranium	20 U	20 U	20 U	26
Vanadium	26	24	19	2.9
Zinc	44	46	40	170
Zirconium	5 U	5 U	5 U	5 U

Notes:

Bold typeface indicates measurements above reporting limit

U - analyte was not detected; associated value is the reporting limit

FO#A - soil sample collected in fallout area **before** the fireworks displayFO#B - soil sample collected in fallout area **after** the fireworks displayLA#A - soil sample collected in launch area **before** the fireworks displayLA#B - soil sample collected in launch area **after** the fireworks display

TABLE 6.4
SUMMARY OF GROUNDWATER ELEVATIONS
Columbia Lake, Waterloo, Ontario

Sample Location	28-Jun-06	01-Jul-06	03-Jul-06	04-Jul-06	07-Jul-06	08-Aug-06	09-Aug-06	19-Oct-06
LY1	--	--	--	--	--	--	0.62	0.61
LY2	7.73	8.83	10.5	11.8	12.5	4.24	--	--
LY3	22.7	22.6	22.4	22.1	22	20.3	--	22.3
LY4	37.8	38.4	40.4	42.5	42.5	37.9	--	35.7
LY5	--	--	--	--	--	8.45	--	9.93
LY6	1.63	1.7	--	1.81	--	2.01	--	--
LY7	28.2	29	28.1	29.2	28.4	21.3	--	17.3
LY8	12.7	12.3	12.9	12.4	12.1	--	--	--
LY9	14.4	13.1	18.6	19.1	--	--	--	--

Notes:

All concentrations are in units of micrograms per liter ($\mu\text{g/l}$)

-- - sample not collected

TABLE 6.5
SUMMARY OF PERCHLORATE CONCENTRATIONS IN PORE WATER

Sample Location Date Sampled	LY3 28-Jun-06	LY3 07-Jul-06	LY3 08-Aug-06	LY6 28-Jun-06	LY6 07-Jul-06	LY6 08-Aug-06	LY7 28-Jun-06	LY7 07-Jul-06	LY7 08-Aug-06	LY8 28-Jun-06	LY8 07-Jul-06	LY9 28-Jun-06	LY9 07-Jul-06
<i>Metals, Total (µg/l)</i>													
Aluminum	5 U	17	8	5 U	53	8	5 U	5.0 U	5 U	5 U	6	5 U	5.0 U
Antimony	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1.0 U
Arsenic	3	4	5	10	9	9	7	5	6	5	3	6	6
Barium	470	350	380	170	170	260	190	200	220	220	250	150	140
Beryllium	0.5 U	0.50 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	0.50 U	0.5 U	0.50 U
Bismuth	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1.0 U
Boron	590	47	67	520	140	110	570	69	120	570	48	410	100
Cadmium	0.1 U	0.10 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	0.10 U	0.1 U	0.10 U
Calcium	130,000	130,000	130,000	84,000	67,000	120,000	99,000	85,000	99,000	97,000	130,000	92,000	78,000
Chromium	5 U	5.0 U	5 U	5 U	5.0 U	5 U	5 U	5.0 U	5 U	5 U	5.0 U	5 U	5.0 U
Cobalt	2.2	1.7	1.6	0.5 U	0.50 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	1.1	0.5 U	0.50 U
Copper	1	4	5	2	2	11	2	3	5	2	1	7	12
Iron	50 U	50 U	50 U	50 U	50 U	50 U	50 U	50 U	50 U	50 U	240	50 U	50 U
Lead	0.5 U	0.50 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	0.50 U	0.5 U	0.50 U
Lithium	12	6	9	19	17	11	21	8	16	19	8	15	9
Magnesium	38,000	38,000	38,000	34,000	48,000	38,000	40,000	32,000	46,000	36,000	37,000	45,000	45,000
Manganese	150	30	19	2 U	5	6	2 U	2	4	14	160	150	81
Molybdenum	7	3	4	9	11	7	12	6	9	10	5	11	12
Nickel	640	200	93	29	12	38	26	13	17	55	99	51	37
Phosphorus	50 U	50 U	56	50 U	50 U	50 U	50 U	50 U	50 U	50 U	50 U	50 U	50 U
Potassium	2,300	2,400	2,300	1,500	1,600	1,500	2,000	1,600	1,600	1,400	1,100	1,600	1,400
Selenium	2 U	2.0 U	2 U	2 U	2.0 U	2 U	2 U	2.0 U	2 U	2 U	2.0 U	2 U	2.0 U
Silicon	51,000	57,000	60,000	56,000	66,000	55,000	54,000	60,000	55,000	50,000	54,000	51,000	62,000
Silver	0.1 U	0.10 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	0.10 U	0.1 U	0.10 U
Sodium	6,500	5,600	5,700	15,000	13,000	34,000	4,000	2,800	3,500	6,800	6,100	5,900	3,900
Strontium	340	210	230	450	260	260	410	190	240	370	270	350	180
Tellurium	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1.0 U
Thallium	0.1 U	0.10 U	0.09	0.1 U	0.10 U	0.08	0.1 U	0.10 U	0.06	0.1 U	0.10 U	0.1 U	0.10 U
Thorium	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1.0 U
Tin	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1.0 U
Titanium	5 U	5.0 U	5 U	5 U	5.0 U	5 U	5 U	5.0 U	5 U	5 U	5.0 U	5 U	5.0 U
Tungsten	2	1	1	3	5	2	5	3	3	4	2	2	4
Uranium	18	7.2	8.5	16	6.2	12	9.4	5.4	6.3	12	11	9.4	7.5
Vanadium	60	64	53	120	160	89	170	110	95	100	26	95	120
Zinc	5 U	5.0 U	5	5 U	5.0 U	5 U	5 U	5.0 U	5	8	5.0 U	13	11
Zirconium	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1 U	1.0 U	1 U	1.0 U

Notes:

U - not detected

TABLE 6.6
SUMMARY OF GROUNDWATER ELEVATIONS

Date	Water Level Elevation (meters above datum)								
	UW1	UW2	UW3	UW4	UW5	UW6	UW7	UW8	Lake
9-May-06	97.797	100.412	-	-	-	-	-	-	-
10-May-06	98.687	101.062	97.967	-	-	-	-	-	-
11-May-06	99.917	101.102	100.547	100.593	-	-	-	-	-
12-May-06	100.137	101.642	100.707	100.783	100.696	100.916	100.072	99.572	-
16-May-06	100.277	101.632	100.807	100.803	100.826	100.966	100.142	100.102	-
17-May-06	100.327	101.657	100.862	100.898	100.871	101.026	100.167	100.142	-
18-May-06	100.372	101.672	100.887	100.958	100.946	101.131	100.217	100.237	99.940
24-May-06	100.386	101.439	100.793	100.870	100.913	101.017	100.174	100.203	99.820
25-May-06	100.376	101.379	100.778	100.830	100.888	101.017	100.172	100.178	99.810
26-May-06	100.366	101.369	100.763	100.810	100.863	100.947	100.169	100.153	99.810
29-May-06	100.281	101.167	100.673	100.728	100.758	100.842	100.112	100.058	99.780
1-Jun-06	100.411	101.597	100.788	-	-	-	-	-	-
4-Jun-06	100.501	102.357	100.818	100.925	100.991	101.097	100.222	100.188	99.840
5-Jun-06	100.401	101.439	100.783	100.855	100.913	101.005	100.189	100.161	99.825
7-Jun-06	100.361	101.284	100.708	100.770	100.828	100.917	100.134	100.093	99.810
22-Jun-06	-	-	-	100.378	-	-	99.874	99.728	-
23-Jun-06	99.726	100.539	100.263	100.350	100.278	100.577	99.847	99.508	99.640
10-Jul-06	99.054	100.339	98.488	100.048	100.083	100.315	99.714	99.528	99.780
23-Aug-06	98.694	100.279	100.288	99.738	99.843	100.132	99.374	99.471	99.750
18-Oct-06	99.971	101.604	100.762	101.134	100.886	101.066	100.105	99.927	99.820
23-Mar-07	100.571	101.604	101.028	101.420	101.358	101.577	100.314	100.533	100.000

Notes:

- - water level not recorded

The South-West culvert on the Southern edge of the landbridge/causeway is used as datum "100 meters" (until it can be tied in to a benchmark.)

TABLE 6.7
SUMMARY OF MEASURED GROUNDWATER PARAMETERS

Identifier	pH	eH (mV)	Date Recorded
Monitoring Wells			
UW1	7.2	129	30-Jun-06
UW2	NM	NM	NA
UW3	7.2	117	30-Jun-06
UW4	7.2	127	30-Jun-06
UW5	7.4	154	30-Jun-06
UW6	6.9	81	30-Jun-06
UW7	7.3	25	30-Jun-06
UW8	7.2	142	30-Jun-06
Lysimeters			
LY1	NM	NM	NA
LY2	7.4	NM	1-Jul-06
LY3	7.5	NM	1-Jul-06
LY4	7.9	NM	1-Jul-06
LY5	7.6	NM	1-Jul-06
LY6	7.9	NM	1-Jul-06
LY7	7.9	NM	1-Jul-06
LY8	7.5	NM	1-Jul-06
LY9	7.5	NM	1-Jul-06

Notes:

NM - not measured

NA - not applicable

TABLE 6.9
SUMMARY METALS CONCENTRATIONS IN GROUNDWATER

Sample Location Date Sampled	UW1 25-Jun-06	UW1 11-Jul-06	UW1 10-Aug-06	UW1 23-Mar-07	UW2 23-Jun-06	UW2 11-Jul-06	UW2 10-Aug-06	UW2 23-Mar-07	UW3 25-Jun-06	UW3 11-Jul-06	UW3 09-Aug-06	UW3 23-Mar-07	UW5 23-Jun-06	UW5 11-Jul-06	UW5 09-Aug-06	UW5 23-Mar-07	UW6 30-Jun-06	UW6 11-Jul-06	UW6 09-Aug-06	UW6 23-Mar-07	
<i>Metals, Total (µg/l)</i>																					
Aluminum	18	2,000	390	28	45	680	3,500	9,100	710	1,700	7,400	350	370	33	100	180	15	17	31	54	
Antimony	1 U	1.0 U	1 U	1 U	1 U	2	3	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	
Arsenic	3	13	17	4	4	8	11	12	3	3	4	3	1	1	1	1 U	7	8	7	1 U	
Barium	17	49	47	49	31	54	83	130	65	69	130	55	11	18	25	130	36	30	29	13	
Beryllium	0.5 U	0.50 U	0.5 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	0.5 U	0.50 U	0.5 U	0.5 U	
Bismuth	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	
Boron	520	28	29	22	610	65	75	63	450	16	24	39	530	11	12	45	610	27	100	21	
Cadmium	0.1 U	0.1	0.1 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1	0.1 U	0.10 U	0.1 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	
Calcium	68,000	160,000	100,000	80,000	89,000	100,000	120,000	170,000	92,000	100,000	150,000	83,000	77,000	87,000	91,000	39,000	130,000	130,000	120,000	120,000	
Chromium	5 U	5.0 U	5 U	5 U	5 U	5.0 U	5 U	13	5 U	5.0 U	10	5 U	5 U	5.0 U	5 U	5 U	5 U	5.0 U	5 U	5 U	
Cobalt	0.8	3.6	1.7	0.5	1	2.1	3.3	7	0.6	1.3	5.8	0.5 U	0.5 U	0.9	1.1	0.8	1.5	1.4	1.5	0.5 U	
Copper	2	5	2	2	1 U	3	7	16	1	2	12	48	1 U	1	1 U	99	2	1.0 U	2	9	
Iron	50 U	13,000	12,000	1,400	50 U	1,700	6,100	15,000	610	2,900	13,000	1,800	290	50 U	420	210	140	1,200	1,800	63	
Lead	0.5 U	10	1.4	0.8	0.5 U	3.2	5	10	0.5 U	3.2	7.3	23	0.5 U	0.7	0.5 U	15	1	0.6	1.1	2.8	
Lithium	6	6	5 U	5	6	16	23	24	11	8	17	6	9	6	7	6	5 U	5.0 U	5 U	5 U	
Magnesium	30,000	53,000	41,000	37,000	25,000	26,000	32,000	46,000	35,000	36,000	44,000	34,000	31,000	35,000	37,000	13,000	37,000	40,000	35,000	35,000	
Manganese	240	750	450	380	800	730	690	810	80	140	330	52	31	20	68	14	870	570	450	4	
Molybdenum	11	12	14	5	21	76	130	88	4	4	4	10	5	6	3	5	7	7	9	2	
Nickel	2	4	2	1 U	3	3	7	14	1 U	1	11	1	1	1.0 U	1 U	1	2	1.0 U	1	1 U	
Phosphorus	50 U	250	100	NA	50 U	130	250	NA	50 U	75	340	NA	50 U	50 U	50 U	NA	50 U	50 U	50 U	NA	
Potassium	1,600	2,800	2,200	1,800	580	1,000	2,200	4,100	1,700	2,200	4,200	1,900	1,600	2,000	2,200	2,500	3,200	3,500	3,400	1,300	
Selenium	2 U	2.0 U	2 U	2 U	2 U	2.0 U	2 U	2 U	2 U	2.0 U	2 U	2 U	2 U	2.0 U	2 U	2 U	2 U	2.0 U	2 U	2 U	
Silicon	7,200	11,000	9,200	8,400	7,700	8,900	15,000	28,000	10,000	11,000	21,000	9,200	8,300	6,100	7,000	3,200	10,000	9,800	9,800	6,200	
Silver	0.1 U	0.10 U	0.1 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	0.1 U	0.10 U	0.1 U	0.1 U	
Sodium	12,000	22,000	21,000	11,000	93,000	200,000	200,000	190,000	10,000	9,400	9,600	28,000	10,000	9,300	7,700	46,000	22,000	20,000	33,000	22,000	
Strontium	160	300	260	200	270	250	270	320	210	210	280	180	140	150	170	76	200	200	180	170	
Tellurium	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	
Thallium	0.1 U	0.10 U	0.050 U	0.05 U	0.1 U	0.10 U	0.06	0.1	0.1 U	0.10 U	0.12	0.05 U	0.1 U	0.10 U	0.050 U	0.05 U	0.1 U	0.10 U	0.050 U	0.05 U	
Thorium	1 U	1.0 U	1 U	1 U	1 U	1.0 U	2	6	1 U	1.0 U	3	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	
Tin	1 U	2	10	5	1 U	2	4	9	1 U	1.0 U	1 U	3	1 U	2	1 U	1	1 U	1.0 U	1	1 U	
Titanium	5 U	100	21	5 U	5 U	12	150	410	17	12	310	14	13	5.0 U	5 U	7	5 U	5.0 U	5 U	5 U	
Tungsten	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	
Uranium	3.5	6.1	4.3	2.9	11	48	73	62	1.1	1.6	1.4	2.7	3.8	3.5	3.6	2.6	4.1	3.9	6	2.1	
Vanadium	2	11	23	1	1 U	5	10	25	2	9	27	2	8	6	13	7	3	19	17	16	
Zinc	5 U	27	14	7	5 U	7	29	57	5 U	9	46	22	5 U	5.0 U	23	31	12	5.0 U	7	8	
Zirconium	1 U	3	1	1 U	1 U	2	4	8	1 U	3	6	1 U	1 U	1.0 U	1 U	1 U	1 U	1.0 U	1 U	1 U	

Notes:
U - not detected
NA - not analyzed

TABLE 6.10
SUMMARY OF ANALYTICAL RESULTS FOR UNSPENT FIREWORKS CHARGES AND DEBRIS
University of Massachusetts, Dartmouth Campus, MA

Sample ID Sample Type Date Sampled	Charge 1_B Fireworks Charge 8/14/2006	Charge 2_B Fireworks Charge 8/14/2006	FOA8B & FOA27B Fireworks Debris 07/05/06
<i>Anions (mg/kg)</i>			
Perchlorate	389,000	355,000	32
<i>Metals, Total (mg/kg)</i>			--
Aluminum	77,000	120,000	2,100
Antimony	1.2 U	1.2 U	2.0U
Arsenic	1.2 U	1.2 U	--
Barium	440	190	55
Beryllium	0.5 U	0.5 U	--
Cadmium	0.76	1	--
Calcium	1,700	720	22,000
Chromium	61	94	--
Cobalt	0.5 U	0.5 U	--
Copper	110	170	--
Iron	540	680	--
Lead	6	7.6	--
Magnesium	80,000	120,000	1,700
Manganese	350	490	--
Nickel	3.9	5.5	--
Potassium	160,000	160,000	4,600
Selenium	5 U	5 U	--
Silver	0.5 U	0.5 U	--
Sodium	120 U	150	9,300
Strontium	18	22	19
Thallium	0.25 U	0.25 U	--
Vanadium	12 U	12 U	--
Zinc	180	260	--

Notes:

-- - data not available

¹ - metals analysis performed by Alpha Woods Hole Lab of Westminister, MA² - perchlorate analysis performed by Shaw Environmental Research Lab of Lawrenceville, NJ

TABLE 6.11
SUMMARY OF ANALYTICAL RESULTS FOR SURFICIAL SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
University of Massachusetts, Dartmouth Campus, MA

Sample Location QA/QC Sample Type Date Sampled	FOA3 A 06/14/06	FOA3 B 07/05/06	FOA4 A 06/14/06	FOA4 B 07/05/06	LA5 A 06/14/06	LA5ADUP Field Duplicate 06/14/06	FOA5 A 06/15/06	FOA5 B 07/05/06	FOA6 A 06/15/06	FOA6 B 07/05/06	FOA7 A 06/15/06	FOA7 B 07/05/06
<i>Anions (mg/kg)</i>												
Perchlorate	0.000690U	0.0039	0.000132J	0.28	0.000483J	0.000408J	0.000750U	0.285	0.000763U	0.0496	0.000750U	0.00224
Nitrate	1.4U	1.4U	1.4U	1.4U	1.1U	1.1U	1.5U	1.6U	2.0	1.5U	1.5U	1.4U
Sulfate	140U	140U	140U	140U	110U	110U	150U	160U	160U	150U	150U	140U
<i>Metals, Total (mg/kg)</i>												
Aluminum	8100	12000	9900	12000	2100	2200	8400	10000	7900	11000	8700	9700
Antimony	2.8U	2.8U	2.7U	2.7U	2.2U	2.2U	3.0U	3.3U	3.1U	2.9U	3.0U	2.8U
Barium	16	21	16	18	8.5	8	14	21	14	23	15	19
Calcium	490	720	560	590	370	330	440	650	430	550	500	680
Magnesium	720	1300	690	1000	590	520	570	1300	530	1700	710	1400
Potassium	260	400	250	380	230	200	150	400	180	710	280	510
Sodium	86J	150	55J	95J	230	120	100J	160	55J	84J	120U	160
Strontium	2.1J	4.8	2.7	4.4	3.8	3.3	6.1	11	4.9	8.5	5.2	7.0

TABLE 6.11
SUMMARY OF ANALYTICAL RESULTS FOR SURFICIAL SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
University of Massachusetts, Dartmouth Campus, MA

Sample Location QA/QC Sample Type Date Sampled	FOA8 A	FOA8 BLP	FOA8 BCLP	FOA9 A	FOA9 B	FOA13 A	FOA13 B	FOA14 A	FOA14 B	FOA15 A	FOA15 BLP	FOA15 BCLP
<i>Anions (mg/kg)</i>												
Perchlorate	0.000750U	0.00708	0.00655	0.000629J	0.324	0.000707U	0.0475	0.000665U	0.0126	0.000751U	0.022	0.000524J
Nitrate	1.4U	1.0U	1.5U	1.4U	1.4U	1.6U	1.4U	1.4U	1.5U	1.5U	1.0U	1.5U
Sulfate	150U	100U	150U	140U	140U	140U	140U	140U	150U	160U	110U	150U
<i>Metals, Total (mg/kg)</i>												
Aluminum	8700	2200	12000	9900	12000	7400	7700	6500	9600	11000	2400	11000
Antimony	3.0U	2.0U	3.0U	2.8U	2.8U	2.8U	2.7U	2.7U	3.0U	3.1U	2.1U	3.0U
Barium	16	11	16	17	22	15	15	13	16	19	11	17
Calcium	760	470	720	520	420	520	630	420	610	830	420	570
Magnesium	610	1300	1000	850	1400	1000	970	1000	1100	1100	1300	1000
Potassium	260	470	390	330	590	280	300	270	370	380	460	320
Sodium	86J	240	110J	100J	140	160	160	120	140	140	220	95J
Strontium	2.6J	1.9J	3.4	2.9	3.4	5.5	7.8	3.8	6.0	4.4	3.0	4.5

TABLE 6.11
SUMMARY OF ANALYTICAL RESULTS FOR SURFICIAL SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
University of Massachusetts, Dartmouth Campus, MA

Sample Location QA/QC Sample Type Date Sampled	FOA16 A	FOA16 BLP	FOA16 BCLP	FOA17 A	FOA17 B	FOA26 A	FOA26 B	FOA27 A	FOA27 BLP	FOA27 BCLP	FOA28 A	FOA28 B
	06/15/06	07/05/06	07/05/06	06/15/06	07/05/06	06/15/06	07/05/06	06/15/06	07/05/06	07/05/06	06/15/06	07/05/06
<i>Anions (mg/kg)</i>												
Perchlorate	0.000668U	5.03	0.0065	0.000529J	0.00253	0.000134J	0.000315J	0.000637U	0.011	0.00936	0.000677U	0.00194
Nitrate	8.3	1.0U	1.4U	1.3U	1.6	1.6	1.4U	1.3U	1.0U	1.5U	1.4U	1.2U
Sulfate	140U	100U	150U	140U	130U	140U	140U	130U	100U	150U	140U	260U
<i>Metals, Total (mg/kg)</i>												
Aluminum	12000	2300	9600	10000	10000	8200	11000	10000	2400	12000	11000	11000
Antimony	2.8U	2.1U	2.9U	2.8U	2.5U	2.8U	2.8U	2.6U	2.1U	2.9U	2.8U	2.6U
Barium	14	11	17	17	18	17	17	14	11	17	16	18
Calcium	540	460	580	740	930	730	680	220	440	660	580	440
Magnesium	1100	1300	1100	1100	980	910	1300	1000	1400	1000	1200	1500
Potassium	360	480	380	340	430	280	390	280	480	350	380	520
Sodium	52J	230	140	130	120	170	130	140	420	150	140	46J
Strontium	3.5	2.1	12	3.6	6.7	4.8	4.3	2J	2J	3.6	3.1	3.8

TABLE 6.11
SUMMARY OF ANALYTICAL RESULTS FOR SURFICIAL SOIL SAMPLES COLLECTED BEFORE AND AFTER A FIREWORKS DISPLAY
University of Massachusetts, Dartmouth Campus, MA

Sample Location QA/QC Sample Type Date Sampled	FOA30 A	FOA30 B	FOA32 A	FOA32 B
<i>Anions (mg/kg)</i>				
Perchlorate	0.000645U	0.000251J	0.000650U	0.000206J
Nitrate	2.0	1.3U	1.3U	1.5U
Sulfate	130U	130U	140U	150U
<i>Metals, Total (mg/kg)</i>				
Aluminum	12000	6200	9100	12000
Antimony	2.6U	2.6U	2.7U	3.0U
Barium	15	14	15	17
Calcium	330	360	360	620
Magnesium	1300	1000	1200	1200
Potassium	420	370	360	380
Sodium	66J	200	130	100J
Strontium	2.8	3.2	3.6	3.1

Notes:

all concentrations are in milligrams per kilogram (mg/kg) on a dry weight basis

FOA#A - Fallout area, sample grid number, pre-fireworks display sample

FOA#B - Fallout area, sample grid number, post fireworks display sample

FOA#BLP - Fallout area, sample grid number, post fireworks display,
launch platform sample (sand)

FOA#BCLP - Fallout area, sample grid number, post fireworks display,
composite sample from edge of launch platform (sand)

U - analyte was not detected; associated value is quantitation limit

J - concentration is estimated; below calibration curve

TABLE 6.12
SUMMARY OF HISTORICAL PERCHLORATE CONCENTRATIONS IN GROUNDWATER
University of Massachusetts, Dartmouth Campus, MA

Well Location	Sample Event									
	Jun-04 (µg/L)	Aug-04 (µg/L)	Sep-04 (µg/L)	Oct-04 (µg/L)	Dec-04 (µg/L)	Feb-05 (µg/L)	Jun-05 (µg/L)	Sep-05 (µg/L)	Apr-06 (µg/L)	25-Jul-06 (µg/L)
UMD-1	5.14	2.39	3.38	1.67	1U	1U	1U	1U	1U	1U
UMD-2	36.2	28.5	34.1	32.8	13.4	9.42*	1.58	1.4	1.74	2.25
UMD-3	7.1	5.37	7.96	7.5	0.915J	1.98	0.361J	1.58	1U	1U
UMD-4	1U	1U	1U	1U	1U	1U	1U	1U	1U	1U
UMD-5	NA	1U	1U	1U	0.644J	0.265J	1U	1U	0.897J	5.16
UMD-6	NA	1U	1U	2.71	2.09	1.98	0.962J	10.4	1.87	2.73
UMD-7	NA	62.2	40.1	31.2	20.5	24.8	24.7	20.2	14.6	12.4
UMD-8	NA	37.4	20.7	37.4	25.8	23	27.9	35	30	22.4

Notes:

NA - Not analyzed

J - Estimated value

U - Not detected. Value is the laboratory reporting limit

* - Sample collected on March 23, 2005

TABLE 6.13
ISOTOPE DATA FOR FIREWORKS, FLARE AND GROUNDWATER SAMPLES
University of Massachusetts, Dartmouth Campus, MA

Sample	Date Received	ClO₄⁻ δ³⁷Cl	ClO₄⁻ δ¹⁸O	ClO₄⁻ Δ¹⁷O
Solids				
Firework - 1	6-Nov-06	0.7	-19.4	0.090
Firework -2	6-Nov-06	0.1	-20.1	0.074
Flare - 1	6-Nov-06	0.1	-13.4	0.126
Groundwater				
Well - UMD-7	6-Nov-06	0.7	-17.1	0.064
Well - UMD - 8a	6-Nov-06	-0.1	-17.2	0.052
Well - UMD-8b	6-Nov-06	0.5	-17.3	0.127

Notes:ClO₄⁻ - Perchlorate

UMD - University of Massachusetts at Dartmouth

These samples were collected and analyzed by P.Hatzinger (Shaw Environmental) and his team under ESTCP Project (ER-0509)

TABLE 7.1
POTENTIAL PERCHLORATE IMPACTS TO THE ENVIRONMENT FROM VARIOUS SOURCES

Source	Amount Produced Annually	% Product Containing Perchlorate	Amount Perchlorate in Original Product	Order of Magnitude Estimate of Perchlorate Mass in Original Product (kg)	Amount Perchlorate after Combustion or Reaction	Order of Magnitude Minimum Perchlorate Mass Potentially Impacting Environment (kg)
Explosives	2.5×10^9 kg ⁵ .	<0.5% (estimated) ⁴ .	5.6%	10^6	0.035% of original	10^{2*}
Road Flare	3×10^7 flares sold ⁶ (estimated)	100%	11.1 g per flare (based on 15-min American flare)	10^5	0.03% of original perchlorate	10^{2*}
Sodium Chlorate	1.1×10^9 kg ⁷ .	100%	41 mg/kg	10^4	--	10^3 (6 % used for agriculture)
Bleach	3.1×10^9 L ⁸ .	100%	0.019 mg/L mean of 6 brands upon initial opening	10^2	0.154 mg/kg (mean, 6 weeks storage)	10^2
Fireworks	1×10^8 kg ⁹ .	50% (assumed)	372,000 mg/kg of charge	10^7	31.8 mg/kg of debris	$10^{-10^{2*}}$ (1-5% debris assumed)
Current Chilean Nitrate	6.8×10^7 kg ¹⁰ .	100%	0.01% ¹⁰ .	10^4	100%	10^4
Precipitation	6×10^{15} L ¹¹ .	100% (assumed)	0.01264 μ g/L ¹ .	10^5	N/A	10^5
Rocket Fuel	1.1×10^7 kg ² .	--	100%	10^7	0.0022% ³ .	$10^2 *$

Notes:

* - combustion residue, does not include spills, poor housekeeping or incomplete combustion/detonation

1. Jackson, 2007, Wet deposition only
2. Dasgupta et al., 2006
3. Jimmie Oxley, 2007 (unpublished data)
4. IME, 2005
5. Kramer, 2003
6. Geosyntec, 2005
7. Dept. of Commerce, 2003
8. Innovation Group, 2003
9. APA, 2007
10. Urbansky et la., 2001
11. NWRFC, 2005

Full citations can be found in the References Section

TABLE 7.2
SOURCE IDENTIFICATION: CO-CONSTITUENTS, ISOTOPIC SIGNATURES, GEOGRAPHIC REGION

Perchlorate Source	Co-constituents	Unique Isotopic Signature ?	Isotopic Markers**	Geographic Region
Fireworks	potassium, aluminum, magnesium, barium, strontium, nitrate	no	$\delta^{37}\text{Cl}$: 0.6 ± 0.9 ; $\delta^{18}\text{O}$: -17.2 ± 2.8 ; $\Delta^{17}\text{O}$: 0.01 ± 0.08	No specific region. Often near surface waters
Blasting Explosives	nitrate, sodium	no	"	KY, WV, WY, mining areas, construction sites
Road Flares	nitrate, strontium, potassium	no	"	No specific region
Sodium Chlorate	chlorate, sodium	no	"	Sodium chlorate defoliant used mostly on cotton in CA and AZ
Bleach (aged)	sodium, hypochlorite	yes*	$\delta^{37}\text{Cl}$: ~ 14 ; $\delta^{18}\text{O}$: ~ -55	No specific region.
Chilean Nitrate Fertilizer	nitrate, sodium	yes	$\delta^{37}\text{Cl}$: -12.8 ± 2.0 ; $\delta^{18}\text{O}$: -6.3 ± 2.5 ; $\Delta^{17}\text{O}$: 9.6 ± 0.7	Historic agricultural areas: fruit, tobacco, cotton crops CA, GA, KY, NC, SC
Rocket Fuel	ammonium	no	$\delta^{37}\text{Cl}$: 0.6 ± 0.9 ; $\delta^{18}\text{O}$: -17.2 ± 2.8 ; $\Delta^{17}\text{O}$: 0.01 ± 0.08	No specific region; associated with DOD and contractor sites

Notes:

* based on limited information

**Research conducted by Hatzinger et al. as part of ESTCP Project ER-0509

FIGURES



Notes:
 Chinese flares of 5 different lengths are shown, corresponding to flares with burn times ranging from 5 to 30 minutes

Photograph of Chinese Road Flares



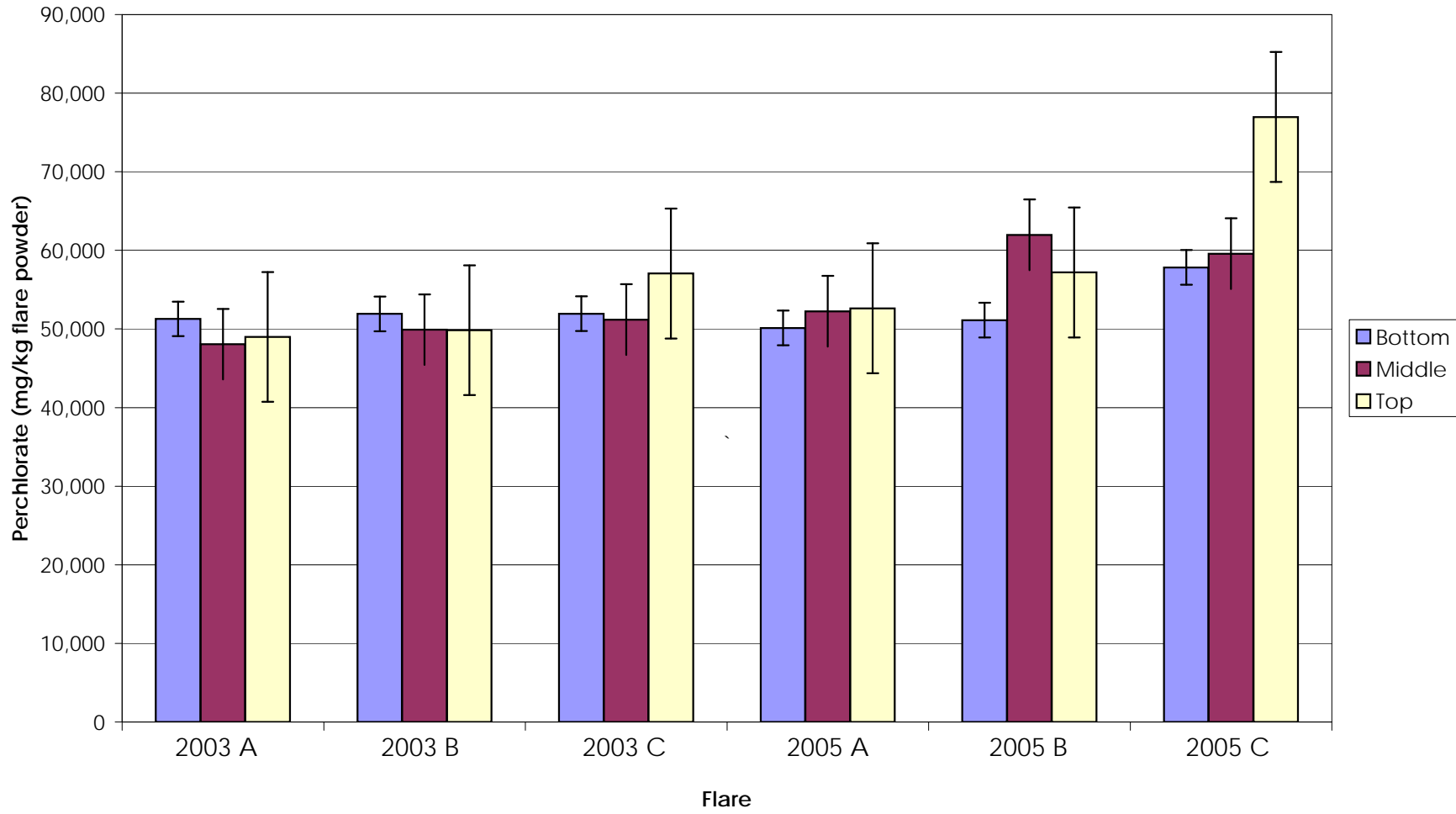
Figure

3.1

Guelph

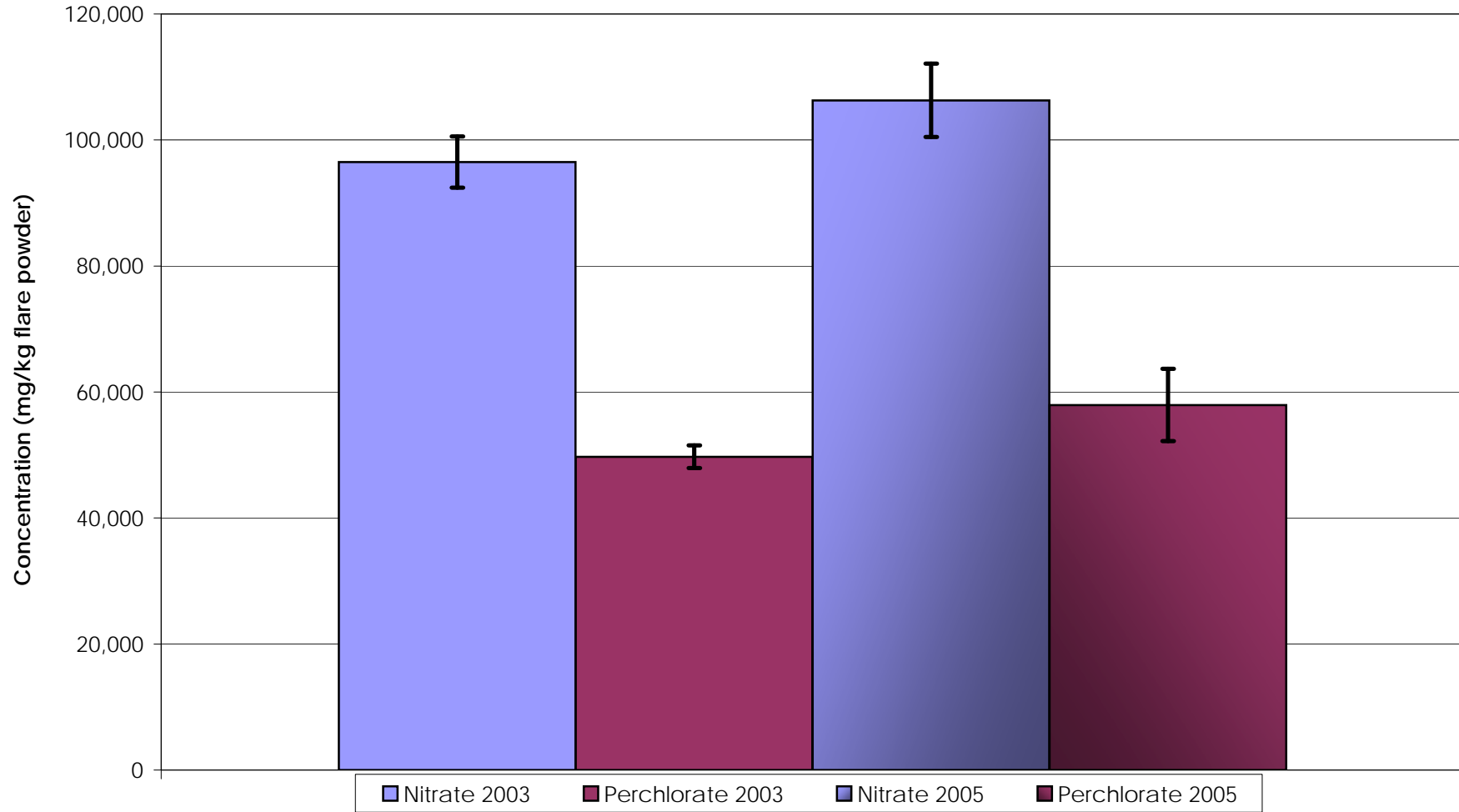
14-Jul-08

P:\PRU\Projects\180197 - Perchlorate\Alternate Sources\Task 1 - Reporting\Final Report\Figures\Figure 3.2 - perchlorate across flare length.xls\Figure 3.2



2003 / 2005 - year of flare production
A, B, C - flare replicate

Perchlorate Concentration along Flare Length, Canadian Flares Manufactured in 2003 and 2005	
Guelph	14-Jul-08
Figure 3.2	



Notes:

Nitrate results were analyzed as Nitrate as Nitrogen

Average Nitrate and Perchlorate Content for Canadian Flares Manufactured in 2003 and 2005



Figure

3.3

Guelph

14-Jul-08



A. Anatomy of a Typical Highway Monitoring Station



B. Primary Monitoring Station Located on I-95

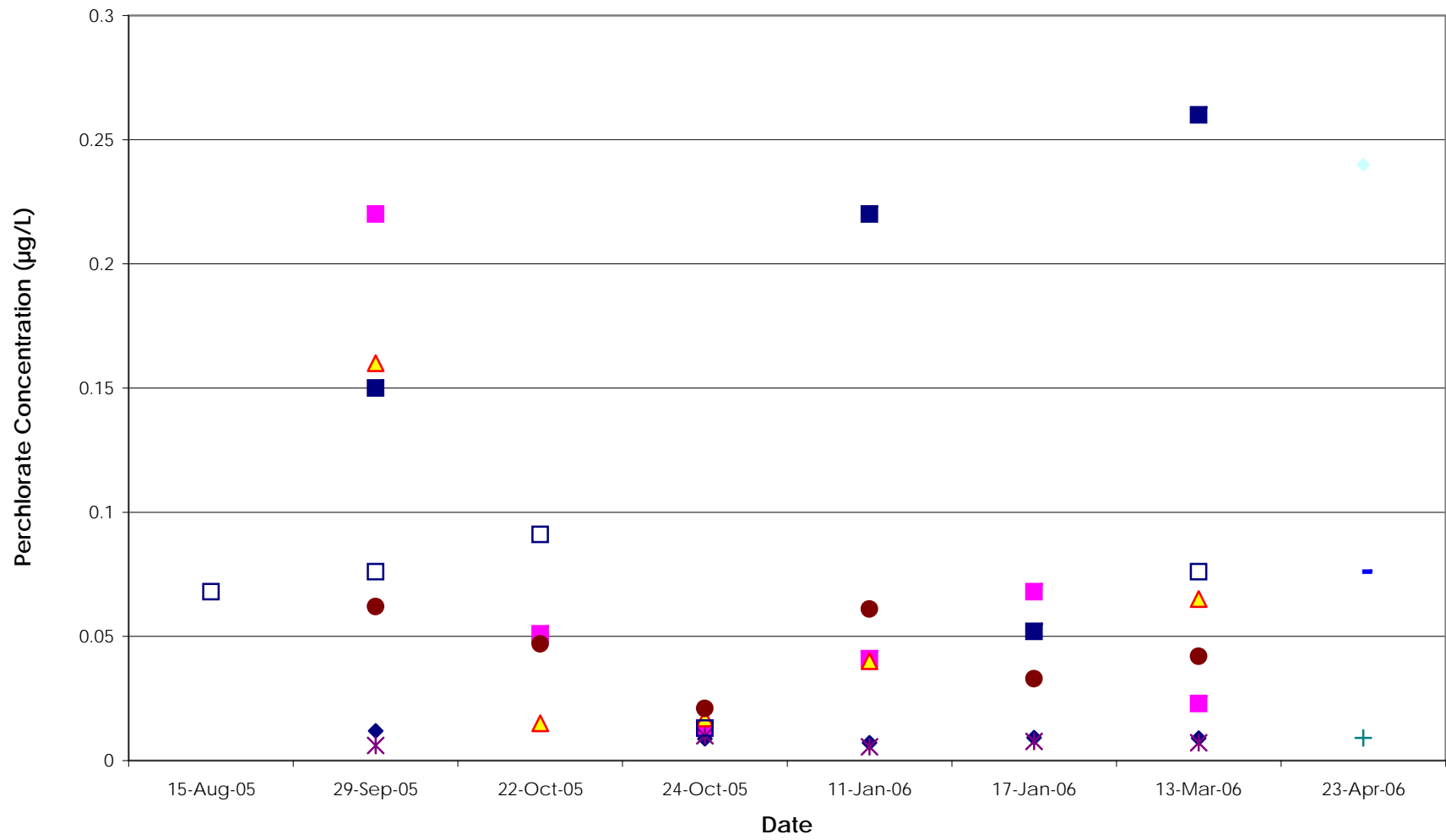
Highway Monitoring Station in Lexington, MA

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Figure
3.4

Guelph

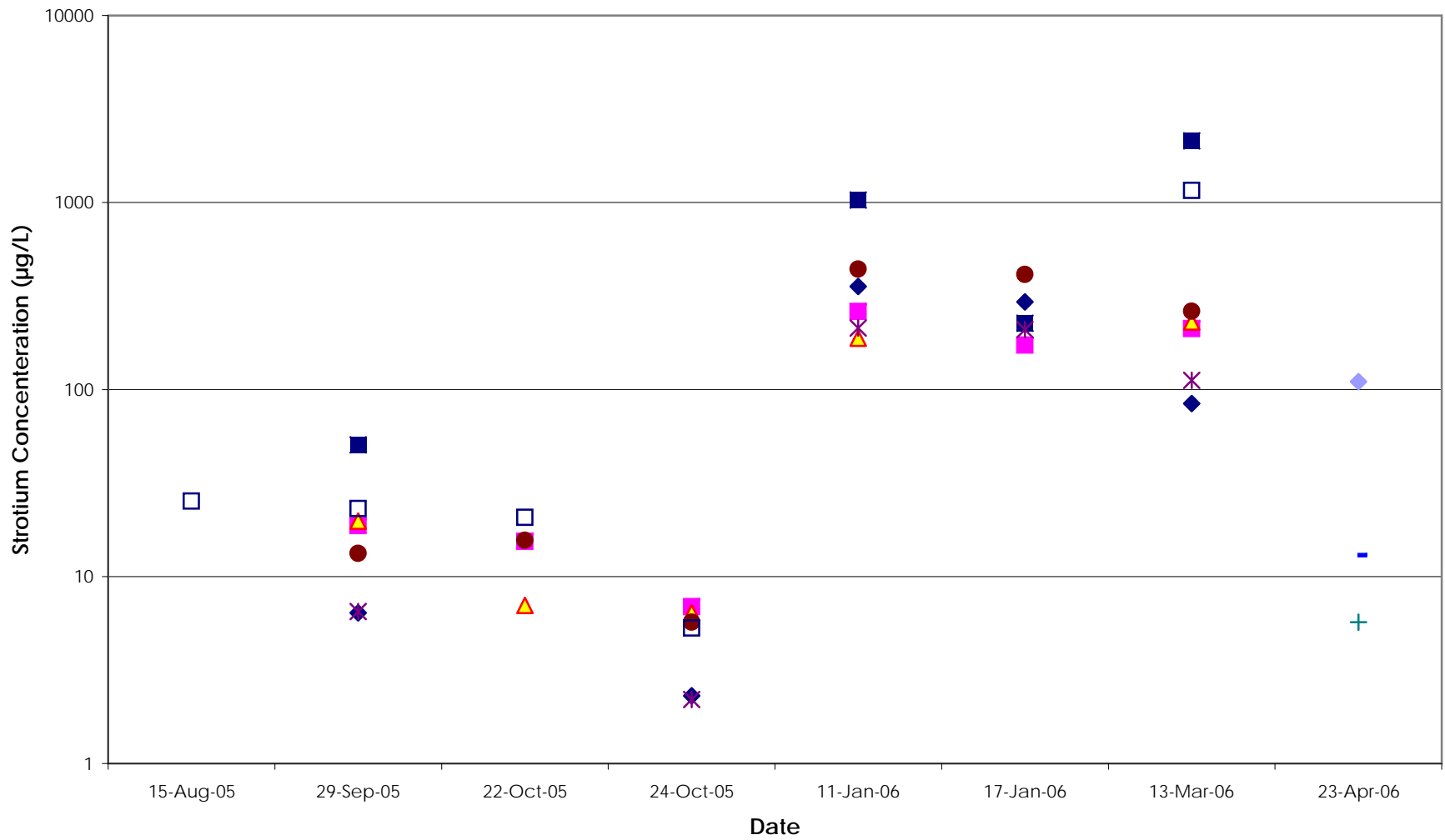
14-July-08



Notes:
µg/L - micrograms per liter

Perchlorate Levels in Highway Runoff - Control Conditions	
	
Guelph	14-July-08

Figure 3.5



- ◆ RT-119 SOUTH
- ▲ I-495 NORTH
- ✕ RT-119 NORTH
- + RT-8
- I-190 SOUTH
- RT-2 EAST
- I-95
- I-495 SOUTH
- I-195 WEST
- ◆ I-93

Notes:
µg/L - micrograms per liter

Strontium Levels in Highway Runoff - Control Conditions



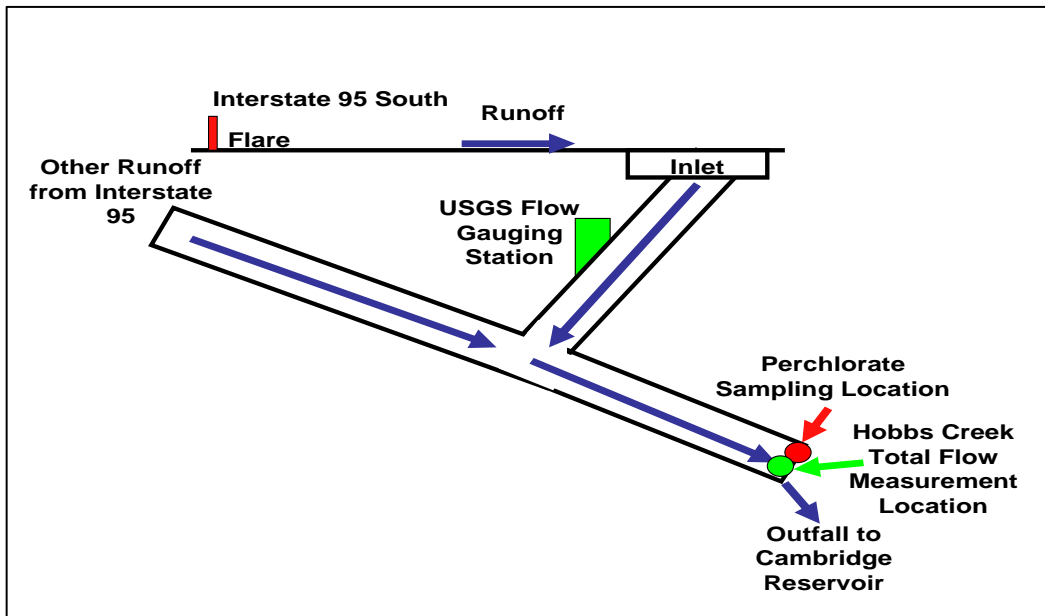
Guelph

14-July-08

Figure
3.6



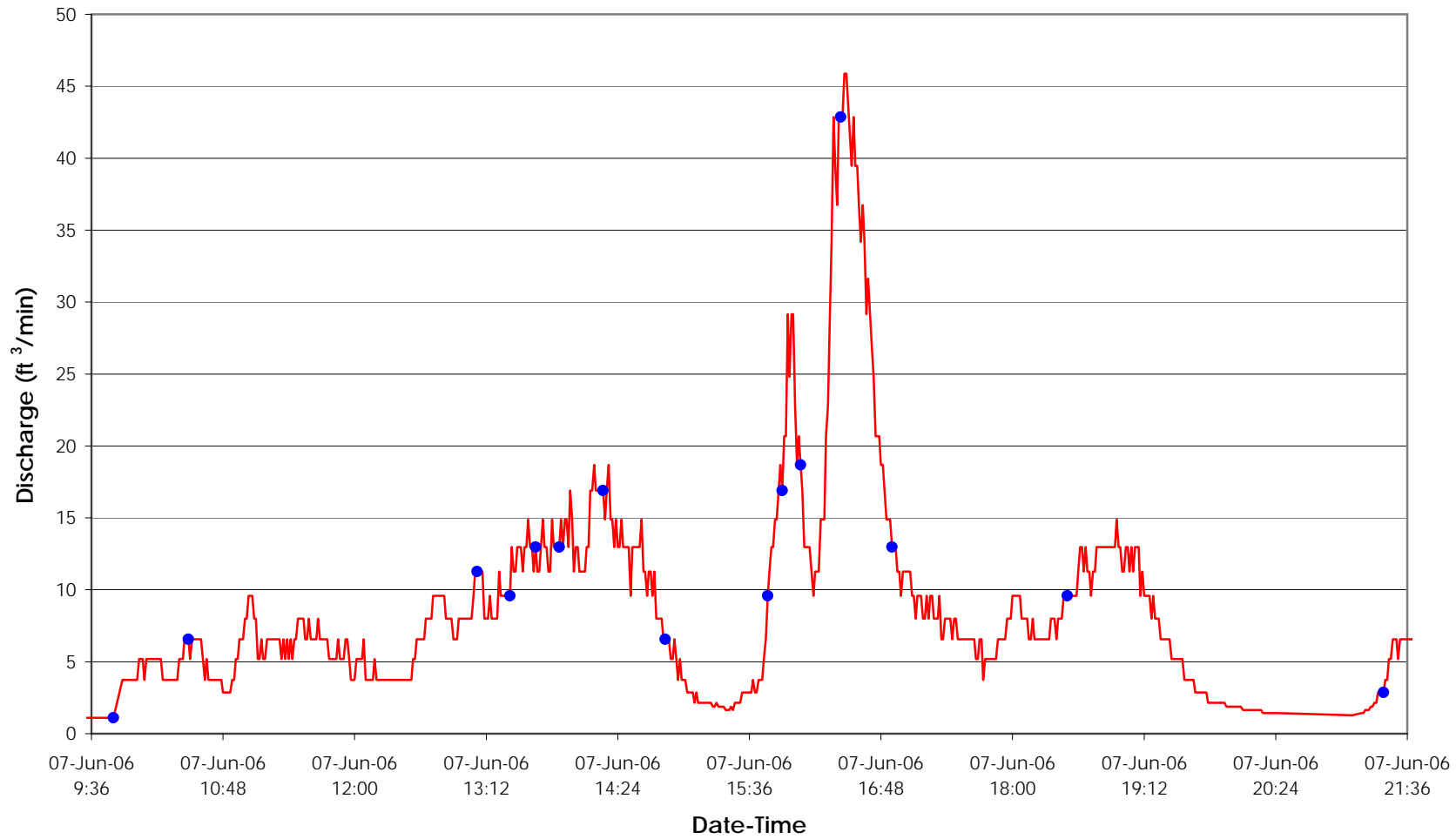
A. Road Flare at Scene of Accident on June 7th



B. Schematic of Sampling and Gauging Locations

Accident Scene Flare Deployment and Monitoring Station Layout	
Guelph	14-July-08

Figure
3.7



— Total Event Flow Hydrograph

● Perchlorate Sampling Points

Notes:
ft³/min - cubic feet per minute

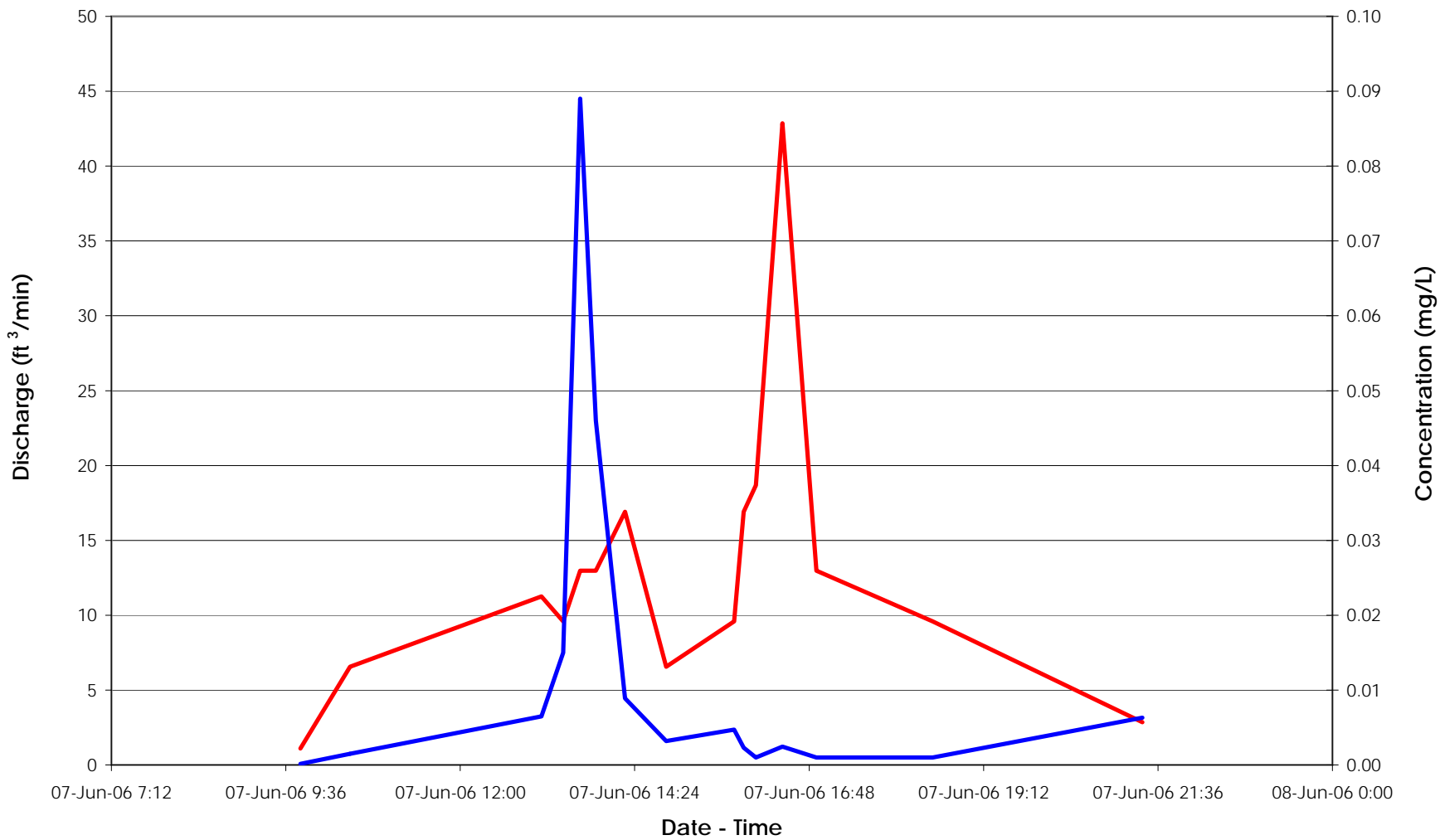
Hydrograph and Perchlorate Sampling Points

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consultants

Figure
3.8

Guelph

14-July-08



— Predicted Hobbs Creek Flow Rate
— Perchlorate Concentration

Notes:
 ft³/min - cubic feet per minute
 mg/L - milligrams per liter

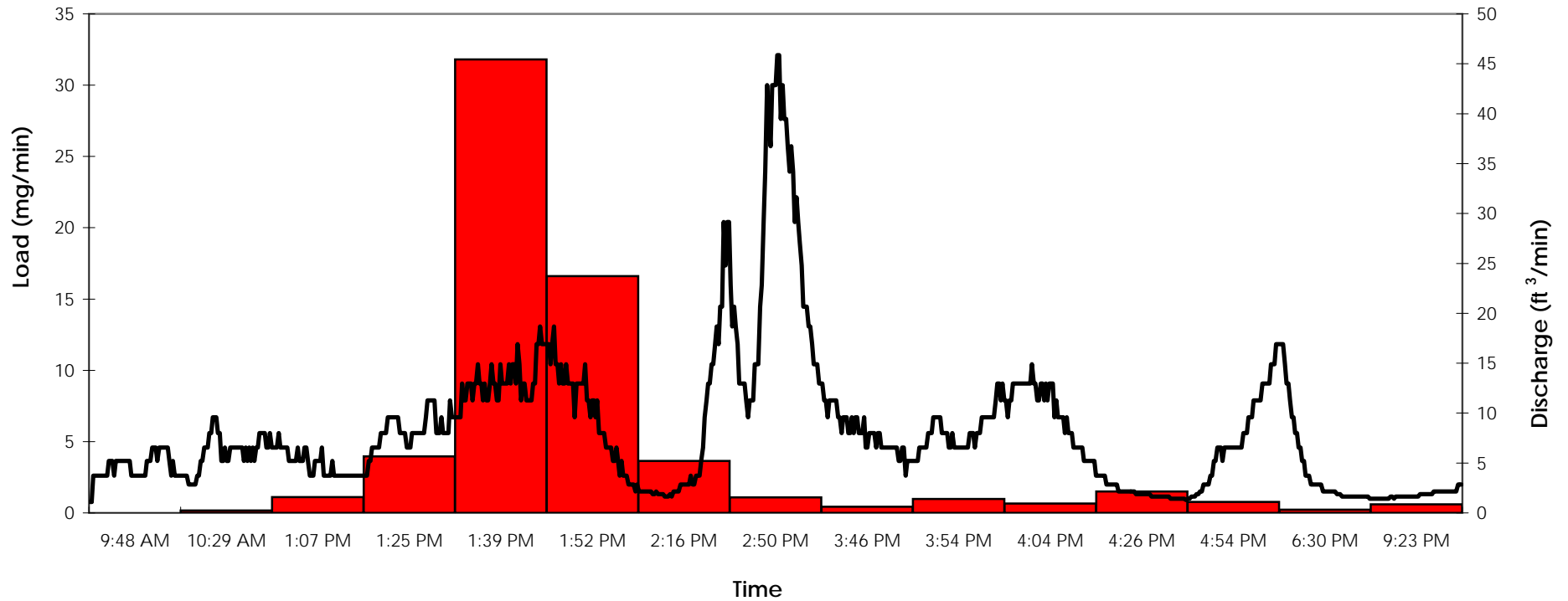
Perchlorate Concentration and Predicted Hobbs Creek Flow Rate Versus Time



Figure
3.9


Guelph

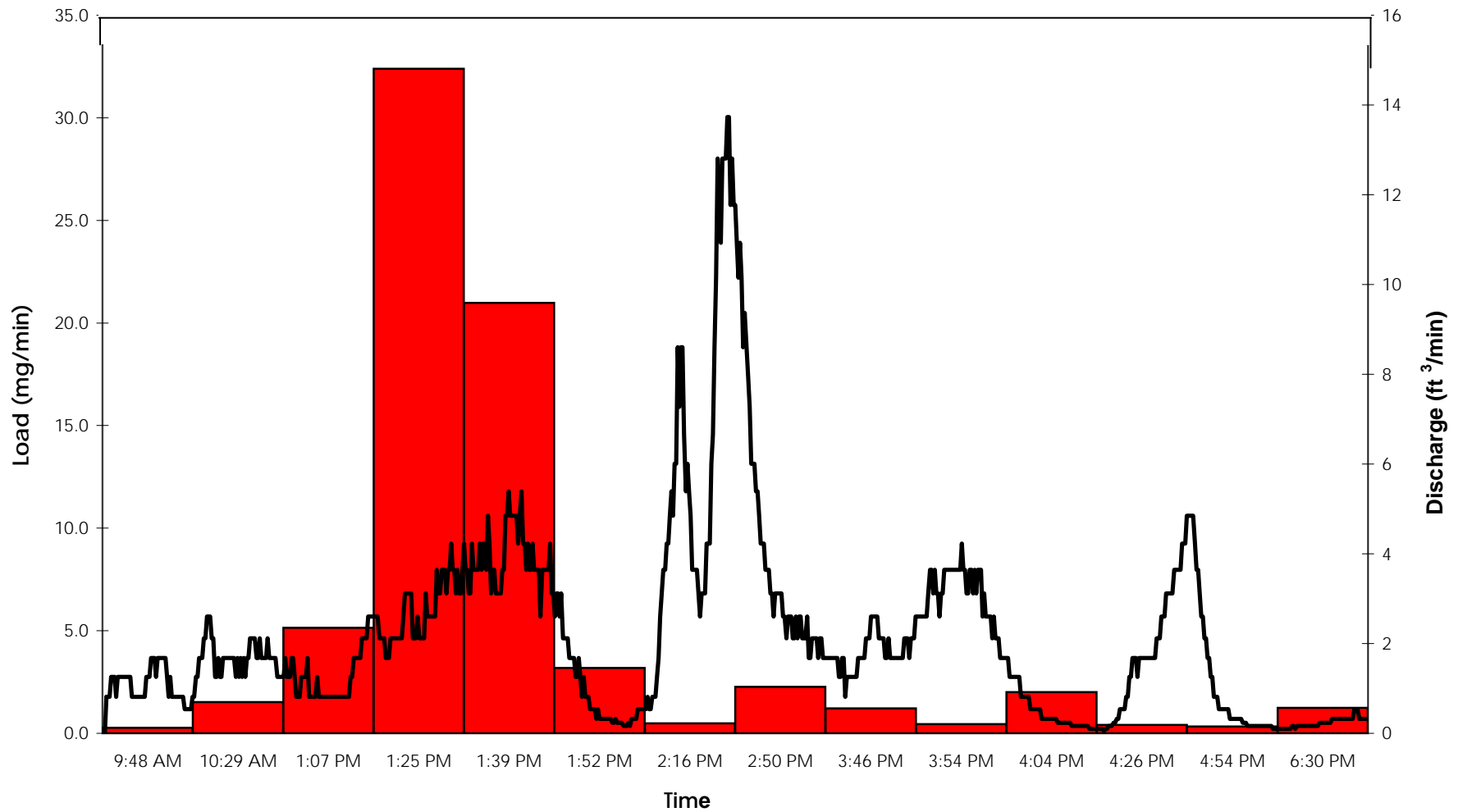
14-July-08



█ Perchlorate Load
— Total Event Flow

Notes:
 ft³/min -cubic feet per minute
 mg/min - milligrams per minute
 All measurements were taken 7-Jun-06

Perchlorate Load to Receiving Water, Accident Scene Flare Deployment	
	
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Figure 3.10	



■ Perchlorate Load

— I-95 Flow

Notes:
 ft³/min - cubic feet per minute
 mg/min - milligrams per minute
 All measurements were taken 7-Jun-06

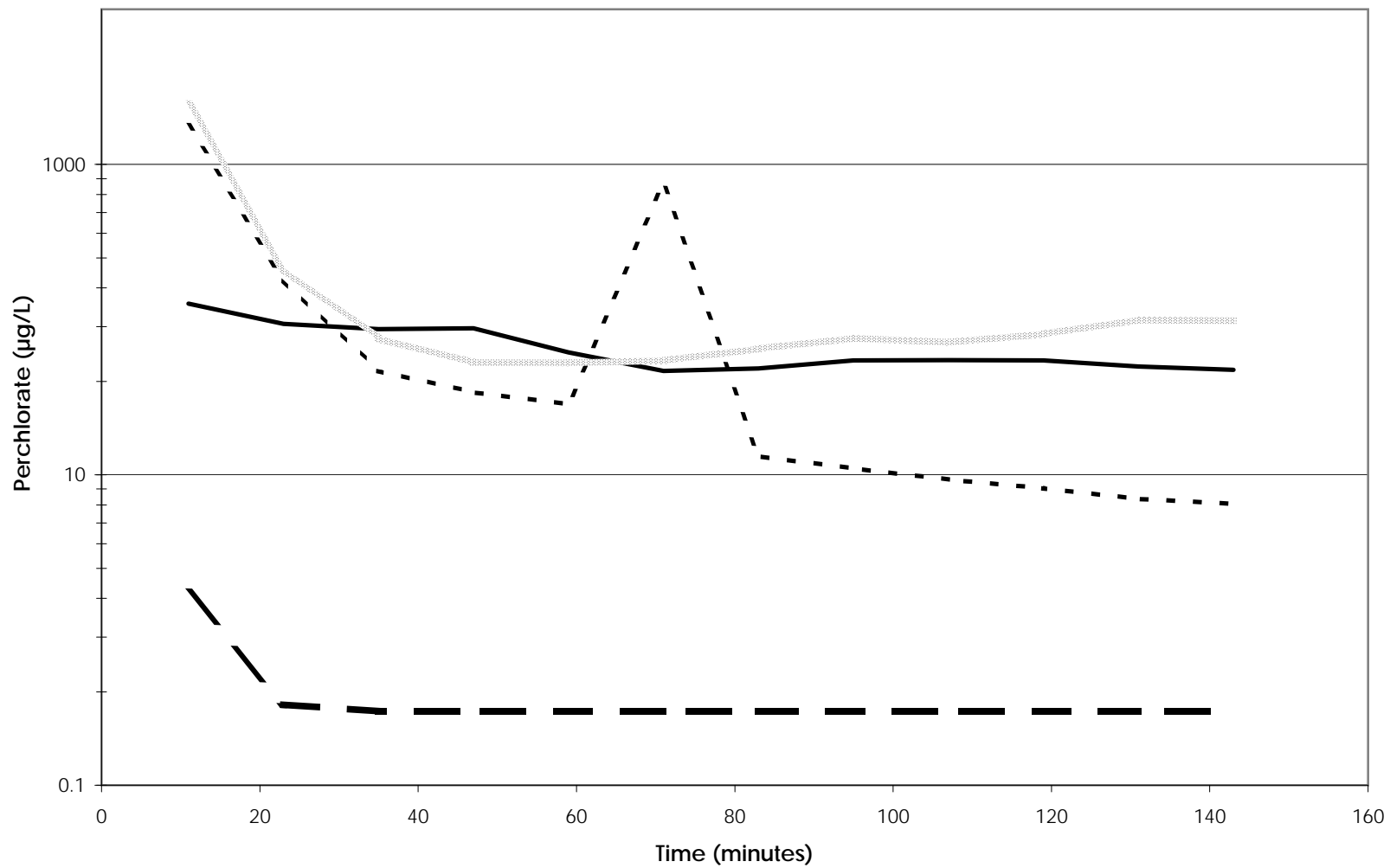
**Estimated Perchlorate Load Leaving I-95,
 Accident Scene Flare Deployment**

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 consultants

Figure
3.11

Guelph

14-July-08



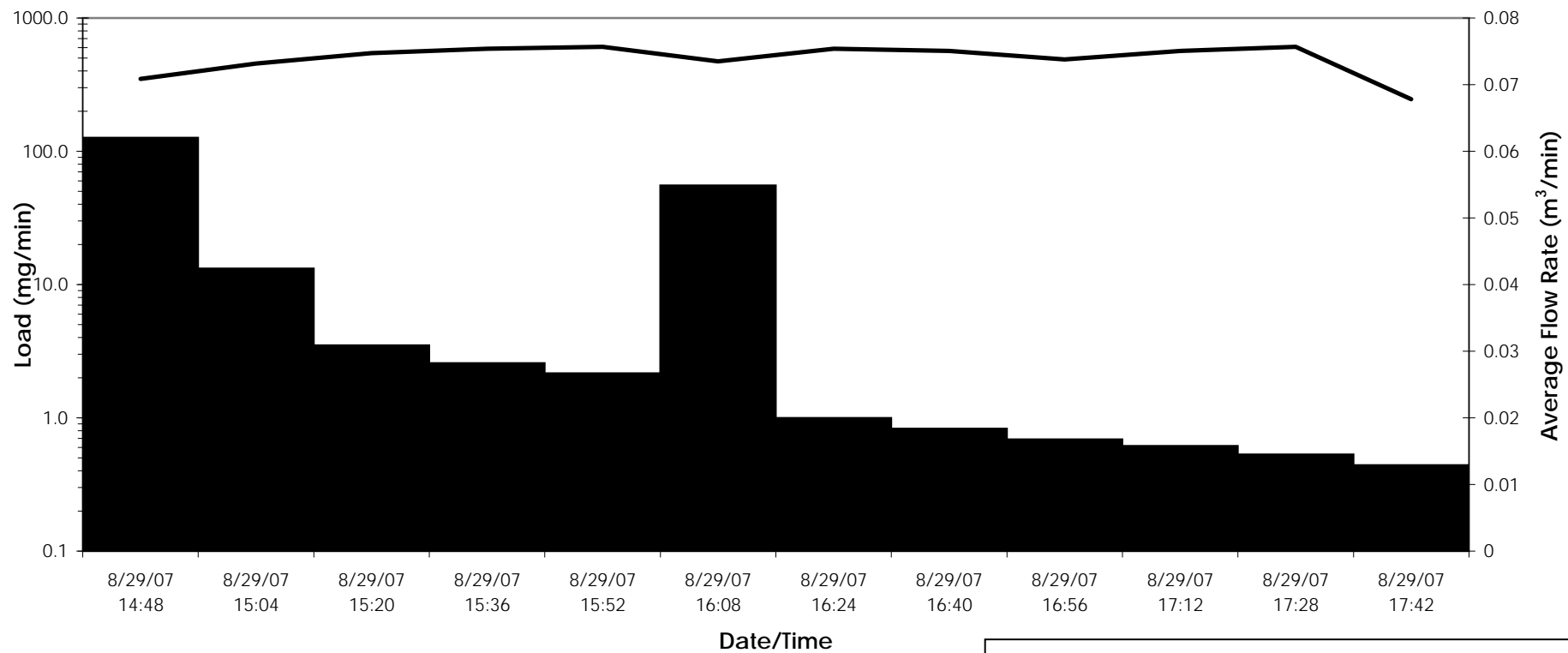
- Completely Burned
- Partially Burned
- - -** Unburned Crushed
-** Partially Burned Crushed

**Perchlorate Concentrations in Runoff,
Controlled Flare Deployment**



Guelph 14-July-2008

Figure 3.12



Load
 Flow Rate

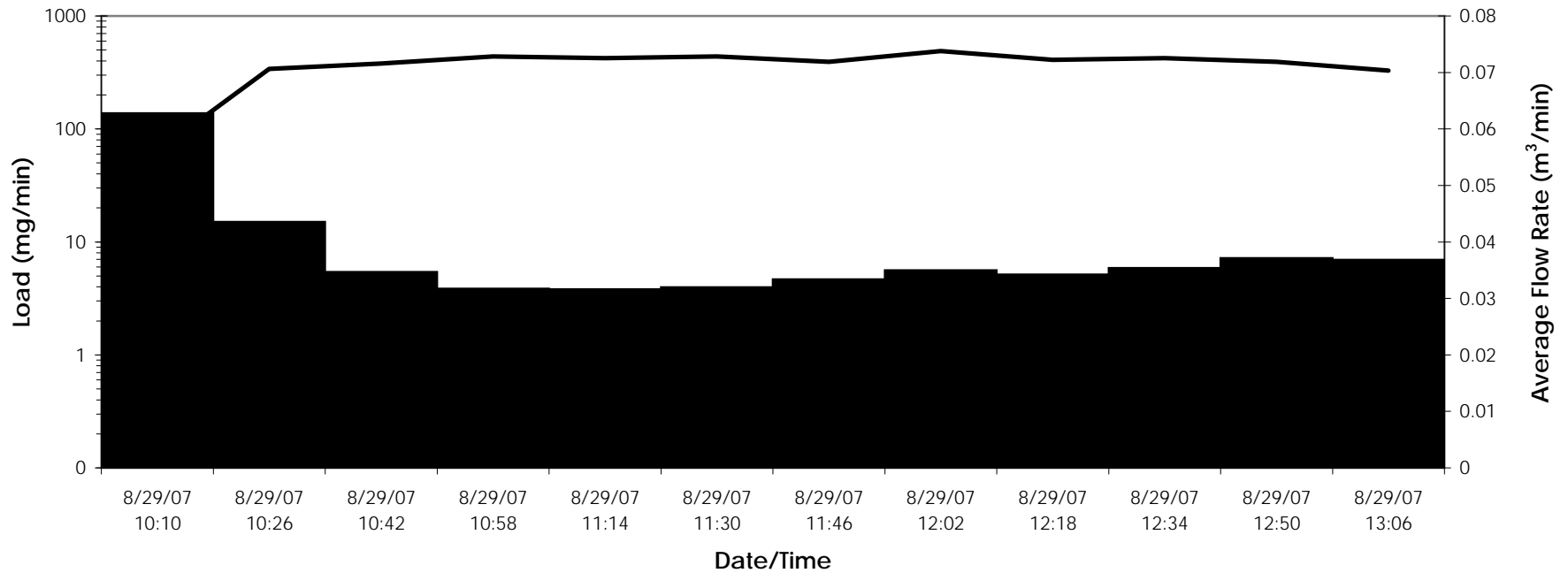
**Unburned Crushed Flare Perchlorate Load in Runoff,
Controlled Flare Deployment**




Figure
3.13

Guelph

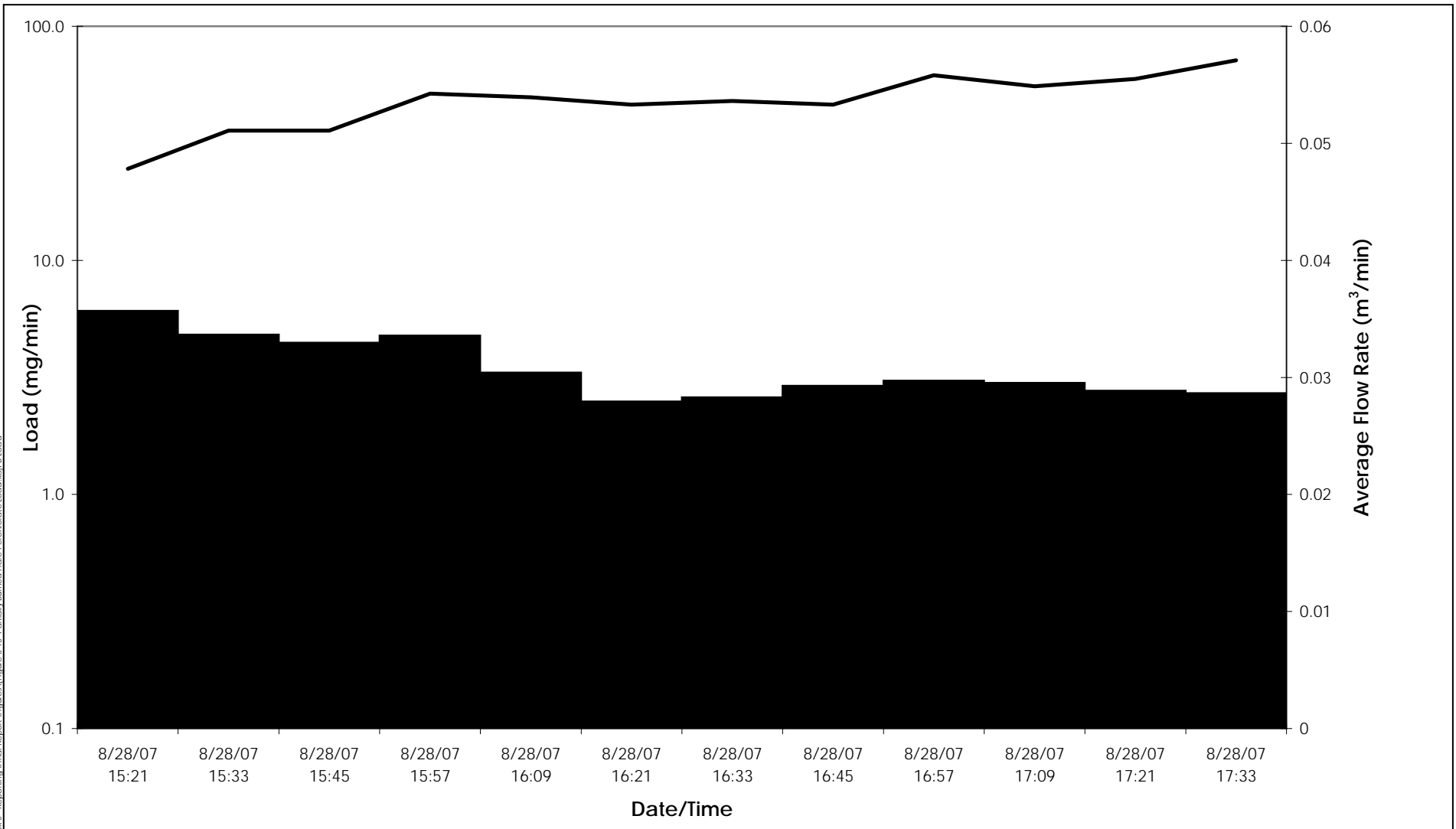
14-July-2008



Load
 Flow Rate

Partially Burned Crushed Flare Perchlorate Load In Runoff, Controlled Flare Deployment	
	
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Figure 3.14	

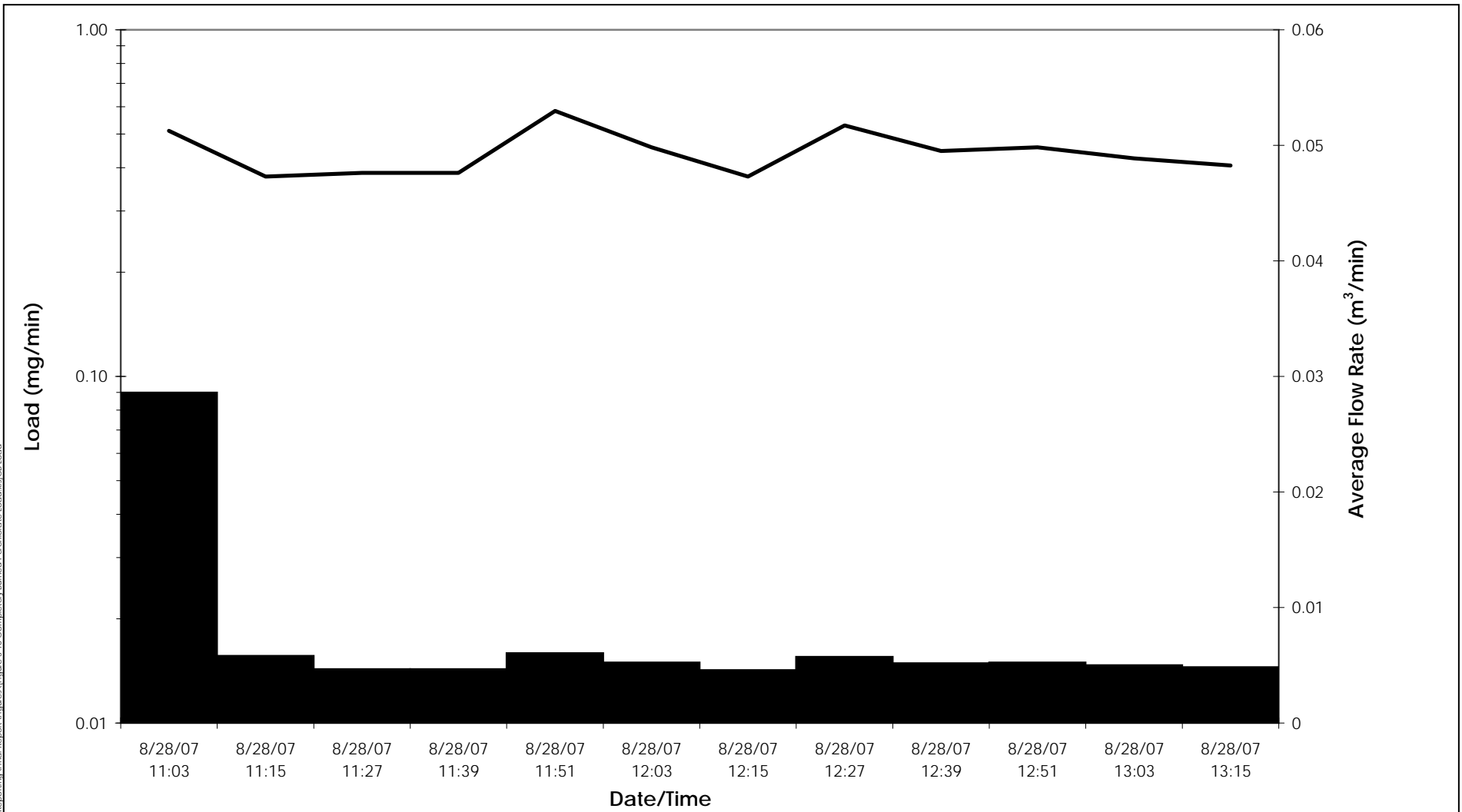
P:\PRA\Projects\100107 - Perchlorate Alternates Sources\Task 5 - Reporting\Final Report\Figures\Figure 3.15- Partially Burned Flare Perchlorate Load.xls\Fig Load



■ Load — Flow Rate

Partially Burned Flare Perchlorate Load in Runoff, Controlled Flare Deployment	
Guelph	14-July-2008
Figure 3.15	

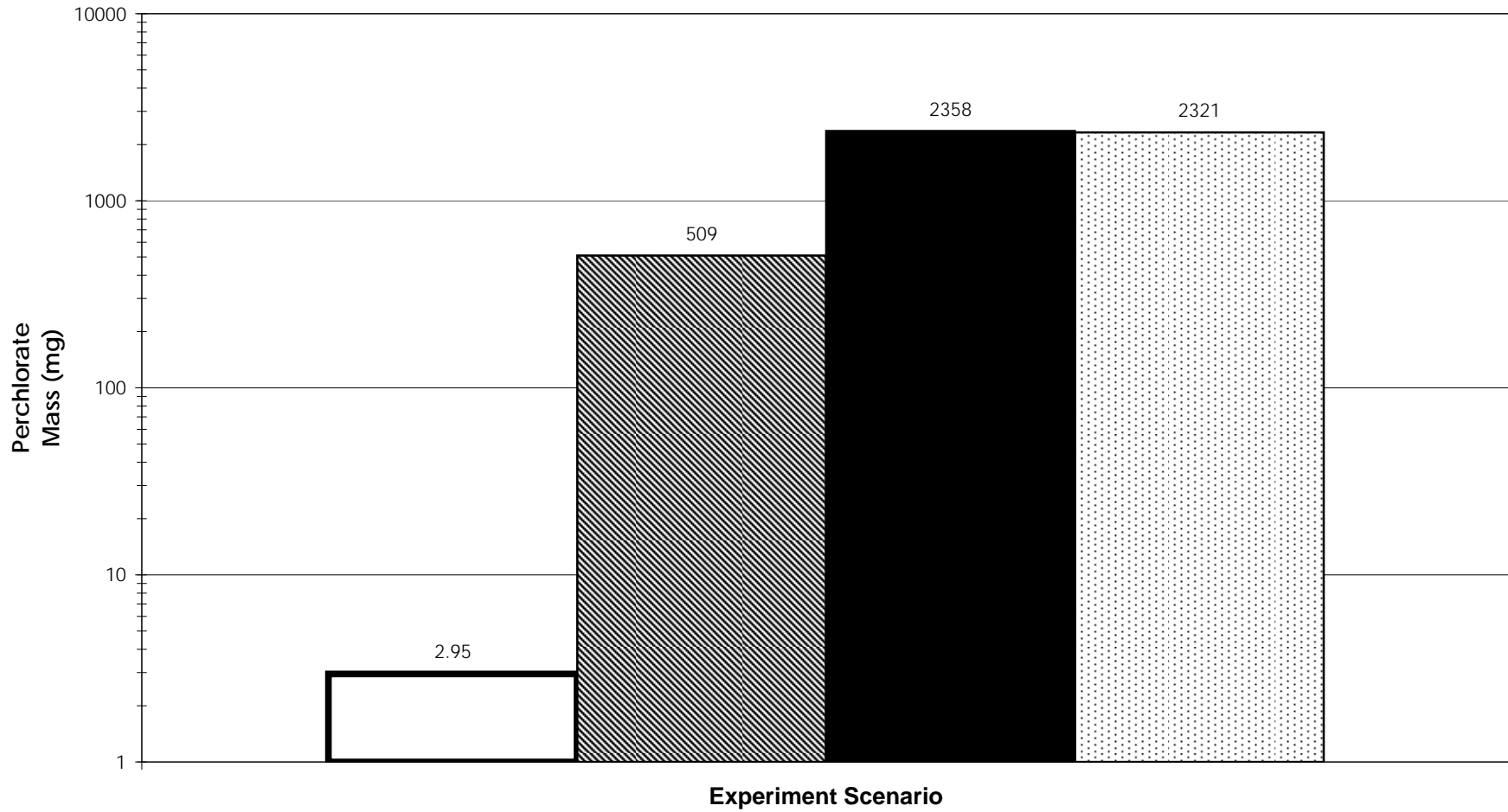
P:\PRA\Projects\10107 - Perchlorate Alternates Sources\Task 5 - Reporting\Final Report\Figures\Figure 3.16-Completely Burned Perchlorate Load.xls\CB_Load



■ Load
— Flow Rate

Completely Burned Perchlorate Load in Runoff, Controlled Flare Deployment	
Guelph	14-July-2008
Figure 3.16	

Flare Condition/Scenario



Flare Condition / Scenario

- Completely Burned
- ▨ Partially Burned
- Unburned Crushed
- Partially Burned Crushed

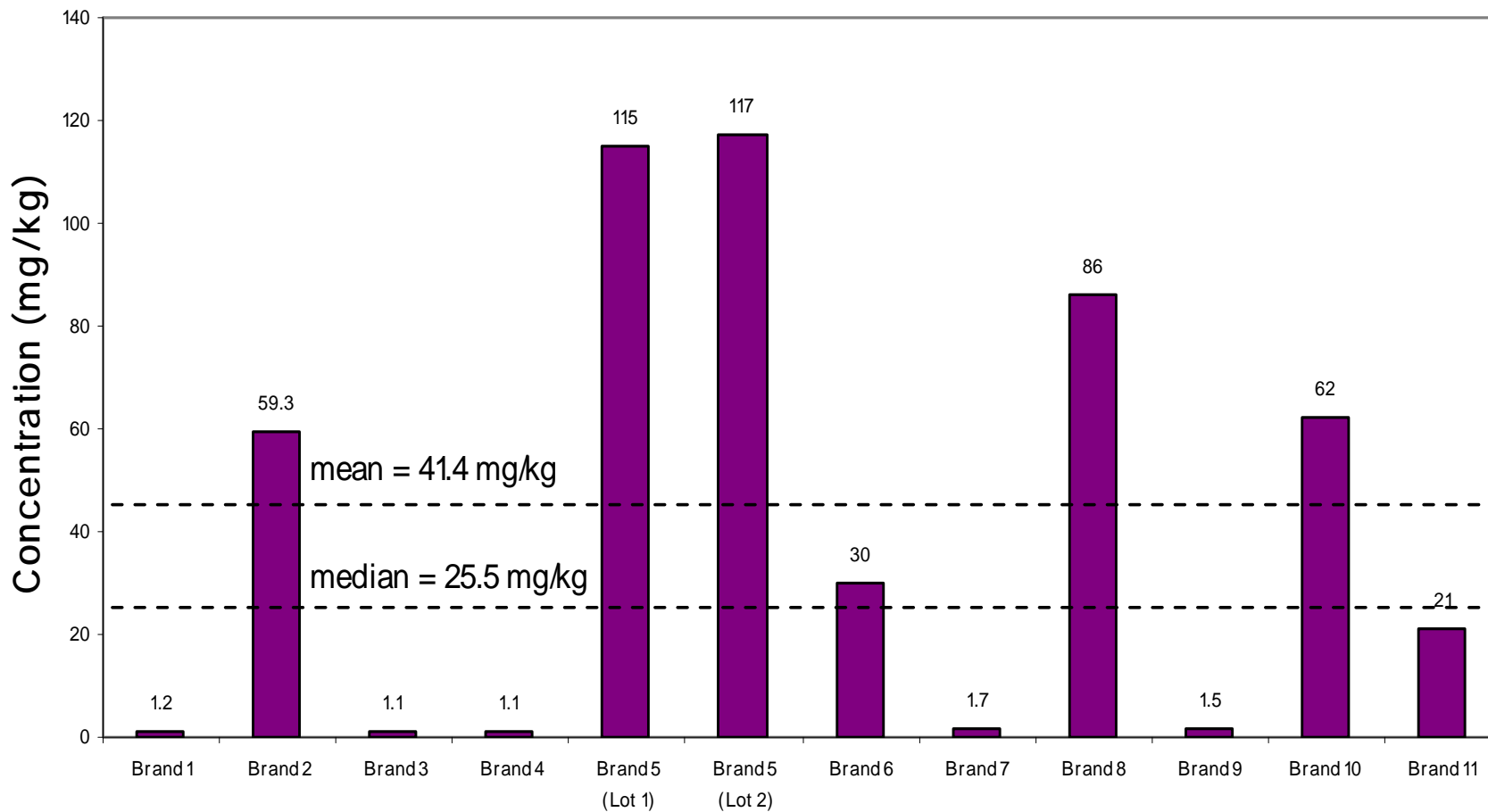
**Total Perchlorate Mass Released per Scenario,
Controlled Flare Deployment**



Figure
3.17

Guelph

14-July-2008



Notes:
mg/kg – milligram per kilogram

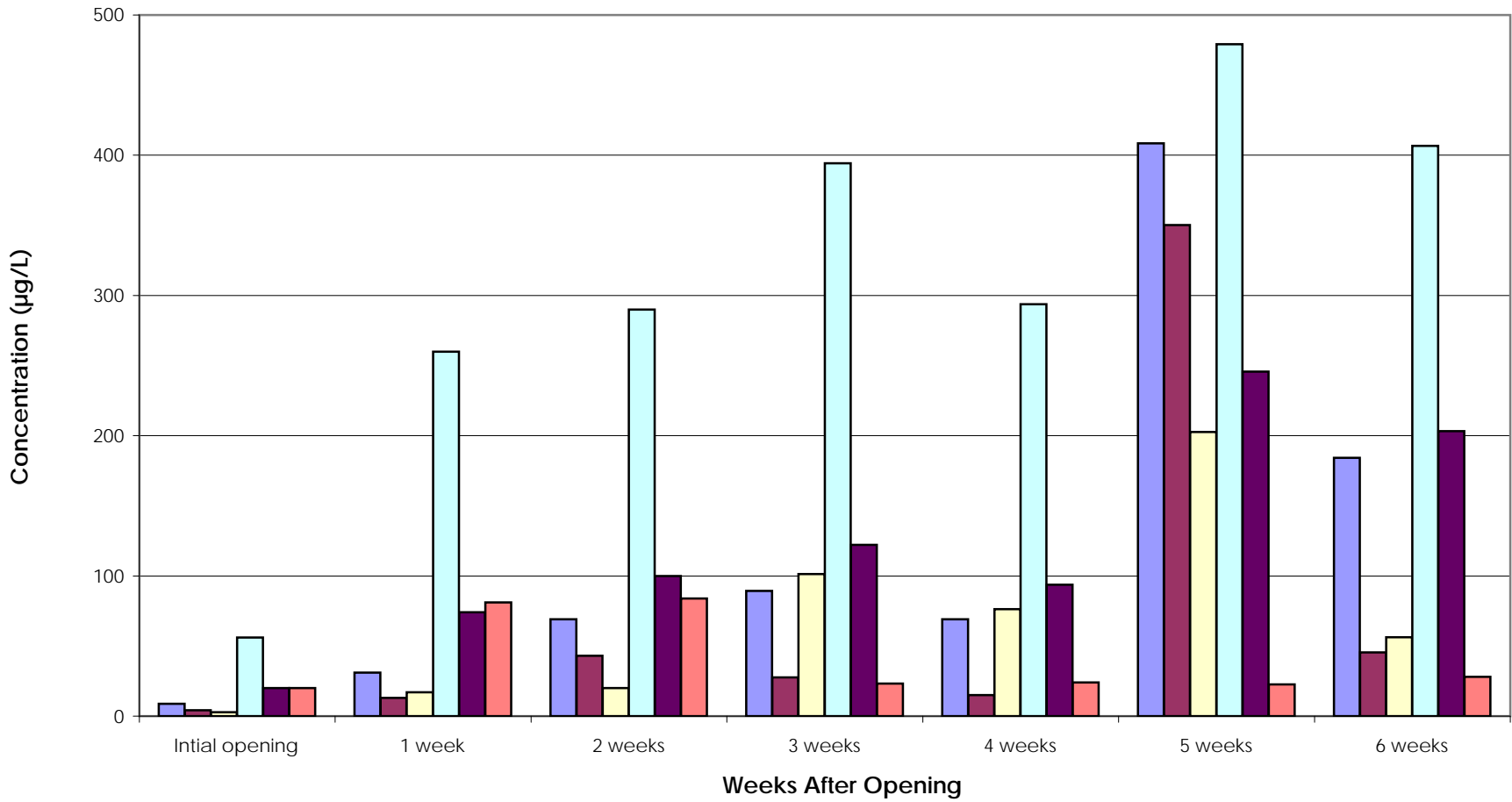
Perchlorate Concentrations in Reagent-Grade Sodium Chlorate



Figure
4.1

Guelph

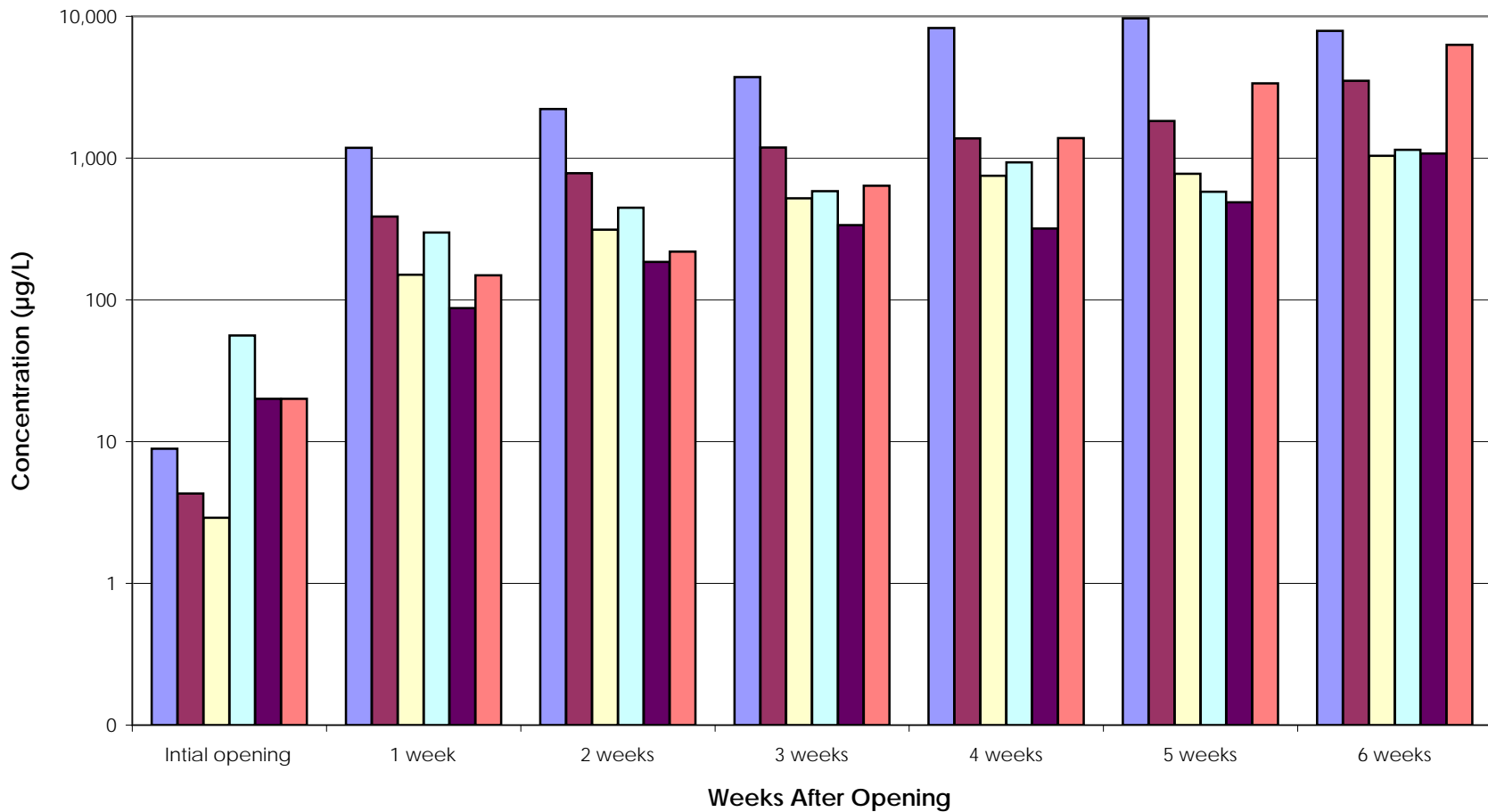
14-July-08



- Brand 1 ■ Brand 2 □ Brand 3
- Brand 4 ■ Brand 5 ■ Brand 6

Notes:
µg/L - micrograms per liter

Perchlorate in Household Bleach Stored in the Dark	
	
Guelph	14-July-08
Figure 4.2	



- Brand 1 ■ Brand 2 ■ Brand 3
- Brand 4 ■ Brand 5 ■ Brand 6

Notes:
µg/L - micrograms per liter

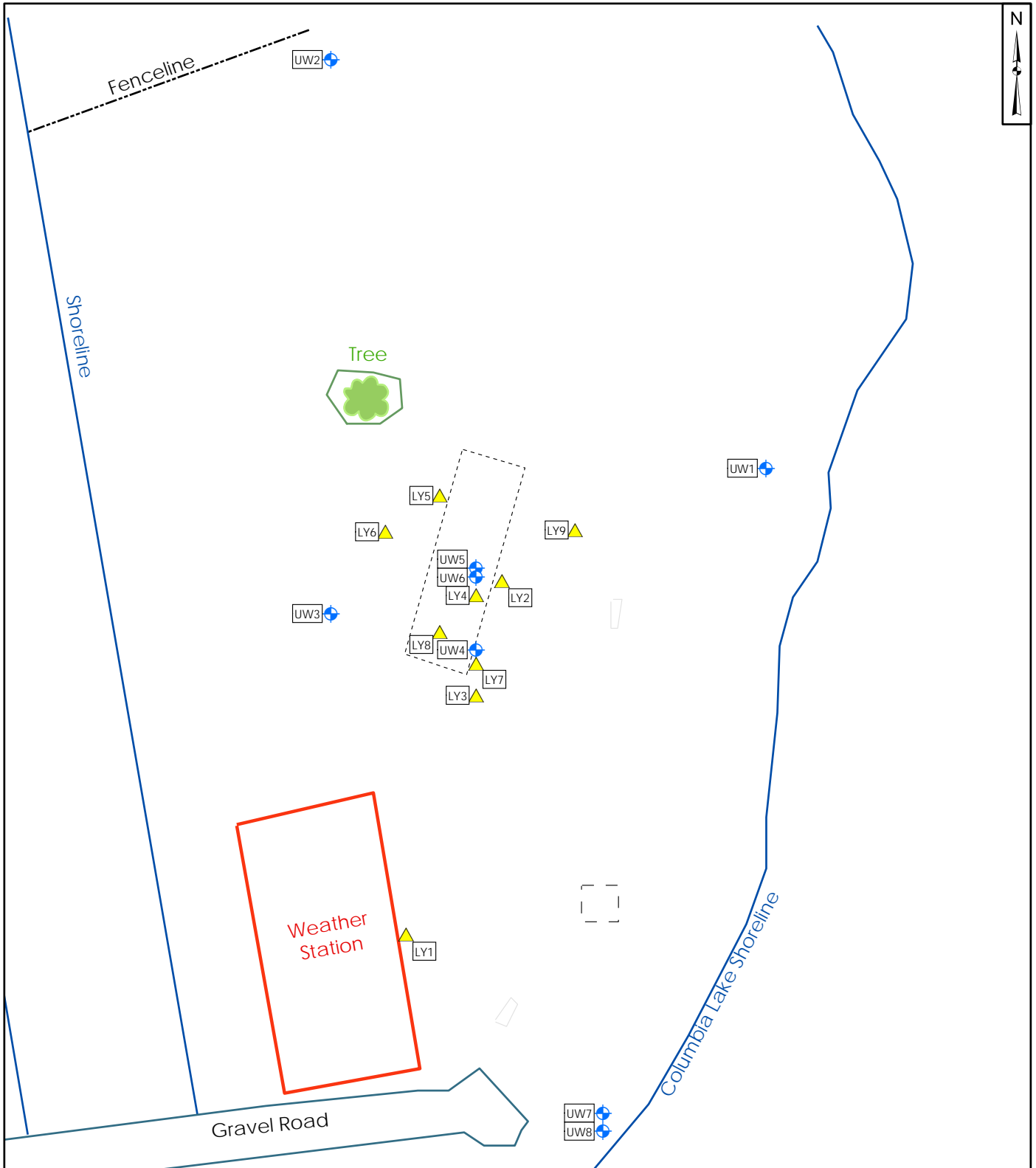
Perchlorate in Household Bleach Exposed to Sunlight







Figure
4.3

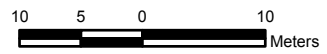
Guelph

14-July-08



P:\PRJ\Projects\180197 - Perchlorate Alternates\Sources\ColumbiaLakeGIS\ColumbiaLake.mxd 12 Jan 2007

-  Lysimeter
-  Monitoring Well
-  Primary Launch Area
-  Secondary Launch Area



Columbia Lake Sampling Locations
Columbia Lake, Waterloo, Ontario

Geosyntec
consultants

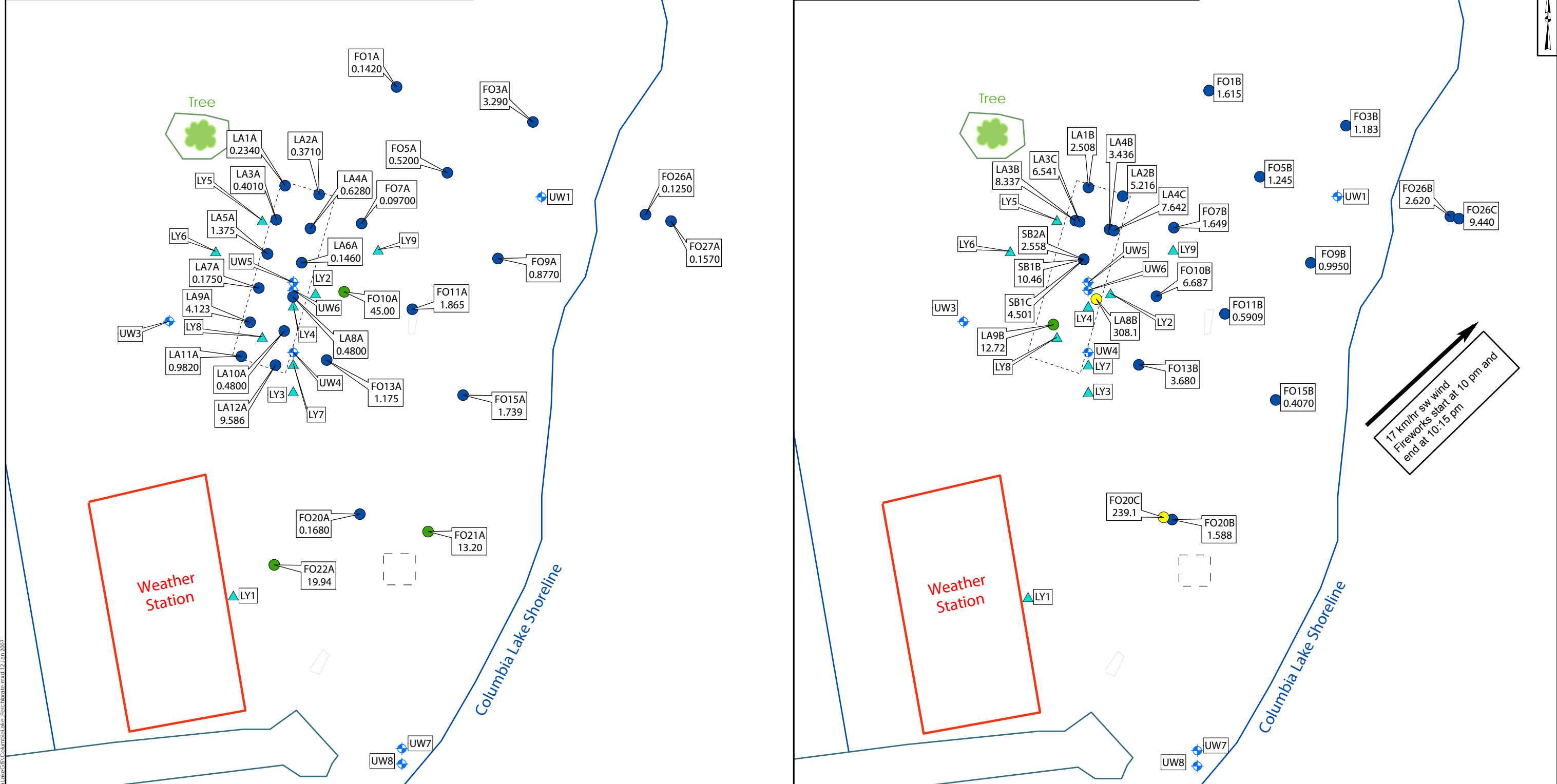
Figure
6.1

Guelph

14-July-2008

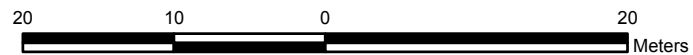
Pre Fireworks Sampling Event A: 29 & 30 June 2006

Post Fireworks Sampling Event B: 2 July 2006



- Concentration ($\mu\text{g}/\text{kg}$)
- Non-Detect (<0.011)
 - ≤ 10
 - $>10 - 100$
 - $>100 - 1,000$
 - $>1,000$
- ▲ Lysimeter
 - ⊕ Monitoring Well
 - Primary Launch Area
 - - - Secondary Launch Area

Note:
 $\mu\text{g}/\text{kg}$ - micrograms per kilogram



Perchlorate Concentrations in Soil
 Columbia Lake, Waterloo, Ontario

Geosyntec
 consultants

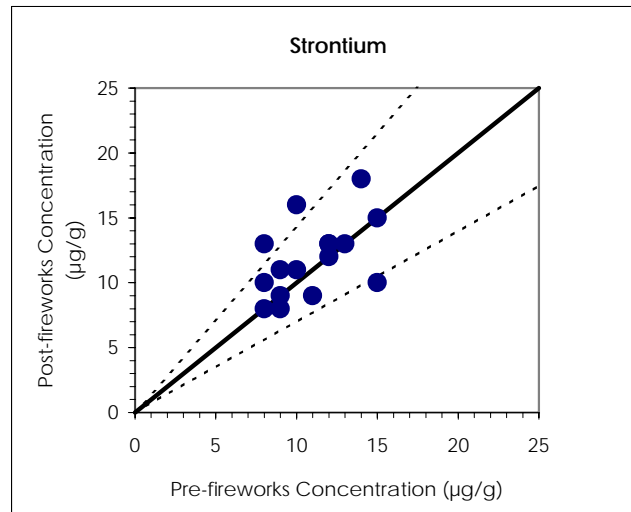
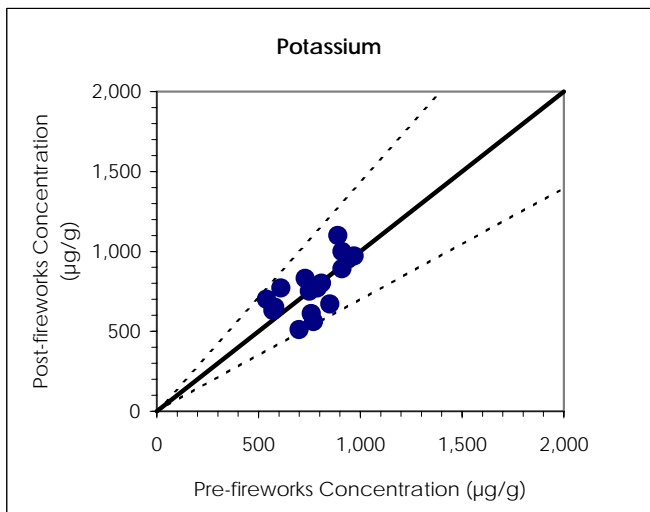
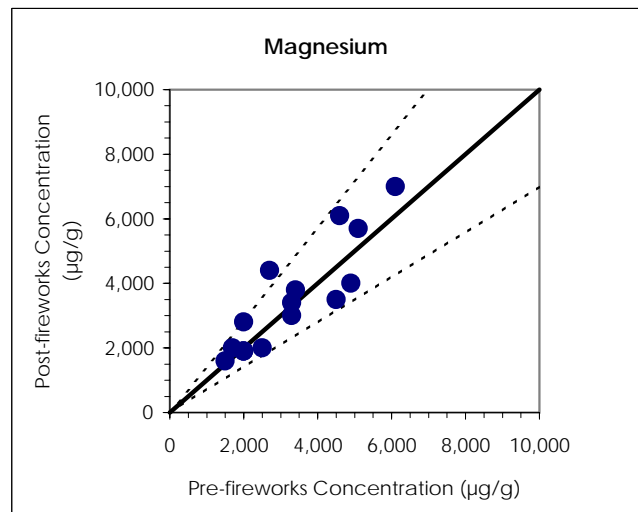
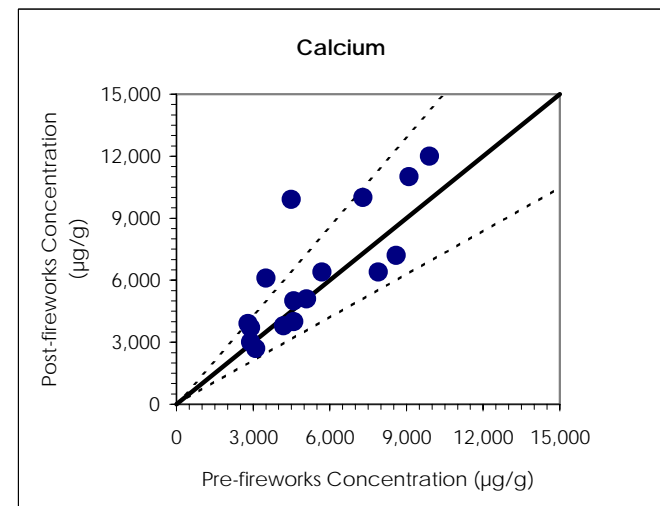
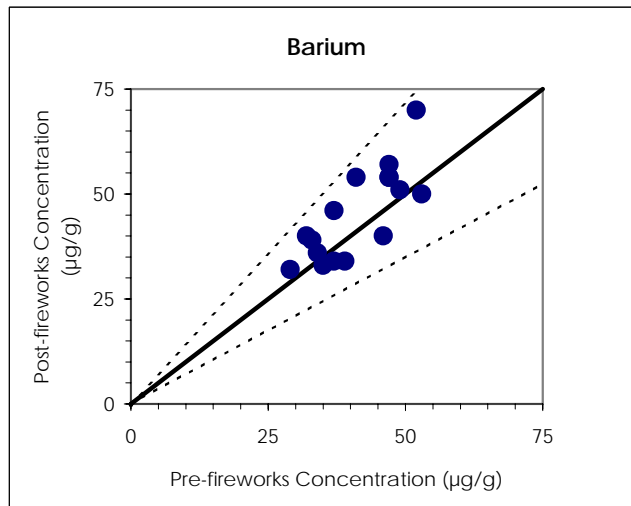
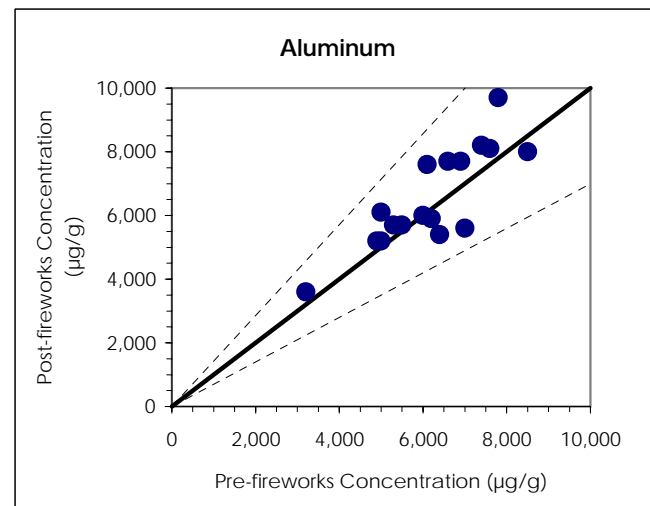
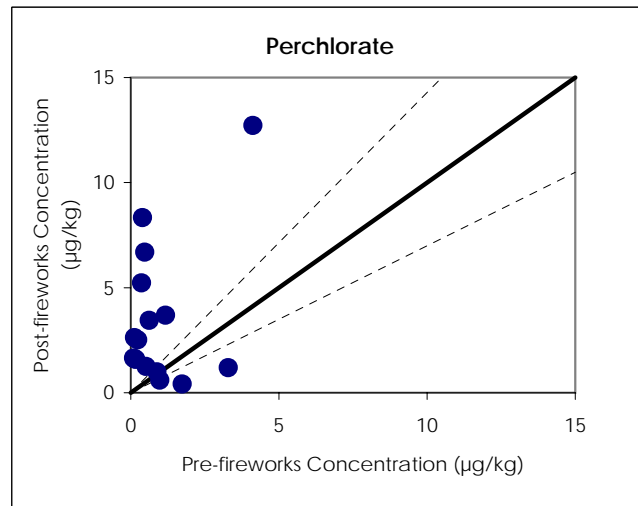
Guelph

14-July-2008

Figure

6.2

P:\BA\Projects\100197 - Perchlorate Alternatives\Columbia Lake\GIS\ColumbiaLake.mxd 12 Jan 2007



**Comparisons of Perchlorate and Metal Concentrations
in Soil Before and After a Fireworks Display
Columbia Lake, Waterloo, Ontario**

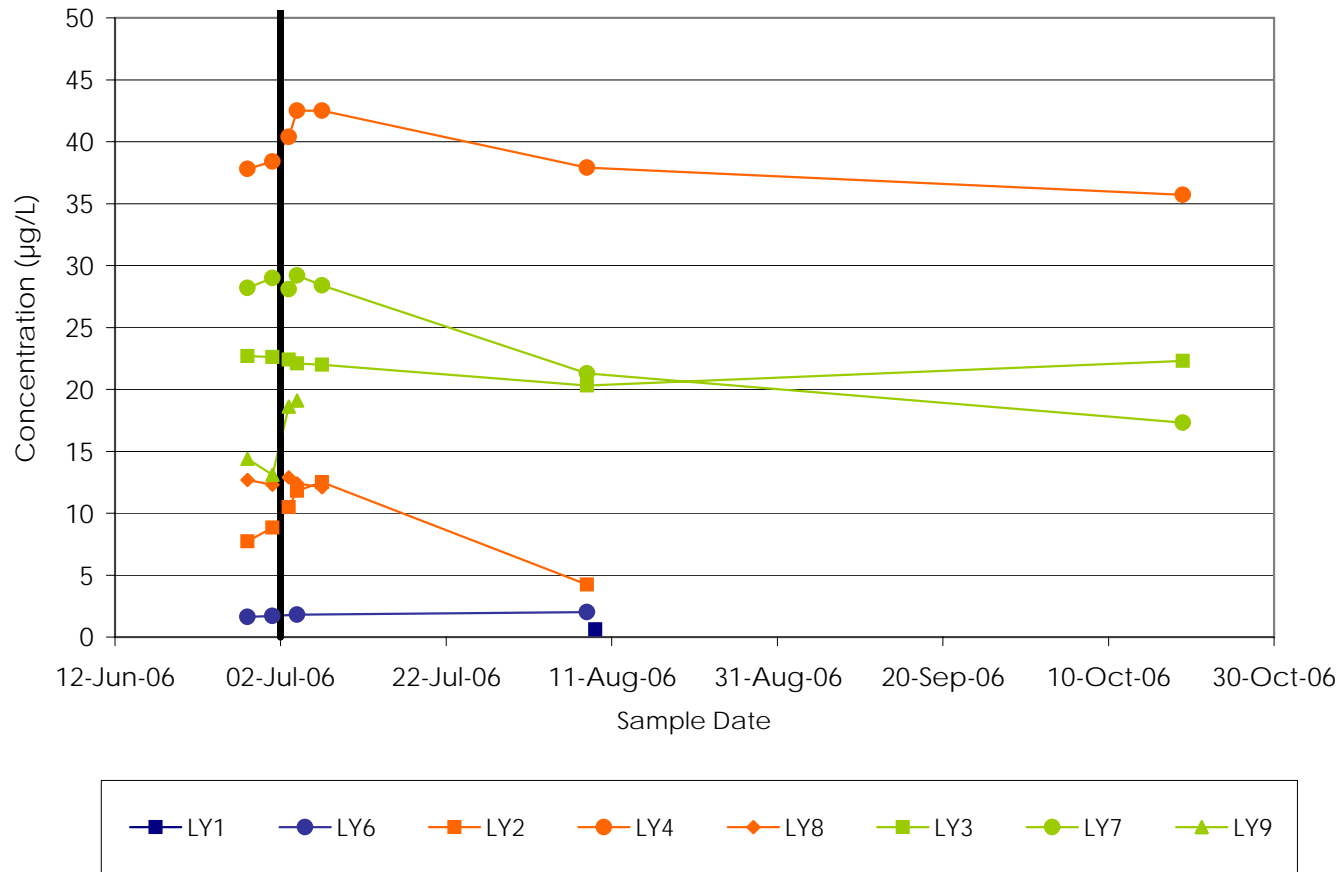


Figure

6.3

Guelph

14- July-2008



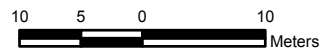
Notes:
 Blue - lysimeter installed upwind of the launch area
 Orange - lysimeter installed within the launch area
 Green - lysimeter installed down wind of the launch area

Perchlorate Concentrations in Pore Water Columbia Lake, Waterloo, Ontario	
Guelph	14-July-2008
Figure 6.4	



P:\PRJ\Projects\180197 - Perchlorate Alternates\Sources\ColumbiaLakeGIS\ColumbiaLake.mxd 10 Jan 2007

- Groundwater Elevation (4-Jun-2006)
- Groundwater Elevation Contour (m)
- Primary Launch Area
- - - Secondary Launch Area



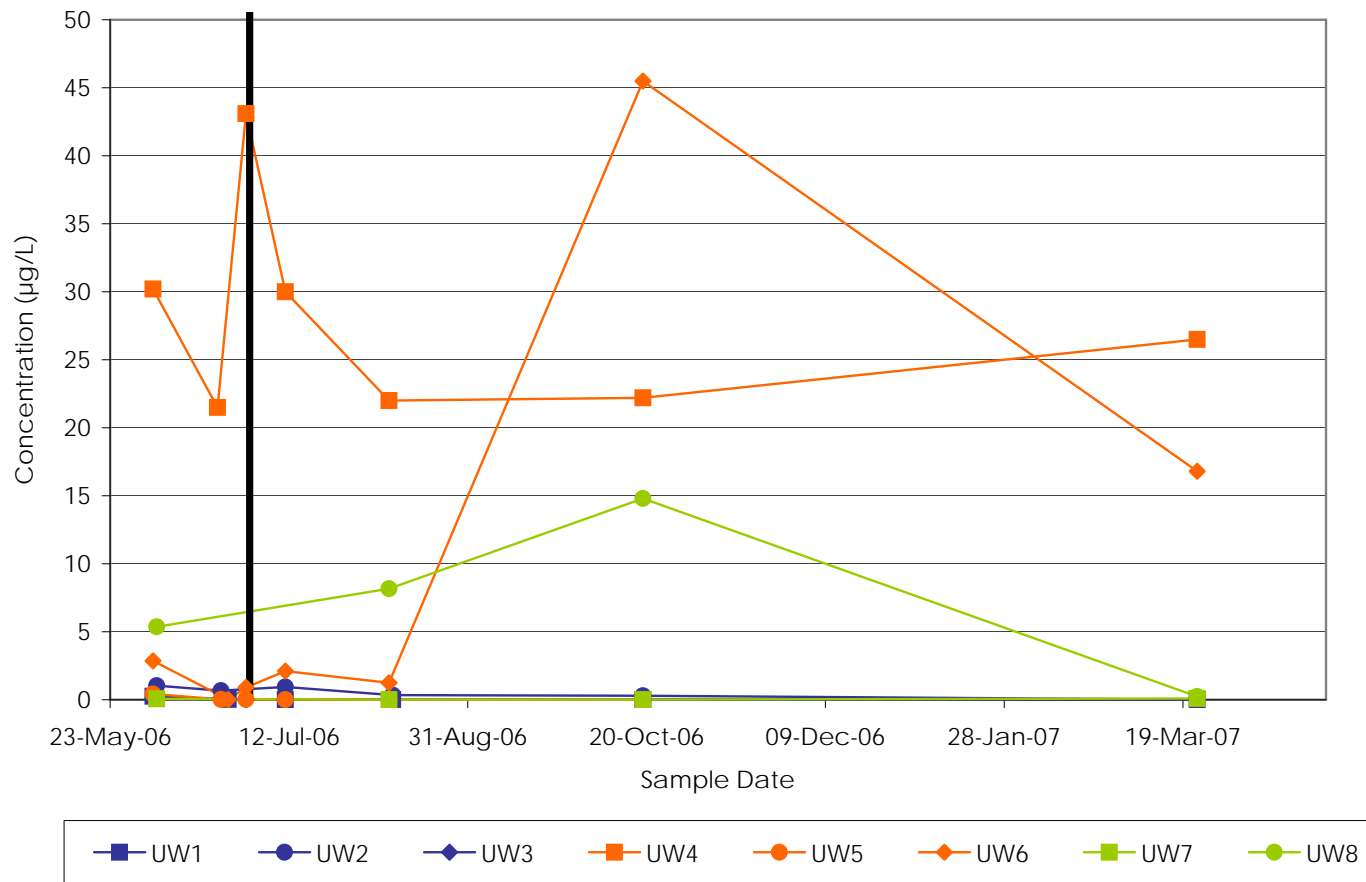
Potentiometric Surface, June 4, 2006
Columbia Lake, Waterloo, Ontario

Geosyntec
 consultants

Figure
6.5

Guelph




14-July-2008



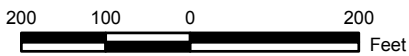
Notes:
 Blue - background monitoring well
 Orange - monitoring well installed within the launch area
 Green - monitoring well installed down gradient of the launch area

Perchlorate Concentrations in Groundwater Columbia Lake, Waterloo, Ontario	
Guelph	14-July-2008
Figure 6.6	



-  Launch Area - 2006
-  Monitoring Well
-  Launch Area - 2005

Note:
Launch areas consisted of poured sand on ground surface and fiberglass ignition cylinders



Fireworks Display Site
University of Massachusetts, Dartmouth Campus

Geosyntec
consultants

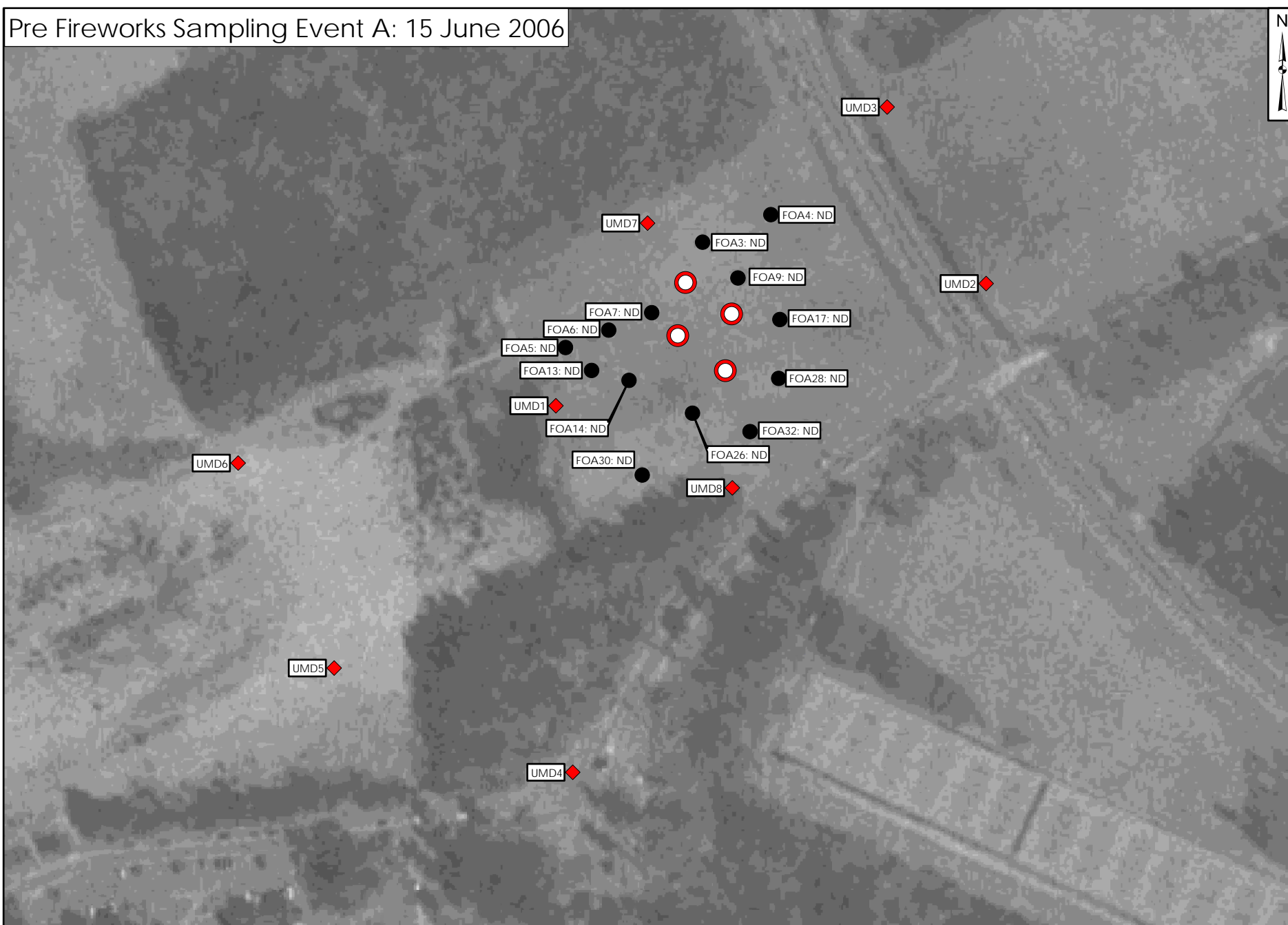
Figure

6.7

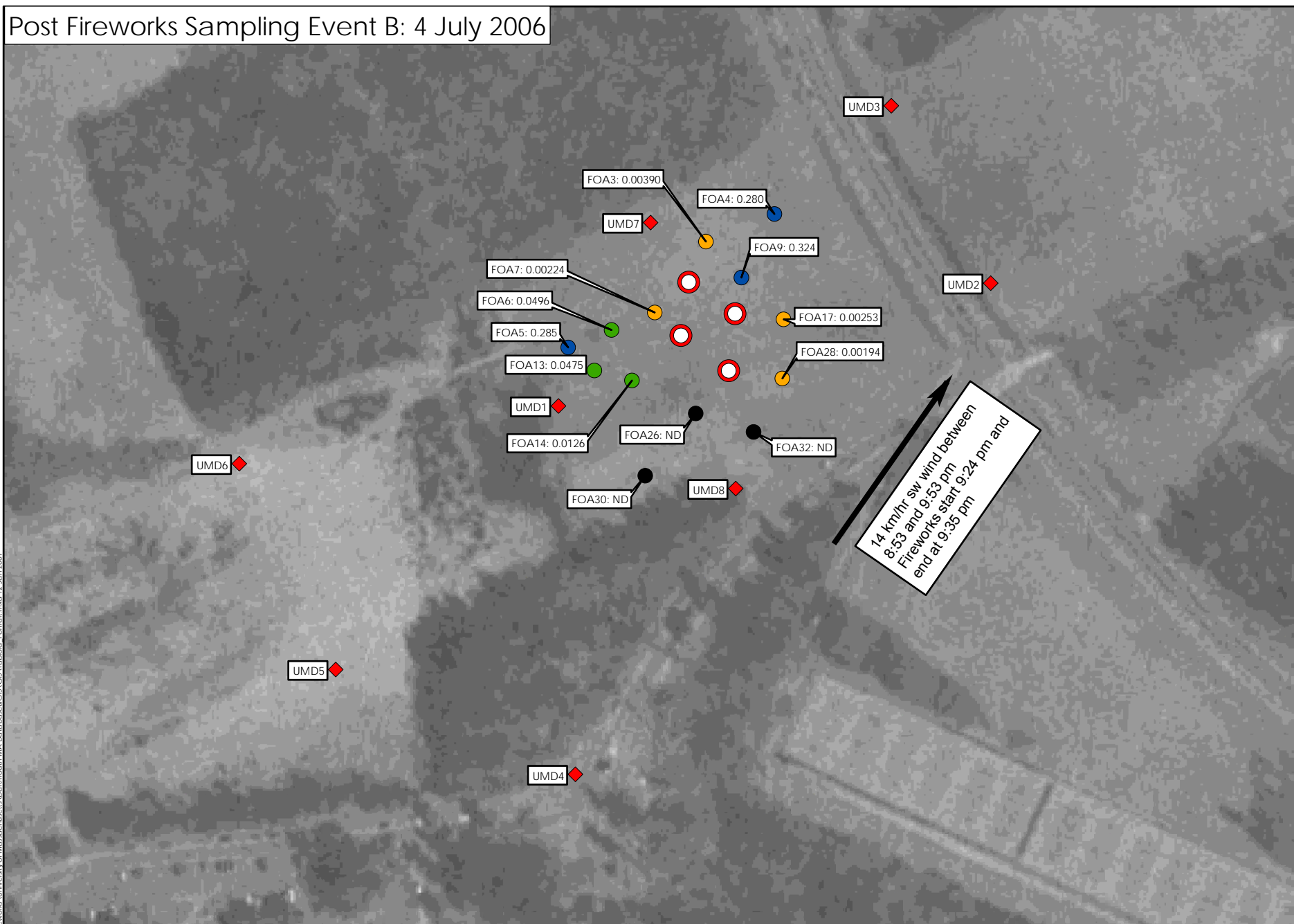
Guelph

13-July-2008

Pre Fireworks Sampling Event A: 15 June 2006



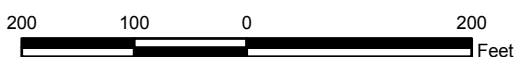
Post Fireworks Sampling Event B: 4 July 2006



Concentration (mg/kg)

- Non-Detect (<0.0008)
- ≤0.010
- >0.010 - 0.10
- >0.10 - 1.0
- >1.0

- Launch area 2006, consisting of poured sand on ground surface and fiberglass ignition cylinders
- ◆ Monitoring Well
- ND - Non-Detect



Perchlorate Concentrations in Soil
University of Massachusetts, Dartmouth Campus

Geosyntec
consultants

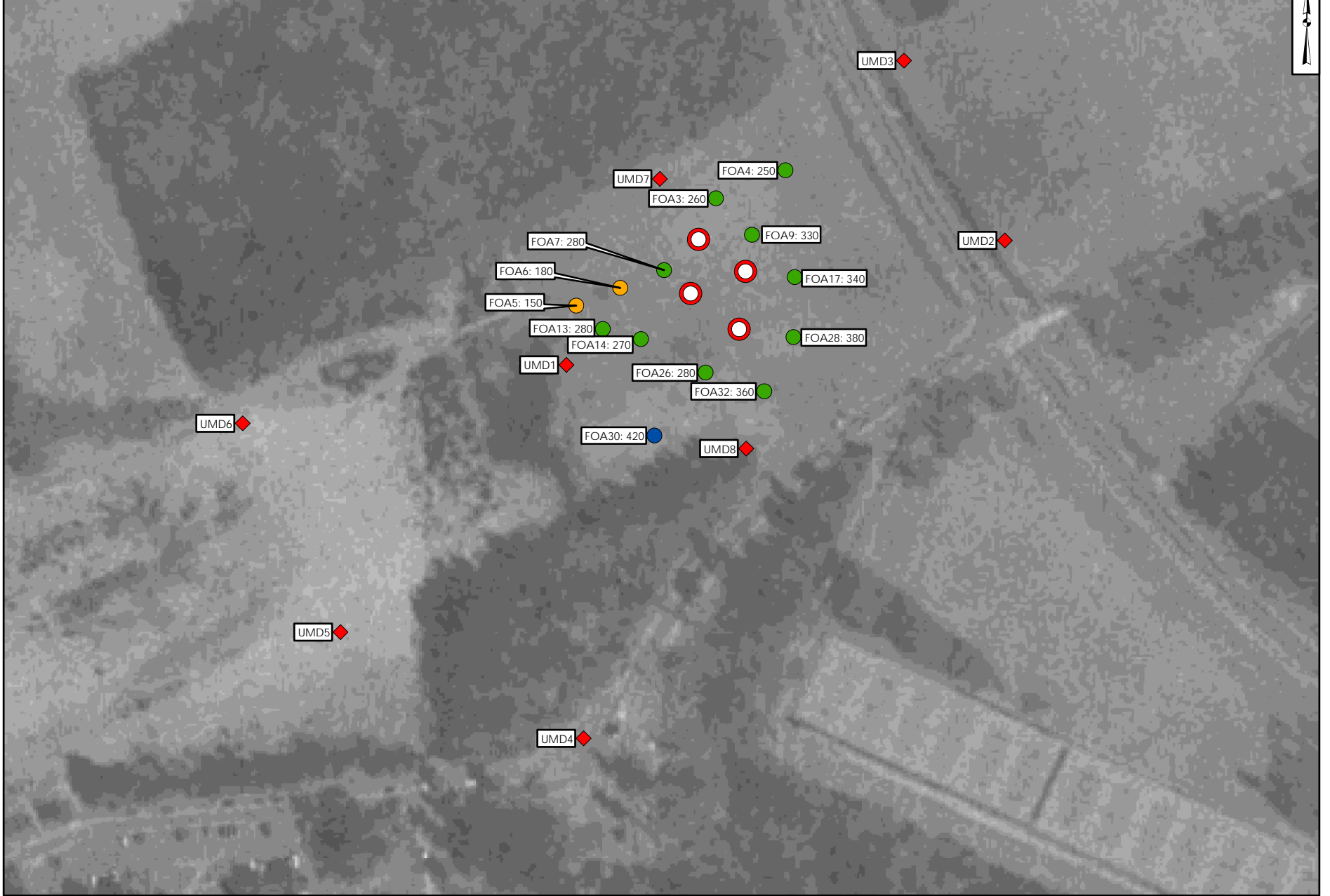
Guelph

14-July-2008

Figure

6.8

Pre Fireworks Sampling Event A: 15 June 2006

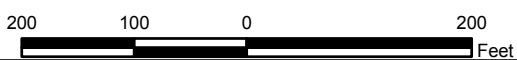


Post Fireworks Sampling Event B: 4 July 2006



Concentration (mg/kg)

- Non-Detect
- ≤200
- >200 - 400
- >400 - 600
- >600
- Launch area 2006, consisting of poured sand on ground surface and fiberglass ignition cylinders
- ◆ Monitoring Well
- ND - Non-Detect



Potassium Concentrations in Soil
University of Massachusetts, Dartmouth Campus

Geosyntec
consultants

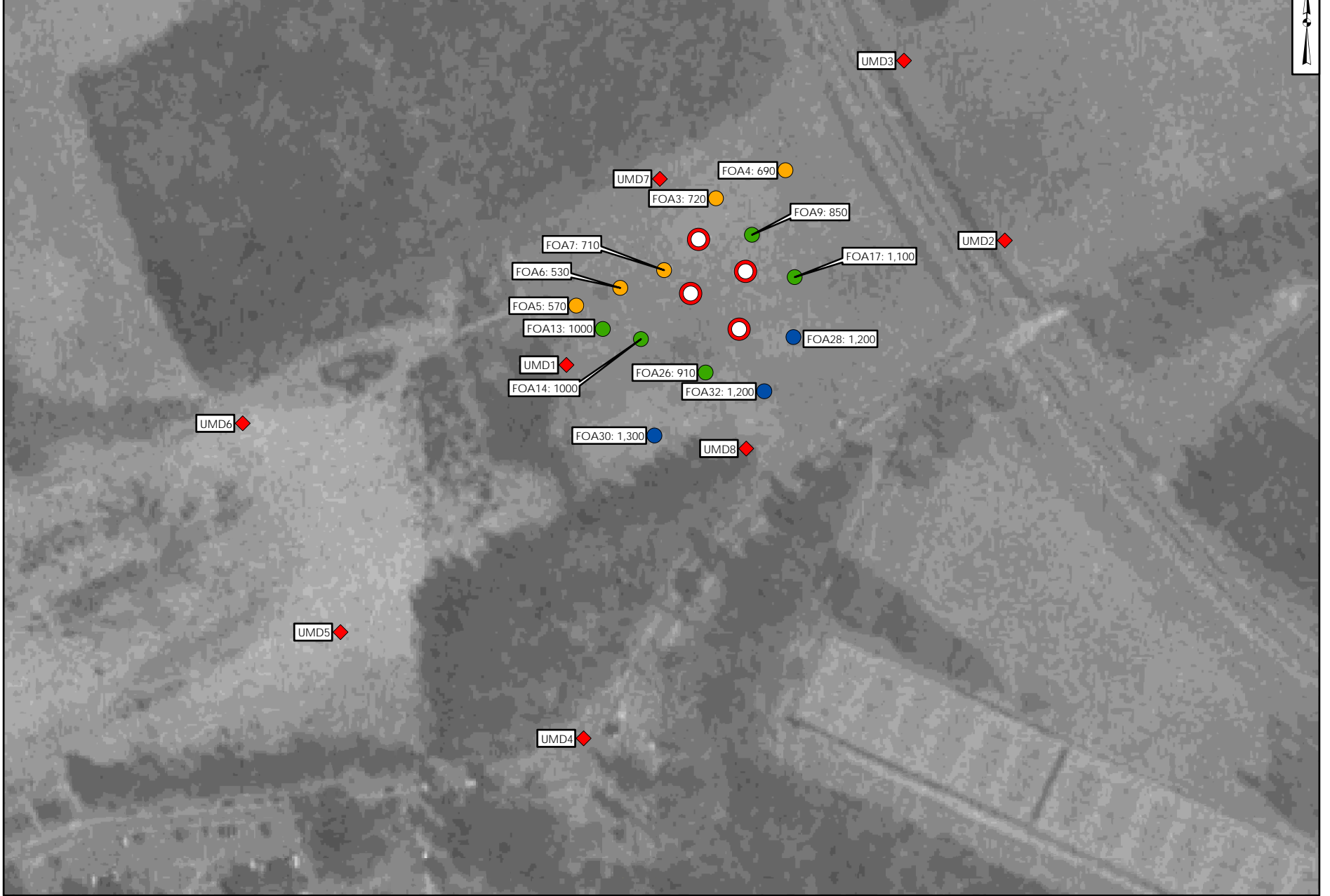
Guelph

14-July-2008

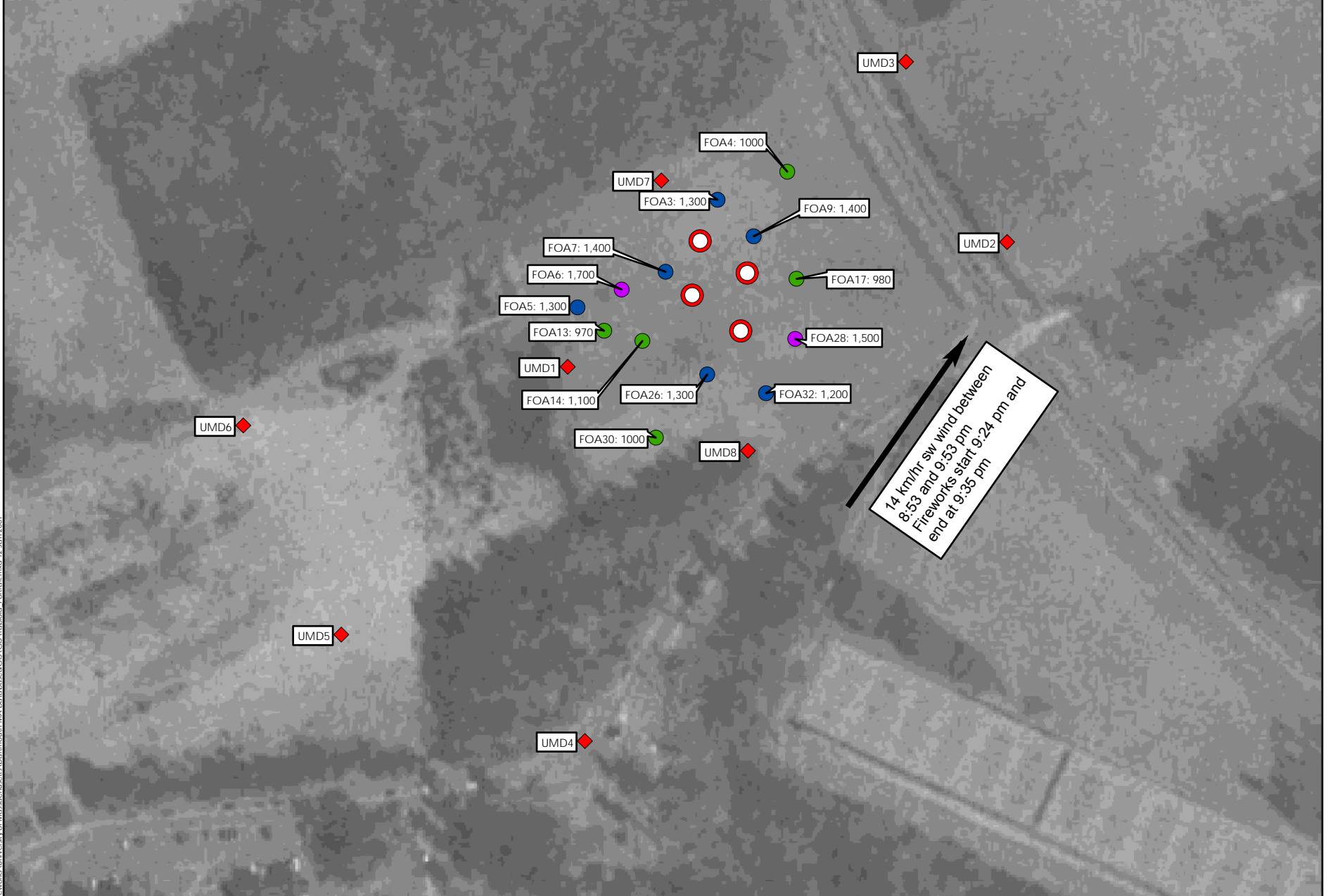
Figure

6.9

Pre Fireworks Sampling Event A: 15 June 2006

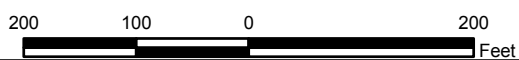


Post Fireworks Sampling Event B: 4 July 2006



Concentration (mg/kg)

- Non-Detect
- ≤800
- >800 - 1,100
- >1,200 - 1,400
- >1,400
- Launch area 2006, consisting of poured sand on ground surface and fiberglass ignition cylinders
- ◆ Monitoring Well
- ND - Non-Detect



Magnesium Concentrations in Soil
University of Massachusetts, Dartmouth Campus

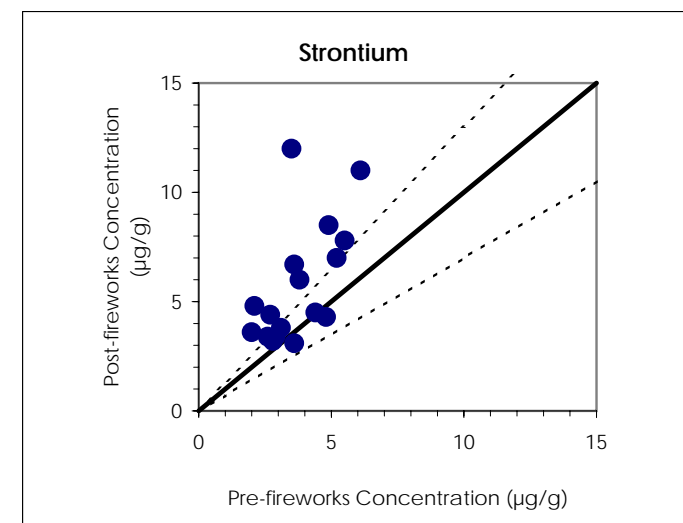
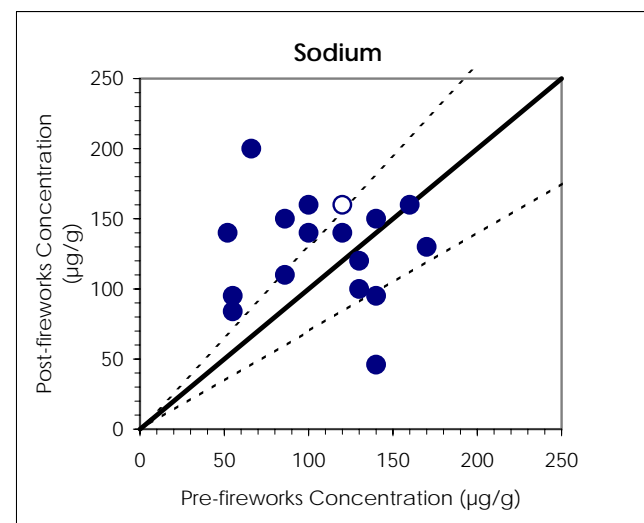
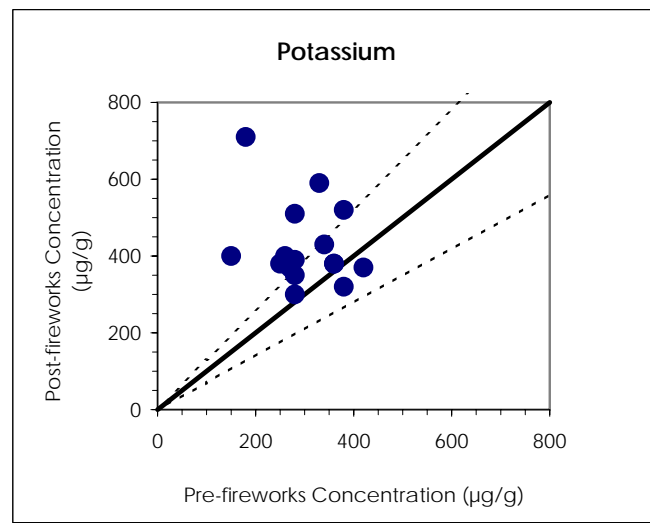
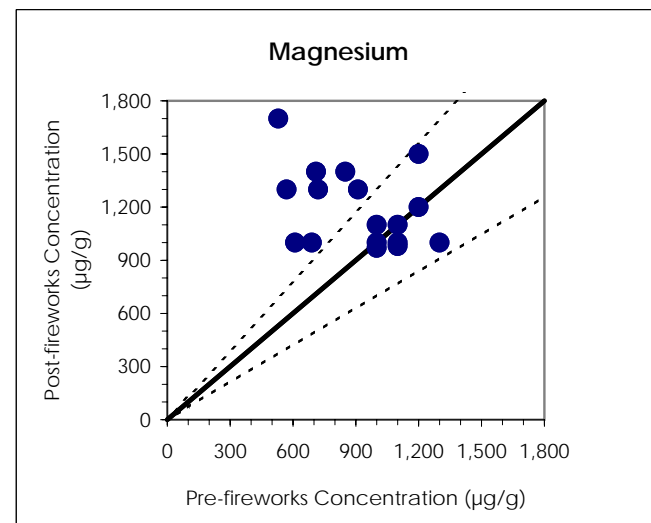
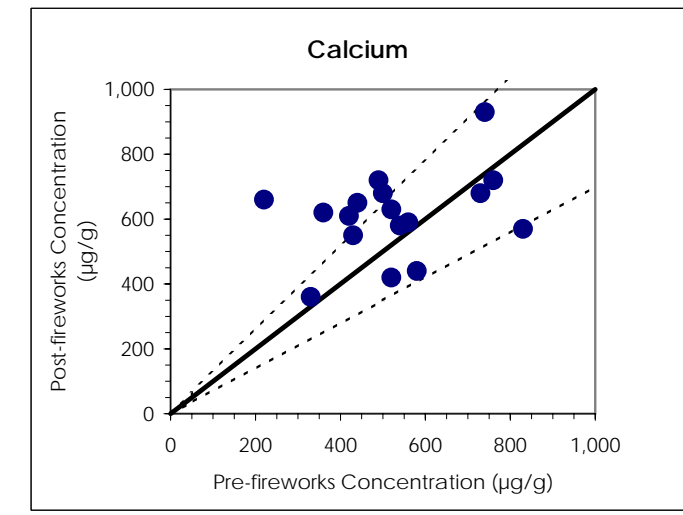
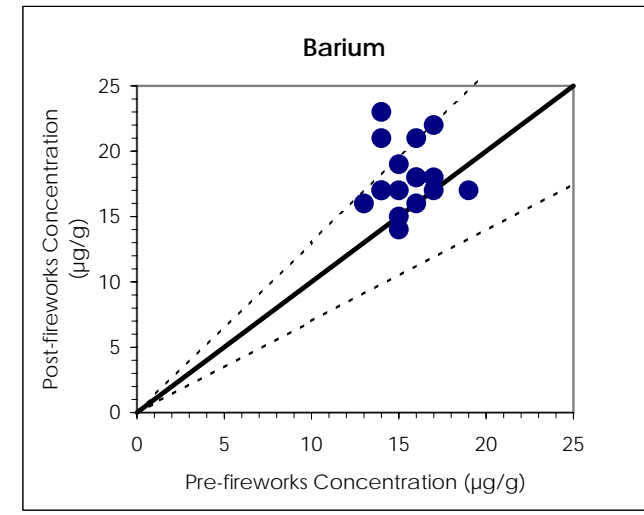
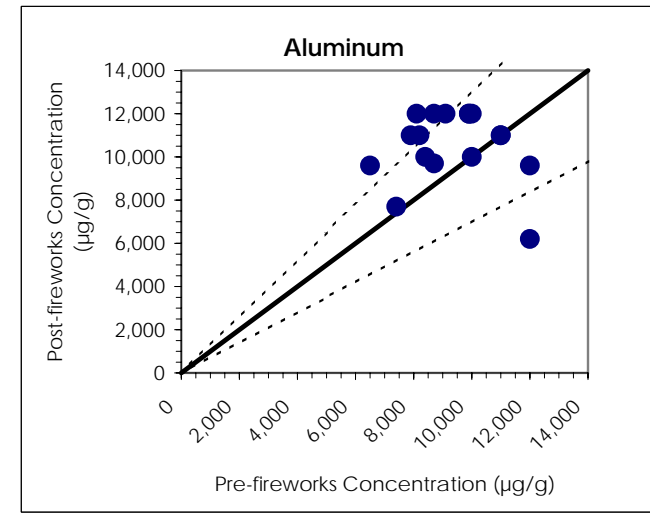
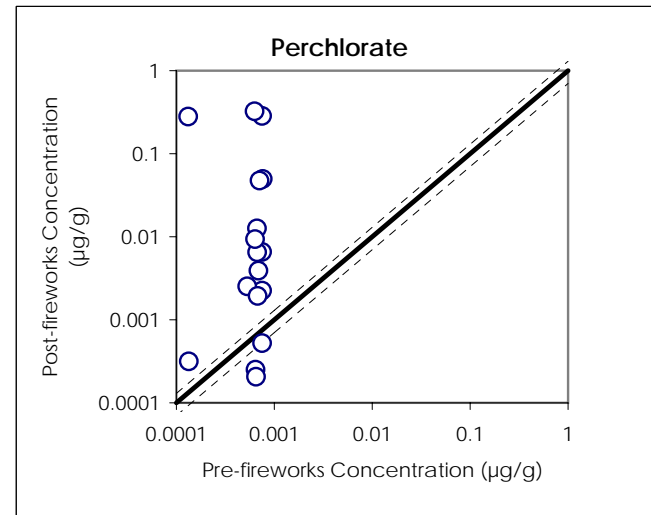
Geosyntec
consultants

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14-July-2008

Figure

6.10



Notes:

For perchlorate, open symbols indicate pre-firework sample where perchlorate concentrations were below the method reporting limit (variable).

For sodium, open symbols indicate pre-fireworks samples where sodium concentrations were below the method reporting limit (variable).

**Sample Comparisons For Select Compounds In Soil
Collected Before and After A Fireworks Display**
University of Massachusetts, Dartmouth Campus, MA



Guelph

14-July-2008

Figure

6.11

APPENDIX A

Hindcasting of Total Flows at Hobbs Creek from 1-95 Flow Rates

Purpose / Scope

The analysis of the June 7, 2006 event required establishing the relationship between two continuous variables, total stream discharge at Hobbs Creek (Figure A-1) and stream discharge at Interstate 95 USGS station. Flows at the I-95 USGS station had been monitored and collected over the period from June to September, whereas stream discharge at Hobbs Creek had been monitored from August 2006 to Sept. 2006. Of interest is the quantification of this relationship into a model for use as a predictive tool during days in which discharge from Interstate 95 was measured but Hobbs Creek stream discharge was not. The regression equation was used to quantify the perchlorate loads to the Cambridge Reservoir, the downstream water body that occurred during an actual flare deployment event on June 7, 2006.



Figure A.1. Hobbs Creek Sampling and Gauging Location

Figure A.2 represents the storm hydrograph for the time period August 20 – September 6, 2006, where both Hobbs Creek and USGS I-95 data were collected. Figure A.3 is a snapshot of the hydrograph from August 20 to August 21, which shows a lag time of approximately 6 minutes between peak flows. The lag time shows that it takes the peak flow 6 minutes to travel from the USGS gauging station to the Hobbs Creek gauging location at the outfall to the Cambridge Reservoir. To accurately predict the flows at Hobbs Creek based on the USGS I-95 station, the peak flows were aligned for use in the regression analysis.

Based on the time-lag hydrograph (Figure A.3), the data were manipulated to line up the peak values. The peak on 8/20/06 at 6:40:30 at the I-95 stations was paired with the peak on 8/20/06 at 6:46:30 at the Hobbs Creek station. By pairing the data, it allowed for a better understanding of the hydraulic properties of the watershed. The relationship between peak flows was used to predict the time at which the peak flow travels through the Hobbs Creek watershed.

Analytical Procedure for Regression Analysis

The regression equation was developed based on a simple linear regression model, which is the most common model used in hydrology to provide a means of predicting or estimating one dependent variable from knowledge of a second independent variable (Haan, 2002). A regression model is used to determine the best fit straight line in order to minimize the deviation between the observed values and the predicted values. When developing a regression equation, it is important to assess if the data be sufficiently described by the regression line. Methods for

assessing the sufficiency of the model were explored as means for choosing the best model that describes the relationship between the flows at the I-95 and the Hobbs Creek stations.

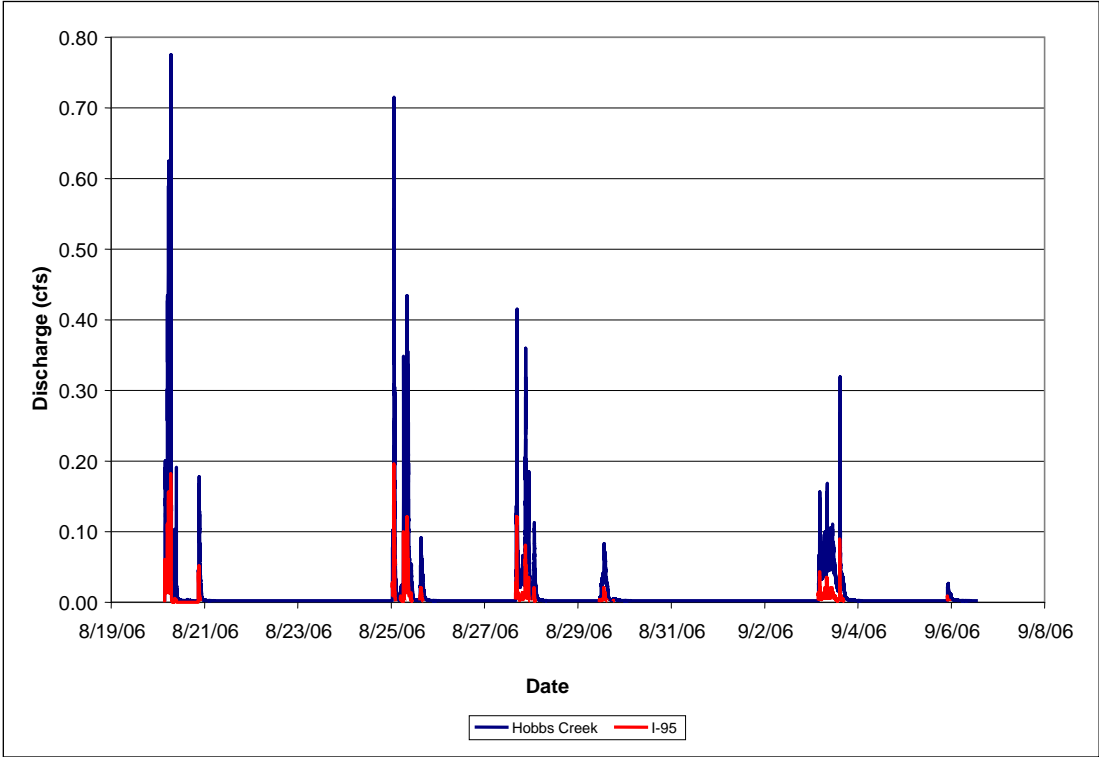


Figure A.2. Hydrograph of Hobbs Creek and I-95.

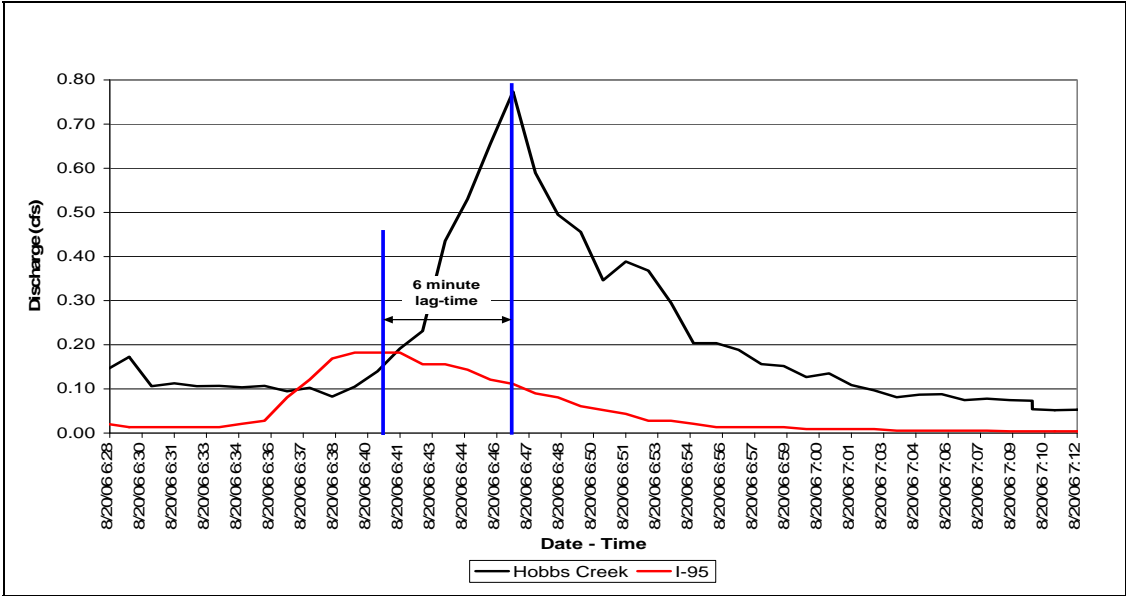


Figure A.3. Time Lag Hydrograph

The statistical software package MiniTab[™] was used in the development of the regression equation to describe the relationship between the flows at I-95 and Hobbs Creek. A simple linear regression equation (Helsel and Hirsch, 1993) is shown below:

$$Y_i = \beta_0 + \beta_1 x_i + \varepsilon_i \quad i=1,2,\dots,n$$

where:

Y_i	is the i^{th} observation of the response (or dependent) variable
X_i	is the i^{th} observation of the explanatory (or independent) variable
β_0	is the intercept
β_1	is the slope
ε_i	is the random error or residual for the i^{th} observation, and
n	is the sample size.

There are five assumptions associated with simple linear regression (Helsel and Hirsch, 1993). These assumptions are as follows:

- Model form is correct: y is linearly related to x .
- Data used to fit the model are representative of data of interest.
- Variance of the residuals is constant (homoscedastic). It does not depend on x or on anything else.
- The residuals are independent.
- The residuals are normally distributed.

To determine if the model form is correct, the data are plotted y versus x to determine if there is a linear trend. If a linear trend exists, one can proceed with the regression analysis. If a linear trend does not exist, further examination into the data is required to see if a transformation of the data can produce a linear trend.

In determining if the data used to fit the model are representative of the data of interest, the R^2 value and t -ratio can be examined. R^2 represents the fraction of variability in y that can be explained by the variability in x . An R^2 value of 1.00 means perfect correlation, a value of -1.00 means perfect inverse correlation, and a value of 0.00 mean no correlation or complete independence (Helsel and Hirsch, 1993). The t -ratio tests the null hypothesis that the coefficient is equal to zero. If $|t| \geq 2$, reject $\beta_1 = 0$ at $\alpha = 0.05$ for reasonably large samples, then there is a statistically significant linear relationship between x and y (Helsel and Hirsch, 1993).

Plotting the residuals versus predicted values enhances the opportunity to see curvature and heteroscedasticity. Heteroscedasticity is caused by non-normality of one of the variables, an indirect relationship between variables, or to the effect of a data transformation. Heteroscedasticity is not fatal to an analysis, but serves to weaken it instead of invalidating the analysis (Helsel and Hirsch, 1993).

A good residual pattern is where there is no relation between residuals and time which would show evidence that there is no correlation. Plotting the residuals on normal probability paper is usually the best indicator of the normal distribution of residuals. If the residuals depart from the normal distribution, then transformation of the y variable might be warranted (Helsel and Hirsch, 1993).

Regression Analysis:

Least-square regression was used for determining the regression equation. The plotted data (Figure A.4) shows a linear relationship, proving the assumption that the model is in the correct form. The regression analysis was performed using 2383 data points. The Hobbs Creek data were recorded every minute, whereas the I-95 data were only collected when stream discharge was greater than 0.001 cfs. The regression equation developed (Equation 1) from this data has an R² value of 88.6%.

$$Y_i = 3.26X_i + 0.0183$$

(Equation 1)

where

- Y_i the ith predicted value of Hobbs Creek
- X_i the ith value of I-95

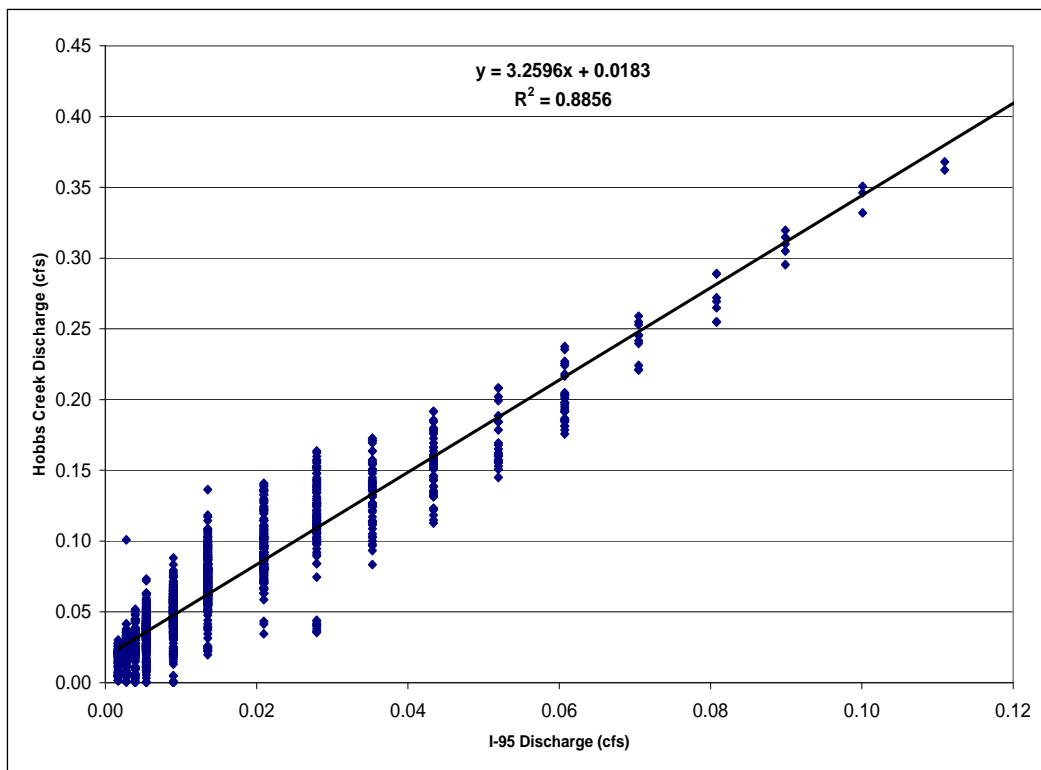


Figure A.4. Scatterplot of Y vs. X with Regression Line

Diagnostic Evaluation of the Regression Model

Diagnostic checks were done to test the model accuracy and to evaluate whether the regression assumptions were valid. Based on the R^2 value (88.6%) and a t-ratio of 135.7, which is ≥ 2 , the model is shown to be representative of the data of interest. These values show that there is a statistically significant relationship between y and x.

Plots of the residuals (Figure A.5 to A.7) show relationships that suggest that the model is a good predictor for the data. Figure A.5 is a normal probability plot of the residuals and indicates that the data are normally distributed, with the exception of a few points at both ends of the line. Figure A.6 shows the residuals versus time and indicates that there is no noticeable correlation between them. The test for heteroscedasticity (Figure A.7) shows some curvature in the data, which would lead one to believe that one of the variables is not normally distributed. Since the values on the other residual plots indicated that the data were normally distributed, no transformations were made to the data. The regression equation developed to describe the data is shown to be an overall good predictor for the total flow Hobbs Creek entering Cambridge Reservoir.

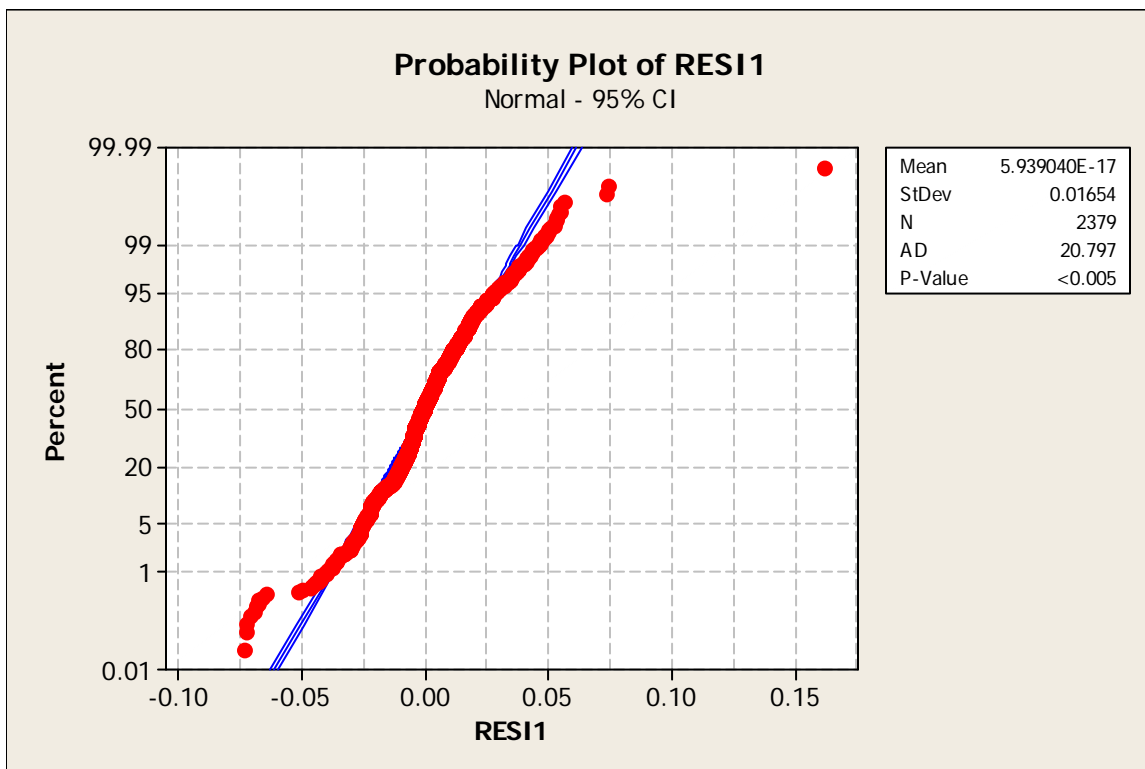


Figure A.5. Normal Probability Plot of Residuals with 95% Confidence Intervals

In the development of the regression equation, points that resembled high influence or leverage on the equation were deleted from the data set. Of the original 2566 data points, 183 (7%) of the data were deleted. These points were determined to be of high leverage by looking at DFITs. DFITs are used to determine if a point is of high influence. A point is determined to be of high influence if:

$$|DFITS| \geq 2 \sqrt{p/n}$$

(Equation 2)

where

p is the number of coefficients in the equation, and
n is the sample size.

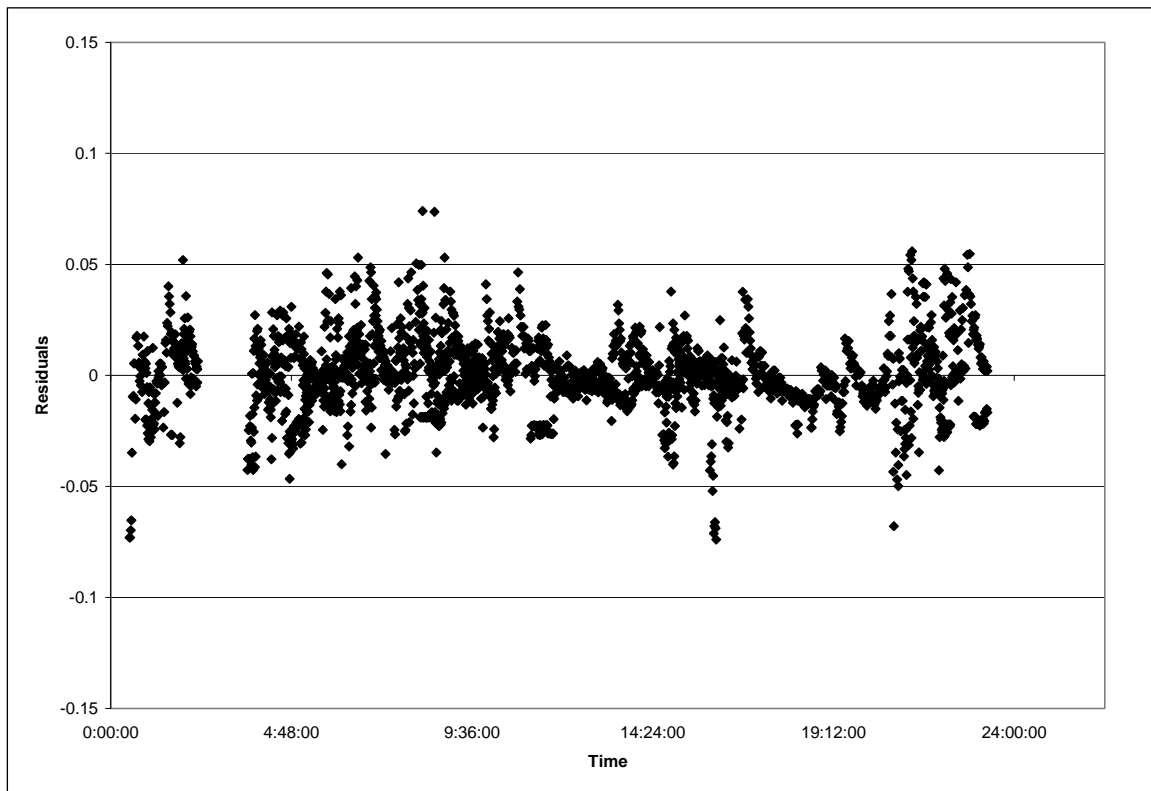


Figure A.6. Plot of Residuals vs. Time

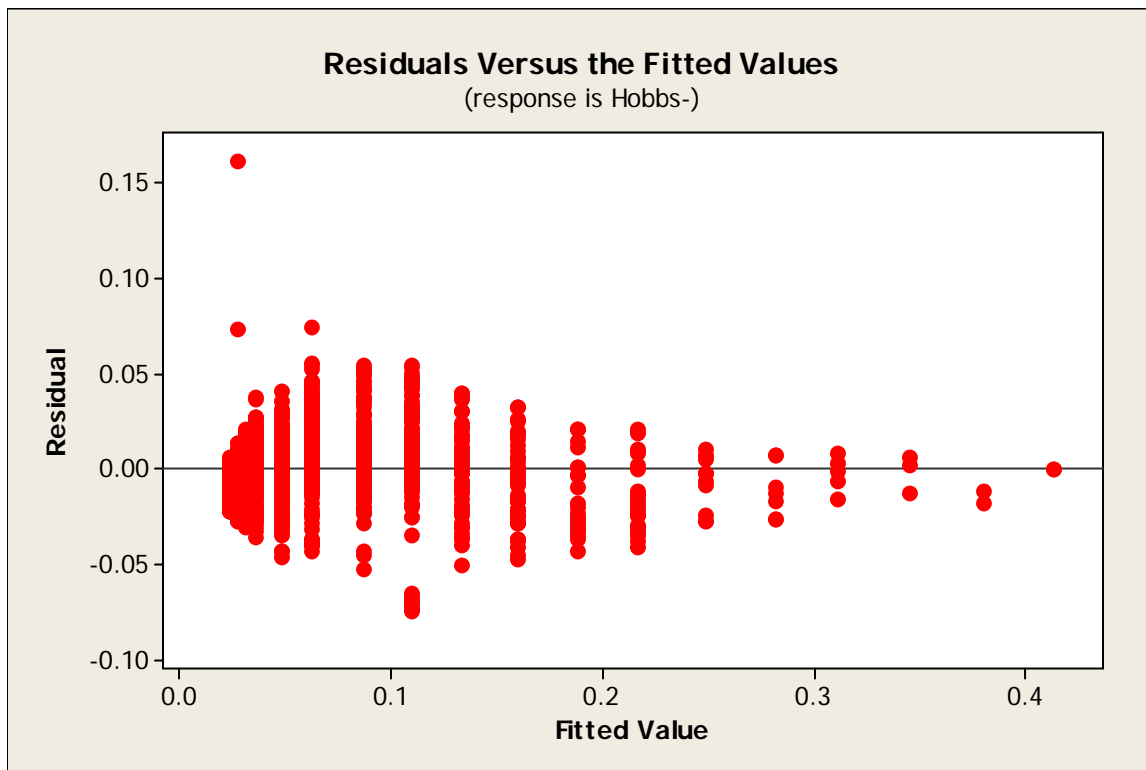


Figure A.7. Residuals versus Predicated Values

Results of the Regression Analysis

A regression equation was developed to predict flows for Hobbs Creek based on stream flow data at the I-95 USGS station. Based on 2383 data points, the final regression equation had an R^2 value of 88.6%. After evaluating the goodness of fit of the regression model on predicting the data, Equation 1 is shown to be a good predictor of total flows at Hobbs Creek. The total predicated flows at Hobbs Creek in Figure A.8 have been realigned to show the 6 minute lag-time between the peak flows.

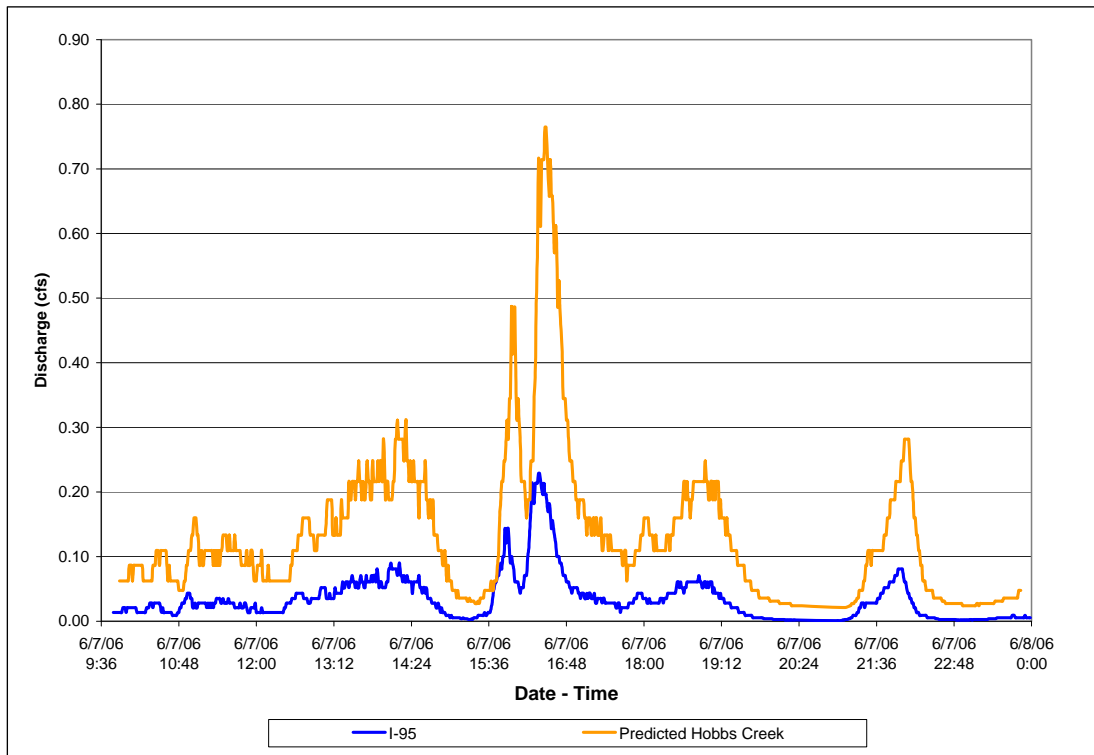


Figure A.8. Total Predicted Flow at Hobbs Creek

For the June 7, 2006 perchlorate concentration spike, the I-95 stream flow was known. By using the regression equation, Figure A.8 shows the predicted Hobbs Creek stream flow during that time. The 95% confidence intervals and 95% prediction intervals were examined to determine how much error was associated with the predicted values. The error associated with the predicted values was minimal. Figure A.9 is a plot of the actual Hobbs Creek total stream flow values versus the predicted total stream flow values on August 25 from 6:11am to 8:53am. This plot shows that there is very little under prediction or over prediction associated with the flows.

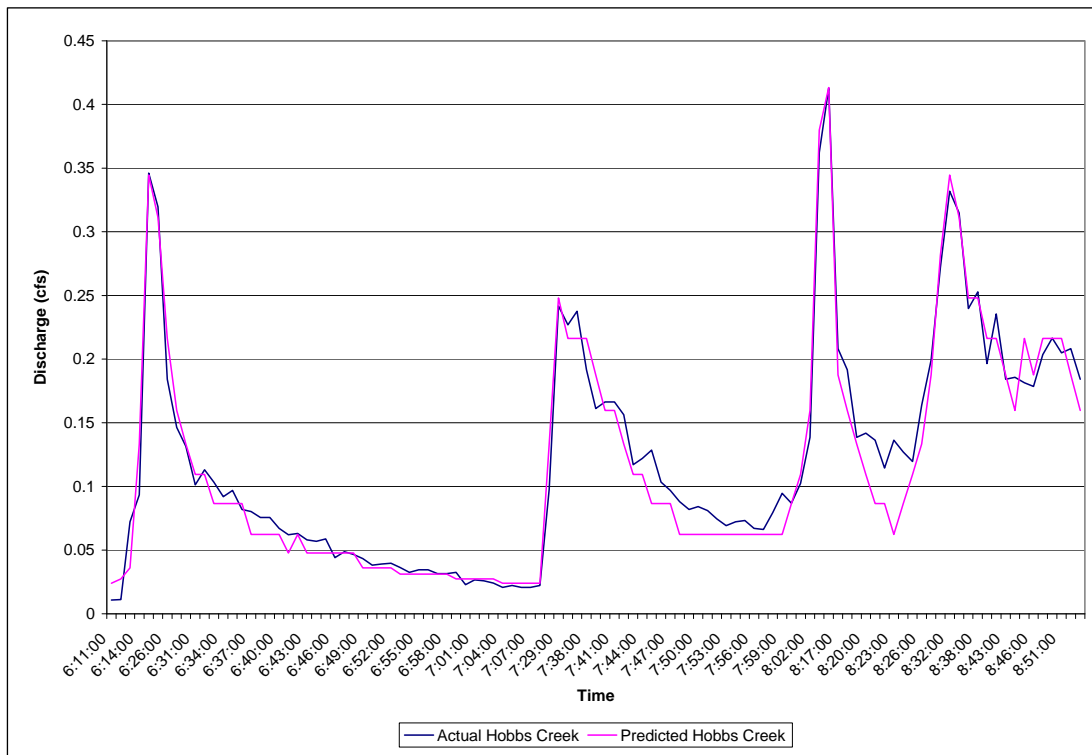


Figure A.9. Graph of Predicted Hobbs Creek and Actual Hobbs Creek Discharge

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