

**EXHIBIT THREE**  
**EVALUATION OF NOVEMBER 2013 DETECTION OF NEW PARAMETERS**  
**CLOSED COLLINSVILLE LANDFILL**  
**COLLINSVILLE, ILLINOIS**

### **EXHIBIT 3-1**

#### **Groundwater Assessment of 31 Additional Parameters under 35 IAC 620.410 and 4<sup>th</sup> Quarter 2013 Monitoring Results Submitted to IEPA in February 2014**

NOTE: This copy excludes the electronic data submitted to the IEPA as Appendix B, Appendix C Field Notes, Appendix D Chain of Custodies and Analytical Results of the above report, and the Analytical Results for Appendix E Historical Leachate Sampling Results that is provided in the data summary tables of this report and the historical letter reports for the leachate sampling.

**GROUNDWATER ASSESSMENT OF 31 ADDITIONAL PARAMETERS UNDER 35  
IAC 620.410 AND 4<sup>TH</sup> QUARTER 2013 MONITORING RESULTS  
CLOSED COLLINSVILLE LANDFILL  
COLLINSVILLE, ILLINOIS**

**FEBRUARY 2014**

**Prepared for:**

**CITY OF COLLINSVILLE  
COLLINSVILLE, ILLINOIS 62234**



**PROJECT NUMBER: 31891**

**PREPARED BY:**



**TETRA TECH, INC.  
1634 Eastport Plaza  
Collinsville, Illinois 62234**

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## ACRONYMS

AN	Ammonium Nitrate
bgs	below ground surface
CCA	Compliance Commitment Agreement
COC	chain of custody
DOT	Department of Transportation
IAC	Illinois Administrative Code
IDW	investigative derived waste
IEPA	Illinois Environmental Protection Agency
LPSTP	Longitudinal Peak Stone Toe Protection
MCCP	Mecoprop
MDEP	Massachusetts Department of Environmental Protection
mg/L	milligram per liter
PCB	polychlorinated biphenyl
SVOC	semi-volatile organic compound
TDS	total dissolved solids
TOC	total organic carbon
TOX	total organic halogens
µg/L	microgram per liter
USEPA	U.S. Environmental Protection Agency
VN	Violation Notice
VOC	volatile organic compound

## EXECUTIVE SUMMARY

Tetra Tech, Inc. (Tetra Tech) was retained by the City of Collinsville, Illinois (the City) to prepare this Groundwater Assessment of 31 Additional Parameters under 35 Illinois Administrative Code (IAC) 620.410 and the 4<sup>th</sup> Quarter 2013 Groundwater Monitoring Results as a part of the Closed City of Collinsville Landfill's monitoring program for Illinois Environmental Protection Agency's (IEPA) review.

The quarterly monitoring was prompted based on Violation Notice M-1998-00195, issued by the IEPA on October 6, 1998. This violation notice was a result of the IEPA's inspection of the landfill completed on April 22, 1998 that identified levels of chloride and Total Dissolved Solids (TDS) in monitoring well MW-1 had exceeded the Class I Groundwater Standards of 200 mg/L and 1,200 mg/L, respectively (35 IAC 620.420(a), except as provided in Section 620.450 or subsection (a)(3) or (d)).

In response to Violation Notice M-1998-00195, Tetra Tech performed several surface and subsurface investigations. The initial investigation was performed in 1999. In order to further assess the elevated concentrations of certain constituents, Tetra Tech prepared a Groundwater Assessment Plan dated May 2000 as a Supplemental Permit Application for the Closed Collinsville Landfill, pursuant to 35 Illinois Administrative Code Subtitle G, Part 807. The IEPA approved Supplemental Permit Number 2000-173-SP on January 3, 2001 to modify the groundwater monitoring program. The annual assessment of the groundwater at the Closed Collinsville Landfill was established under Supplemental Permit Number 2000-173-SP. Since 2000, the requirements of the groundwater monitoring program have been adjusted based on the findings of the 2006 assessment monitoring, but quarterly monitoring and an annual evaluation of the data continues under Supplemental Permit Number 2013-373-SP.

The subject of this report, submitted as a Supplemental Permit Application in accordance with Attachment A, Condition 25 of Supplemental Permit Number 2012-373-SP, includes an evaluation of the 31 additional parameters under 35 IAC 620.410 a), b), and e) and the presentation of the 4<sup>th</sup> Quarter 2013 sampling results collected concurrent with the 31 additional parameters.

4<sup>th</sup> Quarter analytical results detected three of the 31 additional parameters – perchlorate, Mecoprop (MCP) and p-dioxane (1,4-dioxane). Concentrations of perchlorate and MCP exceed the newly established Class I Groundwater Standards and arsenic exceeds the recently revised standard. The presence of perchlorate and arsenic are related to past activities at the former coal mine that once operated at the site. 1,4-Dioxane may be associated with the packaging of dynamite, but the most likely source is current use of herbicides that contain surfactants with 1,4-dioxane as an impurity. Additional monitoring is needed to assess the source of MCP. The three newly detected parameters will be monitored for three additional and consecutive quarters to evaluate background concentrations, identify baseline conditions and further assess the source of the MCP.

## **1.0 INTRODUCTION**

This Groundwater Assessment of 31 Additional Parameters under 35 IAC 620.410 and the 4<sup>th</sup> Quarter 2013 Groundwater Monitoring Results has been prepared by Tetra Tech on behalf of the City for submittal to the IEPA for review and approval.

### **1.1 Purpose and Objective**

According to the approved Supplemental Permit Number 2012-373-SP, Attachment A, Condition 25, the City shall conduct a single sampling event (in conjunction with routine quarterly groundwater monitoring) to determine that all new parameters do not exceed the newly established Class I Groundwater standard for 35 IAC 620.410 a), b), and e). Only parameters which do not currently have an approved background value were evaluated. The objectives of this report are to:

- Identify detected results;
- Compare the results to the newly established Class 1 Groundwater Standards;
- Establishment background concentrations of the detected parameters; and
- For each detected parameter, provide a rationale for why the facility is not the source of the detected parameters.

### **1.2 Statutory Authority**

Authority for responding to releases or threats of release from a landfill affecting groundwater quality is addressed in Title 35, Subtitle F, Chapter 1, Part 620 of the Illinois Environmental Protection Pollution Control Board. Under this act, the City or landfill owner is required to investigate, survey, test, or gather other pertinent data to assess the existence, extent, and nature of specified contaminants in groundwater. In addition, the City is authorized to undertake planning, engineering, and other studies or investigations to prevent, limit, or mitigate the risk to human health or welfare and the environment.



## 2.0 SITE CHARACTERIZATION

The site, shown in Appendix A, Figures 1 and 2, is described as a closed sanitary landfill located along Lebanon Road due east and outside the city limits of Collinsville, Illinois. It is located in the northwest quarter of Section 36, Township 3 North, Range 8 West, Madison County, Illinois. The closed landfill is approximately 22 acres in area and was in operation under the 807 regulations from the early 1970's through 1984 under permit number 1972-71. The site was closed in October 1986. The IEPA certified the landfill was satisfactorily closed in a letter dated October 24, 1986. A leachate collection system was installed after closure. Under permit 2011-EP-1106, collected leachate is transported and discharged to the Collinsville Waste Water Treatment Plant.

Based on previous studies, shallow groundwater at the site is approximately 10 feet below ground surface (bgs) and appears to be flowing in a northwesterly direction from the landfill toward Canteen Creek (Mathes, 1991; Tetra Tech, 2004, Tetra Tech, 2008a). The surface hydrology at the site is defined by ponds and creeks. Two small ponds/lakes are located near the landfill; both are considered upgradient of the landfill. One pond is located southeast of the landfill and the other lies southwest of the landfill. There are also two small creeks in the immediate vicinity of the site. The first creek, known as Canteen Creek, flows west along the northern edge of the landfill (between the landfill and Lebanon Road), and the other flows north along the western edge. The creeks merge at the northwest edge of the City's property. The creeks are sustained and recharged with groundwater (Tetra Tech, 2008).

Based on the results of the 2006-2007 assessment monitoring, the site and surrounding area was part of the Lumaghi Coal Company's Canteen Mine No.2. Aerial photographs and interviews with early landfill operators indicate that coal and coal gob were stored north and south of Canteen Creek from sometime prior to 1943. This area was incorporated into the area that later became the Collinsville Landfill and the land beneath the entire region is mined-out (Tetra Tech, 2008). The former location of the gob piles and the Canteen Mine #2 are shown in Figure 2.

## **3.0 PREVIOUS INVESTIGATIONS**

### **3.1 1998 Violation Notice M-1998-00195**

On April 22, 1998, the IEPA performed an inspection of the Closed Collinsville Landfill and sampled monitoring well MW-1 for inorganics, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), pesticides, herbicides, and polychlorinated biphenyls (PCBs). Results indicated concentrations of inorganic parameters, chloride, and TDS, were above Class I Groundwater Standards and the IEPA issued Violation Notice (VN) M-1998-00195 on October 6, 1998. The current well network including MW-1 is shown on Figure 2.

### **3.2 1999 Limited Surface and Subsurface Investigation**

The 1998 violation prompted the City to perform a groundwater investigation. In March 1999, Tetra Tech performed a limited surface and subsurface investigation, which included the installation of one piezometer, P-2, and the collection of groundwater samples from the existing well MW-1 and piezometer P-2. MW-1 was located along the western toe of the landfill and piezometer P-2 was installed upgradient and southeast of the landfill. Levels of chloride (11 mg/L) and TDS (776 mg/L) in P-2 were below their respective Class I groundwater standards and higher concentrations were found in MW-1, located downgradient of the landfill.

During Tetra Tech's March 1999 investigation, multiple surface water samples were collected from nearby ponds and creeks. The surface water was tested for elevated concentrations of chloride and TDS. The limited investigation verified the presence of chloride and TDS in MW-1 above Class I groundwater standards adjacent to the landfill and identified the absence of elevated chloride and TDS in surface water samples and groundwater upgradient of the landfill.

### **3.3 2000-2007 Groundwater Monitoring and Groundwater Investigations**

#### **3.3.1 Quarterly Assessment Monitoring (Supplemental Permit 2000-173-SP)**

Based on the March 1999 limited groundwater investigation, a Groundwater Assessment Plan (Supplemental Permit 2000-173-SP) was prepared to modify the groundwater monitoring program for the Closed Collinsville Landfill. The IEPA approved this supplemental permit on January 3, 2001. The purpose of the program was to monitor the groundwater and determine whether releases from the facility were occurring or whether constituents in the groundwater were below groundwater quality standards. The groundwater assessment program consisted of quarterly groundwater sampling and comparison of the results to groundwater quality standards cited in the IAC Section 35 Part 620.420(a). The list of parameters specified in the permit included List 1 Field Parameters, List 2 Routine Indicator Parameters, and List 3 Inorganic and Organic Annual Parameters. The list of parameters is identified in Appendix A, Table 1. The landfill was monitored for List 1 and List 2 parameters on a quarterly basis and List 3 parameters annually.

### **3.3.2 2001-2002 Assessment Monitoring (Supplemental Permit 2001-468-SP)**

In 2001, Tetra Tech installed additional piezometers (P-3, P-5, P-6, P7, and P-8) and monitoring wells MW-2 and MW-3. The piezometer and monitoring well locations are shown on Figure 2 in Appendix A. The investigation included an evaluation of the monitoring program and an assessment of groundwater flow and the hydraulic gradient. The annual 2001 Groundwater Assessment Monitoring Report was submitted in June 2003 as part of Supplemental Permit 2001-468-SP, which was approved by the IEPA on August 23, 2003.

The 2001 Groundwater Assessment Monitoring Report (revised in 2002 and 2003) noted several constituents above Class I groundwater standards at various locations. The elevated parameters included chloride, TDS, barium, beryllium, cadmium, chromium, iron, manganese, lead, and nickel. The report questioned the integrity of well MW-1 and further suggested that high turbidity or the presence of abandoned coal mines might account for the elevated levels.

### **3.3.3 2002-2006 Groundwater Monitoring (Supplemental Permits 2002-207-SP, 2002-347-SP, and 2003-417-SP)**

Tetra Tech continued to perform quarterly monitoring under Supplemental Permit No. 2001-468-SP. Three Supplemental Permits were approved during the period 2002-2004. Supplemental Permits Nos. 2001-468-SP and 2002-207-SP were combined and approved on August 26, 2003. The combined permits entailed the submittal of a revised 2001 Groundwater Assessment Monitoring Report (Revised 2003). Supplemental Permit 2003-417-SP was approved on November 30, 2004 and adopted the revised background concentrations for specific non-detected organic parameters and established a contingency to re-establish the background concentrations for field parameters (List 1), filtered and unfiltered inorganic parameters, and pentachlorophenol (parameters from Lists 2 and 3).

Since the third quarter 2002 groundwater sampling events, Tetra Tech performed groundwater sampling in accordance with low-flow sampling methods per guidance in the April 1998 U.S. Environmental Protection Agency (USEPA) *Ground Water Issue for Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*. The presence of silt and clay particles in the sample (turbidity) was believed to contribute to elevated levels of inorganic constituents such as beryllium, chromium, and sulfate. In 2003, quarterly monitoring continued and monitoring well MW-1A was installed to evaluate the integrity of adjacent well MW-1. Monitoring well MW-1 was installed approximately twenty-five years ago and no well construction or boring logs were available for this well. Supplemental Permits 2001-468-SP and 2002-347-SP specified that MW-1 was to remain a part of the monitoring program until results demonstrated the well was improperly constructed or damaged.

In 2004, two surface water samples were added to the monitoring program and background concentrations were reestablished. The surface water locations were sampled quarterly for a year for chloride and TDS. The results of the 2004 quarterly monitoring of the creeks confirmed the low levels of TDS and chloride found in surface water samples in 1999. Concentrations present in Canteen Creek were higher than those found in the unnamed creek located along the western perimeter of the landfill.

In July 2005, Tetra Tech submitted the 2001-2004 results to reestablish the background concentrations for MW-3. The results included background 99% upper confidence limits (UCLs) and for pH, lower confidence limits (LCLs). The results were incorporated with the report that evaluated well turbidity and well integrity (Log Number 2005-167). The 2004 background confidence limits were approved under Supplemental Permit No. 2005-167-SP.

Throughout 2003-2006, quarterly monitoring continued and Tetra Tech initially notified IEPA of a significant change in groundwater quality in the 2003 2nd Quarter Groundwater Monitoring Report submitted July 14, 2003. The significant change was a result of the presence of specific parameters at concentrations that exceeded Class 1 Groundwater Quality Standards, background concentrations, or two times the practical quantitation limit. Each year, Tetra Tech continued to notify the IEPA of a significant change in groundwater quality at the landfill in the Annual 2nd Quarter Groundwater Monitoring Reports. During the 2003-2006 monitoring period, the concentrations of the following parameters indicated a significant change in groundwater quality and resulted in the need for assessment monitoring: Chloride (filtered and unfiltered), manganese (filtered and unfiltered), pH, iron (filtered and unfiltered), TDS (filtered and unfiltered), barium (unfiltered), sulfate (filtered and unfiltered), total organic carbon (TOC), total organic halogens (TOX), sulfate (filtered), specific conductivity, phenols, picloram, and pentachlorophenol.

### **3.3.4 2006-2009 Groundwater and Assessment Monitoring (Supplemental Permits 2005-272-SP, 2006-269-SP, 2006-499-SP, 2007-310-SP, 2008-019-SP, 2009-080-SP, and 2009-358-SP)**

Three Supplemental Permits were approved during the period 2006-2007. Supplemental Permit 2005-272-SP, initially submitted in July 2005, was approved on June 22, 2006. The permit provided for routine quarterly sampling and implementation of the assessment monitoring activities for the facility specified in the Assessment Monitoring Plan. Monitoring well MW-1A was re-designated MW-4 in the permit. Supplemental Permit 2006-269-SP was approved October 12, 2006 and adopted additional assessment monitoring locations and sampling procedures. Supplemental Permit 2006-499-SP, approved on March 6, 2007, clarified the routine groundwater monitoring parameter lists and the additional assessment monitoring parameters.

From 2006-2007, Tetra Tech performed routine quarterly monitoring and assessment monitoring in accordance with Supplemental Permit 2006-499-SP. The Annual 2nd Quarter Groundwater Monitoring Report was submitted July 13, 2007 and was approved February 27, 2008 as Supplemental Permit 2007-310-SP.

Assessment monitoring activities commenced in November 2006 and included installation of three new wells (MW-5, MW-6, and MW-7), one new piezometer (P-14), nine borings, and collection of water samples from seven monitoring wells (MW-1 through MW-7), and seven surface water locations on a quarterly basis for one year. The nine borings were installed along the eastern and southwestern edge of the landfill to evaluate the boundary of the waste. The purpose of the assessment monitoring investigation was to evaluate the sources and extent of the following elevated unfiltered parameters: chloride, TDS, phenols, sulfate, pH, TOC, TOX,

arsenic, thallium, barium, iron, manganese, phenols, pentachlorophenol, and picloram. The concentrations of these parameters had previously exceeded Class I or background UCL and LCL. The Assessment Monitoring Report was submitted to the IEPA on January 14, 2008 as Supplemental Permit Application 2006-499-SP (Log No. 2008-019).

The findings of the assessment monitoring investigation included the following:

- The area surrounding and including the Closed Collinsville Landfill was impacted by coal operations that took place from early 1900 to 1950.
- Coal and gob were present on the northern and southern side of Canteen Creek in the area that now contains the landfill.
- The coal gob present on the south side of Canteen Creek was incorporated into the landfill.
- Surface water samples located along the western and northern perimeter of the former gob storage area exceeded surface water criteria for iron and manganese. Exceedances of upstream concentrations were limited to barium, arsenic, conductivity, chloride, iron, and manganese. Off-site locations did not exceed upstream concentrations or surface water criteria.
- MW-3 is located inside the landfill and is not an upgradient well. Groundwater collected from this well is leachate and not upgradient groundwater.
- Monitoring well MW-6 is upgradient of the landfill and Tetra Tech proposed that IEPA should designate MW-6 as the background well for the site.
- Canteen Creek is a gaining stream and groundwater in the vicinity of the landfill flows northeast and discharges to this creek. Groundwater within the landfill discharges to Canteen Creek and has not impacted downstream or downgradient locations.
- The source of the groundwater quality regarding low pH, chloride, TDS, TOX, arsenic, iron, thallium, and manganese is the presence of gob and coal within the landfill.
- The source of the groundwater quality regarding high pH, sulfate, TOC, barium, conductivity, phenols, and pentachlorophenol was the use of MW-3 as an upgradient well, when the well is actually in the landfill.
- The source of picloram may be due to the widespread use of the herbicide in the surrounding area or may be the landfill.

Approval of the Assessment Monitoring Report was deferred until the assessment monitoring results and environmental closure were formally discussed with the IEPA at a meeting in Springfield, Illinois on July 16, 2008.

The Annual 2nd Quarter Groundwater Monitoring Report for 2007-2008 was submitted to the IEPA as a supplemental permit application on July 10, 2008 (Log Number 2008-283). Approval of this permit application was deferred pending the outcome of the July 2008 meeting. The permit was approved November 8, 2008 and MW-5, MW-7, and P-14 were designated as piezometers and were removed from the sampling network. Water levels are obtained from MW-5, MW-7, and P-14 on a quarterly basis, but no groundwater samples are collected.

During the July 2008 meeting, the assessment monitoring results were discussed and the path forward was evaluated. Meeting participants agreed that the most effective approach to closure was development of a petition for adjusted standards based on the impact of previous coal mining where the landfill is located. Following the City's development of the petition, IEPA's legal counsel would evaluate and comment on the petition before final revision and submittal to the Illinois Pollution Control Board.

Following the July 2008 meeting, IEPA's approval of the Assessment Monitoring Report was initially denied due to the need for supplemental data, withdrawal of specific recommendations for land use controls, and revisions of the statistical calculations for confidence limits established for the assessment monitoring parameters associated with the new background well MW-6. Addenda to the report were submitted on September 5, 2008, October 10, 2008, October 30, 2008, and November 5, 2008. Supplemental Permit Applications associated with the Assessment Monitoring Report (Log No. 2008-019) and the Annual Monitoring Report (Log No. 2008-283) were approved as Supplemental Permit 2008-019-SP on November 21, 2008. This permit approved the assessment monitoring results and the new background monitoring well MW-6 and included a requirement to establish the background confidence limits for List 2 and List 3 parameters not previously included in the assessment monitoring.

During the 2006-2009 monitoring years, Tetra Tech continued to notify IEPA of a significant change in groundwater quality in the annual reports for the following parameters: Chloride (filtered and unfiltered), manganese (filtered and unfiltered), pH, iron (filtered and unfiltered), arsenic (filtered and unfiltered), lead (filtered), antimony (unfiltered), TDS (filtered and unfiltered), barium (unfiltered), TOX, sulfate (filtered and unfiltered), thallium (unfiltered), cobalt (unfiltered), specific conductance, fluoride (unfiltered), methylene chloride (unfiltered), and phenols. Beginning in March 2009, Tetra Tech notified the IEPA of significant change in groundwater quality on a quarterly basis and in the annual report for one or more of the above parameters.

On February 13, 2009, a Supplemental Permit Application requesting a reduction in the List 3 Organic Parameters was submitted to IEPA (Log No. 2009-080). The request was based on the limited detection of organic parameters in previous leachate samples, samples collected from MW-3 (located in the landfill) and a temporary well installed in the center of the landfill on October 25, 2008. Addenda were submitted on April 22, 2009 and April 23, 2009. The application was approved as Supplemental Permit No. 2009-080-SP on May 1, 2009. With the exception of the quarterly sampling (for one year) to establish the new background well MW-6, List 3 organic parameters for the remaining wells (MW-1, MW-2, and MW-4) were limited to benzene, monochlorobenzene, dichloromethane, pentachlorophenol, para-dichlorobenzene, and picloram. The Annual 2nd Quarter 2009 Groundwater Monitoring Report was submitted July 13, 2009 as a Supplemental Permit Application (Log No. 2009-358) and was approved as Supplemental Permit No. 2009-358-SP on November 10, 2009.

On March 10, 2009, IEPA issued VN M-2009-1006 to the City of Collinsville detailing 22 alleged violations of permit requirements associated with the Closed Collinsville Landfill. The alleged violations primarily concerned formal quarterly notification of a significant change in

groundwater quality and receipt of electronic data and reports. In response to the violation notice, a meeting was held at the Regional IEPA office in Collinsville, Illinois and a proposed Compliance Commitment Agreement (CCA) was submitted to IEPA on May 4, 2009. IEPA approved the proposed CCA on May 26, 2009 pending receipt of the alleged missing data and reports within the proposed schedule. On January 27, 2010, the City of Collinsville received a letter from IEPA stating that the Closed Collinsville Landfill had returned to compliance for the alleged violations and IEPA had verified receipt of all missing data.

### **3.3.5 2010 VN M-2010-01006**

On April 22, 2010, IEPA issued VN M-2010-01006 to the City of Collinsville detailing nine violations associated with the Closed Collinsville Landfill. The alleged violations primarily concerned the presence of seeps on the upper surface of the landfill. In response to the violation notice, The City of Collinsville repaired those areas where seeps may have been present. In addition, Tetra Tech prepared and submitted, on the behalf of the City of Collinsville, a CCA to IEPA on May 7, 2010 and prepared an inspection checklist for the City of Collinsville who now inspects the landfill on a monthly basis. On September 2010, IEPA issued a letter stating the Closed Collinsville Landfill had returned to compliance.

### **3.3.6 2010-2011 Groundwater and Assessment Monitoring (Supplemental Permits 2010-159-SP, 2010-342-SP, 2011-165-SP, and 2011-313-SP)**

The Supplemental Permit 2010-159-SP was issued August 31, 2010 in response to the April 14, 2010 submittal of the 2010 Re-Establishment of the Background MW-6 Statistical Results, and subsequent Addendum submitted July 29, 2010. During the Assessment Monitoring investigation in 2006, results suggested that the former background well, MW3, was installed within the landfill. Therefore, MW3 was not a background or upgradient well. MW6 was installed during the 2006 investigation as an upgradient well and analytical, hydrogeologic, and probing results indicated that MW6 met qualifications for a background well for the landfill.

Supplemental Permit 2010-342-SP, submitted as a Supplemental Permit Application on July 2010, was approved on March 31, 2011. The permit provided for routine quarterly sampling. Supplemental Permit 2011-165-SP was approved September 23, 2011 and accepted the 2011 review of 12 months of data for MW-1, MW-2, and MW-4 and comparison of the data to the recently established background values for MW-6. Supplemental Permit 2011-313-SP, approved on October 6, 2011, provided for routine quarterly sampling.

During the 2010-2011 monitoring year, Tetra Tech prepared and notified IEPA of a significant change in groundwater quality for the following parameters: chloride (filtered and unfiltered), manganese (filtered and unfiltered), low pH, iron (filtered), ammonia as N, arsenic (filtered and unfiltered), TDS (filtered and unfiltered), barium (unfiltered), cyanide, TOX, sulfate (filtered and unfiltered), and boron (unfiltered).

### **3.3.7 2011-2012 Groundwater and Assessment Monitoring and Other Activities (Supplemental Permits 2012-336-SP, 2012-348-SP, and 2012-313-SP-SP)**

The Annual 2nd Quarter 2012 Groundwater Monitoring Report was submitted July 12, 2012 as a Supplemental Permit Application (Log No. 2012-336) and was approved as Supplemental Permit No. 2012-336-SP on October 11, 2012.

### 3.3.7.1 Revised Petition for Adjusted Standards

In response to the presence of coal and gob beneath the northern half of the landfill, the City in partnership with the City's attorney for landfill closure and Tetra Tech, developed a Draft Petition for Adjusted Standards and supporting documentation. The purpose of the Petition was to move the landfill toward final environmental closure. The historic use, storage, and impact of coal waste at the landfill and surrounding areas documented in the Assessment Monitoring Report was the basis for the Petition and was in accordance with 35 IAC 620.440(c). The Draft Petition was submitted to IEPA on July 2, 2009. A revised Draft Petition was submitted to IEPA on January 30, 2012 for review prior to submittal to the Illinois Water Pollution Control Board. Based on telephonic communications with IEPA, the Agency has completed their review, and the petition will be forwarded to IEPA Legal Counsel.

### 3.3.7.2 Violation Notice L-2012-MD-025

On March 27, 2012, Madison County Government Planning and Development Department issued Violation Notice L-2012-MD-025 to the City of Collinsville detailing six violations associated with the Closed Collinsville Landfill. The alleged violations concerned the presence of seeps along the northern toe of the landfill and trash and seeps on a steep bank of nearby Canteen Creek. The presence of seeps along the northern perimeter of the landfill had been the subject of the VN issued in 2010. On June 4, 2012, the City submitted a response to VN M-2012-MD-025 and requested to enter into a CCA with the Madison County Planning and Development Department (Attachment 1). The issues and the proposed resolutions were:

1. Solution for Seeps – Installation of a supplemental leachate management system (French Drain).
2. Solution for Erosion along Canteen Creek – Longitudinal Peak Stone Toe Protection (LPSTP).
3. Solution for Early Detection of Seeps and Erosion Issues in the Creek – Inspection of the Creek.

The Madison County Planning and Development Department issued a proposed CCA to the City on June 25, 2012 and the City signed the agreement on July 7, 2012. The CCA accepted the resolutions identified above.

**Supplemental Leachate Management System** - Tetra Tech submitted the plan and design for the supplemental leachate management system to IEPA as a Supplemental Permit Application on June 28, 2012 followed by Addendum 1 and Addendum 2. The application was approved on October 29, 2012 as Supplemental Permit 2012-313 SP. Construction of the French drain began in January 2013 and the installation was completed in June 2013. Construction of the pump house and installation of the pump is scheduled to begin during the summer months if weather permits. A Completion Report will be submitted following receipt of the analytical results for the leachate installation of the pump and optimization of the pump rate and depth of pump.

**Installation of the LPSTP** – Tetra Tech submitted the plan and design for installation of LPSTP along a portion of Canteen Creek to IEPA as a Supplemental Permit Application on July 20,



2012 and the application was approved on October 18, 2012 as Supplemental Permit 2012-348-SP. Construction began in November 2012 and the majority of the construction was completed in November. Willow stakes were installed in March and sufficient growth was recorded in June 2013 to preparation the Completion Report. The Completion Report for the LPSTP was submitted in August 2013 as a Supplemental Permit Application (Log No. 2013-373) and was approved as Supplemental Permit No. 2013-373-SP on October 30, 2013.

### **3.3.7.3 Groundwater Monitoring 2012-2013 (Supplemental Permits 2013-325-SP)**

The Annual 2nd Quarter 2013 Groundwater Monitoring Report was submitted July 3, 2013 as a Supplemental Permit Application (Log No. 2013-325) and was approved as Supplemental Permit No. 2013-325-SP on October 3, 2013.

Supplemental Permit 2013 Permit No. 2013-373-SP associated with completion of the LPSTP was approved in 2013 and is described above.

During the 2012-2013 monitoring years, Tetra Tech prepared and notified IEPA of a significant change in groundwater quality basis for the following parameters: chloride (filtered and unfiltered), manganese (filtered and unfiltered), low pH, specific conductance, iron (filtered and dissolved), ammonia as nitrogen, arsenic (filtered and unfiltered), TDS (filtered and unfiltered), barium (unfiltered), sulfate, copper (unfiltered), and boron (unfiltered). Tetra Tech continues to perform quarterly monitoring under Supplemental Permit 2013-373-SP.

## 4.0 2013 4<sup>TH</sup> QUARTER SAMPLING PROCEDURES, METHODS AND ANALYSIS PARAMETERS

Tetra Tech collected the 4th Quarter groundwater samples in accordance with the schedule and methodology for sample collection in accordance with Supplemental Permit Number 2013-373-SP. Samples were collected on November 25, 2013.

### 4.1 Sampling Procedures

Prior to sample collection, Tetra Tech personnel record the static water levels on a quarterly basis with an electronic water level indicator at locations P-6, P-14, MW-1, MW-2, MW-3, MW-4, MW-5, MW-6 and MW-7. In accordance with the Groundwater Assessment Plan and the April 1998 USEPA *Groundwater Issue for Low-Flow (Minimal Drawdown) Groundwater Sampling Procedures*, Tetra Tech purged and sampled the monitoring wells using the low-flow method with a peristaltic pump (MW-1, MW-2, and MW-4) and dedicated tubing or a whale pump (MW-6) with dedicated tubing. Tetra Tech monitored and recorded List 1 field parameters until they stabilized. In a letter to the IEPA dated May 15, 2006, Tetra Tech made a formal proposal to conduct low-flow sampling at the landfill, which was approved (Supplemental Permit 2005-272-SP) on June 22, 2006.

Purge water was placed into Department of Transportation (DOT) approved 55-gallon closed-top metal drums located inside the Leachate Extraction Building 01 near the northwestern boundary of the Closed Landfill. Disposition of the wastewater generated during this assessment is described in Section 4.4 – Investigative-Derived Waste (IDW) Management.

Groundwater collected during the fourth quarter of 2013 were analyzed for the List 1 – Field Parameters and List 2 – Filtered and Unfiltered Routine Indicator Parameters and 31 additional parameters recently added to 35 IAC 620.410 a), b), and e) in accordance with Supplemental Permit No. 2013-373-SP, Attachment A, Conditions 21 and 25:

List 1 Parameters	List 2 Parameters	Additional Parameters in 35 IAC 620.410 a), b), and e)	
Temperature	<b>Filtered</b>	Perchlorate	Vanadium
Specific conductance	Ammonia as Nitrogen	Acenaphthene	Acetone
pH	Arsenic	Anthracene	Benzo(a)anthracene
Elevation of groundwater	Cadmium	Benzo(b)floranthene	Benzo(k)anthracene
Depth of water	Chloride	Benzoic acid	2-Butanone
Bottom well elevation	Iron	Carbon disulfide	Chloroform
Depth to water	Lead	Chrysene	Dibenzo(a,h)anthracene
	Manganese	Dicamba	Dichlorodifluoromethane
	Mercury	1,1-Dichloroethae	Diethyl phthalate
	Sulfate	Di-n-butyl phthalate	Fluoranthene
	Total Dissolved Solids	Fluorene	Indeno(1,2,3)pyrene
	<b>List 2 Unfiltered</b>	Isopropylbenzene	Mecoprop

List 1 Parameters	List 2 Parameters	Additional Parameters in 35 IAC 620.410 a), b), and e)	
	Cyanide	2-Methylnaphthalene	2-Methylphenol (o-cresol)
	Phenols	Naphthalene	p-Dioxane (1,4-Dioxane)
	Total Organic Carbon	Pyrene	alpha-BHC
	Total Organic Halogens	Trichlorofluoromethane	

The monitoring results were recorded on the IEPA's Chemical Analysis Form and submitted electronically. Copies of the electronic communications sent to IEPA along with the electronic data submittals are located in Appendix B.

Tetra Tech monitored and recorded the List 1 – Field Parameters with a YSI Model 556, an electronic water level indicator, and a Hach 2100 Turbidity Meter. The YSI 556 analyzes water quality parameters that include pH, specific conductance, dissolved oxygen, temperature, and oxidation reduction potential. List 1 – Field Parameters were recorded prior to the collection of groundwater samples. Copies of the field notes are located in Appendix C.

Groundwater samples for List 2 – Routine Indicator and the additional parameters recently added to 36 IAC 620.410 were collected using dedicated polyethylene tubing. The samples were collected after the field parameters stabilized. Groundwater samples were placed in the appropriate sample containers and delivered to the laboratory for analysis.

#### **4.2 Sample Handling, Preservation, Shipping, Chain-of-Custody and Quality Control Samples**

Field personnel used chemical resistant gloves while collecting groundwater samples. A clean pair of gloves was used for each sample collected. Approved USEPA sample containers were used throughout the project.

Groundwater samples were placed in the appropriate sample containers, sealed, and stored on ice in a thermally insulated shipping container for laboratory analysis. Samples were hand delivered by Tetra Tech to the NELAC-approved laboratory, Teklab, Inc. in Collinsville, Illinois.

A chain-of-custody (COC) record maintained sample custody and a listing of samples. The COC form was placed within each shipping container. The COC record was completed at the site by the individual designated by the Project Manager as responsible for sample shipment. Original COCs, signed by the field samplers and laboratory personnel, were returned to Tetra Tech with the analytical results. Copies of the COCs and the laboratory analytical results are included in Appendix D.

Duplicate samples are quality control samples designed to evaluate the laboratories ability to reproduce analytical results. The field duplicate and the primary field sample are defined as two water samples collected independently at the same sampling location during a single act of sampling. Tetra Tech submitted "blind" to the laboratory the sample "Field Dup" as a quality control sample. The groundwater sample, "Field Dup," was collected independently with the

groundwater sample from MW-1 for the third quarter 2011, fourth quarter 2011, first quarter 2012, and second quarter 2012.

### **4.3 Decontamination Procedures**

During the groundwater sampling field activities, the field equipment was decontaminated with Alconox soap and rinsed with distilled water after each sampling location. Dedicated polyethylene tubing was used during the groundwater purging and sampling, therefore decontamination of groundwater sampling tubing was not required between sampling locations.

### **4.4 Investigative-Derived Waste (IDW) Management**

IDW consisted of fluids from monitoring well purging activities and decontamination water. Decontamination and purge water was placed in DOT approved 55-gallon closed-top metal drums. The 55-gallon closed-top metal drums are located inside the Leachate Extraction Building 01 near the northwestern boundary of the Closed Collinsville Landfill. The City of Collinsville collects the water from the metal drums on a routine basis and transports the water for disposal at the City of Collinsville Waste Water Treatment Plant (2011-EP-1106).

Discarded materials, including personnel protective equipment, towels, and plastic bags, were disposed of in accordance with applicable regulations at the end of each day or work shift.

## 5.0 2013 4<sup>TH</sup> QUARTER GROUNDWATER RESULTS

This section includes analytical results for the 31 additional parameters recently added to 35 IAC 620.410 and the routine 4<sup>th</sup> Quarter results for samples collected at the Closed Collinsville Landfill on November 25, 2013.

Groundwater constituents at MW-1, MW-2, MW-4 and MW-6 were analyzed for the routine List 1 and 2 inorganic parameters every quarter in conjunction with the 31 additional parameters. A list of the parameters is provided in Section 4.1. Groundwater samples were compared to Illinois Class 1 groundwater standards as stated in Condition 25 of Permit Number 2013-373-SP Attachment A, “the facility shall conduct a single sampling event (in conjunction with routine quarterly groundwater monitoring) to determine that all new parameters do not exceed newly established Class 1 Groundwater Standards for 35 IAC 620.410 a), b) and e).

### 5.1 Parameters Exceeding Class I Standards in the Groundwater

The 2013 Assessment Monitoring Report (Tetra Tech, 2013) identified the presence of low pH, chloride, TDS, manganese, and iron at concentrations above Class I Standards. The above parameters continue to exceed Class I Standards and since the standard for arsenic was lowered, the arsenic concentration in MW-4 exceeded the new Class I Groundwater Standard of 10 µg/L. Tetra Tech evaluated the source of these parameters including arsenic (above the background concentration) as part of the assessment monitoring program under Supplemental Permit 2006-499-SP. Based on the results of the assessment monitoring, the primary source of the parameters present in the groundwater above Class I Standards is the presence of coal mining waste on the property for more than 60 years prior to the opening of the landfill. The Assessment Monitoring Report was submitted to the IEPA January 14, 2008 and was approved as Supplemental Permit 2008-019-SP. Adjusted standards have been developed in accordance with 35 IAC 620.440(c) based upon the historical impact of gob storage at the site that predates the landfill.

As shown in Table 1 (Appendix A), the samples collected from monitoring wells MW-1, MW-2, MW-4, and MW-6 were reported with concentrations of several parameters exceeding Class I Standards including two parameters that are included on the list of 31 additional parameters added to 35 IAC 620.410.

4th Quarter 2013 sampling results above Class 1 Standards are:

- **List 1** – Field parameters exceeding the Class I Standards: pH (6.44 in MW-1).
- **List 2** – Filtered routine indicator parameters exceeding the Class I Standards: arsenic (10.9 µg/L in MW-4); chloride (365 mg/L in MW-1 and 403 mg/L in MW-4), manganese (3,120 µg/L in MW-1; 7,340 µg/L in MW-4; and 224 µg/L in MW-6), and TDS (1,400 mg/L in MW-1 and 1,430 mg/L in MW-4). No unfiltered List 2 parameters exceeded standards.
- **List 3 - 31 Additional Parameters (unfiltered)** – The additional parameters detected during 4<sup>th</sup> Quarter included perchlorate, Mecoprop (MCP), and p-dioxane. The detected

parameters included on the list of 31 additional parameters exceeding the Class I Standards: perchlorate (40 µg/L in MW-1; 51 µg/L in MW4 and 7.8 µg/L in the background well MW-6) and MCPP in the duplicate sample of MW-1 (9.72 µg/L).

## 6.0 ASSESSMENT OF SOURCES AND EXTENT

The additional parameters detected during the 4<sup>th</sup> Quarter include perchlorate, MCP, and p-dioxane. Perchlorate and MCP exceeded the newly established Class I Groundwater Standards. Additionally, arsenic exceeded the revised lower standard of 10 µg/L. The extent and most likely source of each detected parameter is discussed below.

### 6.1 Introduction

The Lumaghi Coal Company owned the project site and surrounding land and mined coal on their property from approximately 1900 until the 1950s (Canteen Mine #2). The underground mine covered the project site and a large portion of the surrounding property. Other mines were present in the region and the subsurface from Glen Carbon, Illinois to southern Belleville, Illinois is characterized by exposed or water-filled room and pillar caverns from historic coal mining (Tetra Tech, 2008). During operation of the mines, activities that took place on the surface and in the subsurface included movement of coal, coal stripping and washing, equipment refueling, air venting, water pumping, blasting, milling, and maintenance of mine equipment and machinery. Each of these activities or a combination of these activities can result in contamination (Teaf, Mulisch, Kuperberg and Wcislo, 2006).

A large volume of coal and gob were moved to the landfill after the ore was extracted, stripped of pyrite pyritic rock, and washed. Gob is a coal waste that originates from the initial physical processing of coal that strips off the undesirable high sulfur pyrite. Coal associated with the Herrin Number 5 coal seam mined beneath the project site contained three percent sulfur (USGS, 2002). Coal waste such as gob contains a higher percentage of pyrite and other sulfide minerals than the processed coal. The sulfur-containing waste produces acid mine drainage when exposed to air (oxidation) or contact with surface water or groundwater (Anderson, et.al., 2000; Rose and Cravotta, 1998; USGS, 2004).

The coal and gob were stored in the northern half of the landfill and were exposed to the process of oxidation from the time of placement sometime before 1941 (the earliest aerial photograph of the area) until burial and incorporation into the landfill between 1968 and 1974 (based on aerial photos). Additionally, during active mining, groundwater was constantly pumped from the mine to keep the mine dry. Over the lifetime of a mine, the pumping creates a cone of depression leaving rock with remnants of exposed pyritic coal seams to an oxidizing environment for a long period of time (Teaf, et al., 2006). The oxidation of high sulfur coal and the resulting decrease in pH and high concentrations of other chemicals was discussed in the 2008 Groundwater Assessment report.

Based on the results of the 2008 assessment, the primary source of the high concentrations of chloride, manganese, low pH, specific conductance, iron, ammonia, arsenic, TDS, barium, sulfate, copper, and boron found in the groundwater at the landfill above Class I Standards and background criteria were attributed to the presence of coal mining waste and oxidation of those wastes (Tetra Tech, 2008).

A new literature search was performed to evaluate the source(s) of the elevated concentration of arsenic, perchlorate, 1,4-dioxane, and MCPP.

### **6.1.1 Arsenic**

Arsenic concentrations in MW-4 have historically and periodically exceeded the background concentration of 5.0 µg/L but did not exceed the Class 1 Groundwater Standard of 50 µg/L. Recently, the arsenic standard was lowered to 10 µg/L. The 4<sup>th</sup> Quarter results were compared to the recently lowered groundwater standard and the concentration of arsenic in MW-4 of 10.9 µg/L slightly exceeds the revised Class 1 Groundwater Standard. The arsenic exceedence in MW-4 is a direct result of the high sulfide content of the gob and the long-term exposure (oxidation) of pyritic coal.

The latest version of the Petition for Adjusted Standards requests that Class II Groundwater Standards be applied to inorganic parameters not specifically identified in the petition. Arsenic was not specifically listed; thus, the Class II Standard of 0.100 mg/L or 100 µg/L will be applied to arsenic at the site.

To date, the extent of arsenic is limited to the northern half of the landfill where coal was actively stored prior to incorporation of the landfill sometime after 1970.

### **6.1.2 Perchlorate**

Perchlorate is an anion consisting of a chlorine atom bonded to four oxygen atoms (ClO<sub>4</sub><sup>-</sup>). The anion typically bonds to ammonium, sodium, or potassium ions. Sources include natural sources such as Chilean nitrate, evaporate deposits and some potassium ores, and manmade manufactured perchlorate (Interstate Technology and Regulatory Council, 2005).

Man-made or natural perchlorate may be used in blasting agents, the manufacture, testing or disposal of military solid rocket propellant and munitions, commercial and military explosives, fireworks, safety flares, and industrial applications including the use of sodium hypochlorite solutions at water and wastewater treatment systems (GeoSyntec Consultants, 2005). According to the Massachusetts Department of Environmental Protection (MDEP), the largest source of perchlorates that contributes to groundwater contamination includes explosives and blasting agents (MDEP, 2006).

The dominant commercial explosives used during early coal mining activities until approximately 1945 included black powder, pellet powder, and ammonia dynamite. Perchlorate-containing detonators were used as blasting agents (oxidizers) to activate the explosives (Interstate Technology and Regulatory Council, 2005).

Early explosives were made with Chilean nitrate. The naturally occurring nitrate from Chile was primarily sodium nitrate and prior to 1930, contained up to 7% perchlorate. Chilean nitrate was the dominant source of saltpeter used in the manufacture of black powder. The use of black powder as a commercial explosive peaked in 1917, but the material is still used in limited situations today (GeoSyntec Consultants, 2005). Black powder substitutes often contained perchlorate and the use of these substitutes in commercial explosives continues to increase. Dynamite typically used in coal mines prior to 1950 was typically ammonia dynamite or AN



(ammonium nitrate) dynamite (GeoSyntec Consultants, 2005). This type of dynamite contains nitroglycerin and ammonium nitrate. Perchlorates are present in ammonium nitrate. Dynamite in common use today typically contains emulsions or gels and has a higher concentration of perchlorates (MDEP, 2006). The AN dynamite was packaged in paper tubes and sealed at both ends with paraffin wax and was often wrapped in paraffin wax-coated paper (Betts, 1996).

Though Canteen Mine #2 associated with the Closed Collinsville Landfill closed in 1950, a 1957 Illinois Coal Report listed the types of explosives used at the four remaining mines in Madison County as black powder, pellet powder, and dynamite. Permissible pounds allowed for the four mines with limited coal production (nearing closure) totaled 100,000 pounds (State of Illinois 1957). The dynamite at that time would have been AN dynamite (GeoSyntec Consultants, 2005).

Nitrate and perchlorate are both negatively charged ions and, as such, are highly mobile in soils. The negative charge prevents adsorption. Nitrates and perchlorates are both highly soluble in water. Additionally, nitrate and perchlorate are persistent in the groundwater and not easily degraded (MDEP, 2006). While most of the perchlorate present in black powder, AN dynamite and detonators are expected to be consumed upon detonation, poor housekeeping, spillage, improper use or misfires could leave residues of perchlorate in the soil or mine. Nitrate and perchlorate residues that remain in the soil or mines after blasting would have dissolved on contact with groundwater (GeoSyntec Consultants, 2005 and MDEP, 2006).

Since early operation of the landfill to the present time, no sources of military propellants or munitions, commercial explosives or blasting agents, fireworks, or flares have been identified that would have resulted in disposal of a significant source of perchlorate contamination at the landfill. The landfill closed prior to common use of perchlorates with industrial applications (GeoSyntec Consultants, 2005 and MDEP, 2006). Therefore, the most likely source of the perchlorates is the widespread use of explosives containing Chilean nitrate and blasting agents such as ammonium nitrate and ammonium perchlorate (used in AN dynamite and detonators). Additionally, the prevalence of nitrate in the groundwater is most likely due to the use of nitrate blasting agents rather than oxidation of the pyritic coal and gob.

Perchlorate was found above the newly established Class I Groundwater Standard of 4.9  $\mu\text{g/L}$  in MW-1, MW-4, and the background well MW-6. Concentrations ranged from 7.8  $\mu\text{g/L}$  (MW-6) to 51  $\mu\text{g/L}$  (MW-4). Based on the widespread prevalence of perchlorates, the upward vertical conductivity of the deeper mine water (artesian well MW-7), the length of time explosives and blasting agents were used (life of the mine), and the lack of other sources of perchlorates, the operation of the mine is the most likely source of perchlorates at the Closed Collinsville Landfill.

### **6.1.3 1,4-Dioxane or p-Dioxane**

The organic chemical 1,4-dioxane or p-dioxane is a synthetic industrial chemical or a impurity created during the manufacture of various products. This organic compound is completely miscible in water, highly mobile, persistent and does not biodegrade (USEPA, 2013). The compound is widely used as a solvent, chemical stabilizer, and a wetting or dispersing agent. It is present in paint strippers, dyes, varnishes, paint and paint thinners, greases, and waxes. Additionally, the compound is found as an impurity in antifreeze, de-icing fluids, deodorants,

shampoos, and cosmetics and is used in the manufacture of plastics and pharmaceuticals (Mohr, 2001). According to the USEPA, 1,4-dioxane is found in crops, food additives, and food packaging and appears to be ubiquitous in the environment (USEPA, 2013). However, one possible source of 1,4-dioxane present at the mine throughout its operation is the paraffin wax used in the paper to wrap dynamite and the ends of the actual tubes or “sticks” of dynamite (Betts 1996). The waxes may have contained trace amount of 1,4-dioxane as an impurity. Residues of the paraffin wax may have remained after blasting and any 1,4-dioxane would dissolve on contact with the groundwater.

The compound 1,4-dioxane is often found as a impurity in surfactants used in pesticides and herbicides. According to the Director of the City’s Street Department, Polaris/liberate lecitech /Roundup® Pro are herbicides applied to target locations (the area surrounding the four leachate collection buildings) and spot applied to the gravel road that traverses the landfill. The herbicides are applied during the growing season and applied in accordance with manufacturers specifications (Cheatham 2014). According to David H. Monroe, an Industrial and Environmental Toxicologist, in an October 16, 1989 letter to the National Campaign Against the Misuse of Pesticide, most polyalkoxylated surfactants such as the polyoxyethylene alkylamine in RoundUp are contaminated with 1,4-dioxane. A study done by Monroe on Vision, a glyphosate product by Monsanto, revealed that it contained 1,4-dioxane at a level of 350 ppm (<http://www.naturescountrystore.com/roundup/page2.html>, 2014).

1,4-Dioxane was detected in the northern half of the landfill at the locations of the highest detections of perchlorate and the location of the gob piles. Concentrations ranged from 4.3 µg/L to 6.12 µg/L, but did not exceed the Class I Groundwater Standard of 7.7 µg/L. Though there are many possible sources of 1,4-dioxane that might have been disposed at the landfill, no chlorinated solvents or chemicals associated with varnishes, paint, paint thinners, or antifreeze have been detected in landfill leachate (Appendix E). The organic chemicals detected in leachate samples include low levels of phenols (78 µg/L in MW03 in 2006), pentachlorophenol (6 µg/L in LS-1 in 2010), benzene (12.3 µg/L in TWP-L04 in 2008), monochlorobenzene (14.0 µg/L in TWP-L04 in 2008), paradichlorobenzene (7.63 µg/L in TWP-L04 in 2008) and picloram (0.234 µg/L in MW-3 in 2008). Pentachlorophenol, benzene, monochlorobenzene, and paradichlorobenzene have not been detected outside the landfill. Phenols and picloram have each been found on one occasion in MW-6 located upgradient and outside the landfill. The concentration of phenol (19 µg/L) in MW-6 exceeded the background 99% UCL of 15 µg/L in February 2010 and the picloram concentration of 0.941 µg/L was detected in MW-6 in November 2006 but did not exceed background criteria. Neither parameter exceeded the Class I Groundwater Standards or is associated with 1,4-dioxane.

The most likely source of the herbicides is the routine application of herbicides with trace concentrations of 1,4-dioxane

#### **6.1.4 Mecoprop (MCP)**

MCP, 2-(2-methyl-4-chlorophenoxy) propionic acid, is a member of the chlorophenoxy herbicide group that includes 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2,4-D and is commonly used in the United States. MCP is an herbicide applied to lawns or other types of turf for post-emergent control of broadleaf weeds typically found in lawns and sports fields. The

herbicide was registered in 1964 and as much as six million pounds are used annually (Carex Canada, 2014). In 1980, during the closing years of landfill operation, manufacturers increased the concentration of MCPP in the commercially available products. MCPP can be applied as a stand-alone broadleaf weed killer or with a mixture of other herbicides such as MCPA, dicamba, carfentrazone, sulfentrazone, 2,4-D, 2,4-DP, and monosodium methyl arsenate (MSMA). MCPP is also present in some formulations of weed and feed products. Scott's Ortho Weed Killer for Lawns with Crabgrass Control contains 22% MCPP (Carex Canada, 2014; McAfee and Baumann, 2007; and Beyond Pesticides, 1999). According to the City's Director of Streets, Ortho Products are used by the property owner adjacent to the landfill.

MCPP is miscible in water and is, therefore, a mobile compound and the third most detected herbicide in the United States (Cox, 2004). MCPP was detected in the duplicate sample collected from MW-1 (9.72  $\mu\text{g/L}$ ). The concentration slightly exceeded the Class 1 Groundwater Standard of 7.0  $\mu\text{g/L}$ , but the parameter was not detected in the primary sample. The actual presence or absence of MCPP above the criteria will be further confirmed during quarterly monitoring.

The source of MCPP is not known. The herbicide has been widely used and is heavily used today. The detection may be the result of disposal of herbicide containers that contained MCPP residues, use of the herbicide at the landfill or adjacent properties to minimize broadleaf weeds, use of the herbicide on adjacent property, or common dumping of trash in wooded areas adjacent to the landfill. Litter including varying sizes and shapes of plastic bottles and containers, tires, paper, and other trash is present in the wooded areas along Lebanon Road including the area adjacent to the landfill and areas adjacent to MW-1 and MW-4.

## 7.0 SUMMARY AND CONCLUSIONS

This groundwater evaluation of 4<sup>th</sup> Quarter monitoring results and the presence or absence of one or more of the 31 additional parameters was performed as a requirement of Supplemental Permit 2013-373-SP.

The objectives of this evaluation were to:

- Evaluate the presence or absence of the 31 additional parameters in conjunction with routine quarterly monitoring;
- Compare the analytical results to the recently revised or newly established Class 1 Groundwater Quality Standards;
- Provide rationale for the presence of the new detected parameters at the landfill; and
- Collect groundwater samples in conjunction with routine groundwater monitoring for four consecutive quarters for the detected compounds and statistically calculate background UCLs for these parameters in accordance with Supplemental Permit 2013-373, Attachment B.

Samples for the routine and 31 additional parameters were collected during the 4<sup>th</sup> Quarter sampling event. Based on the laboratory results, routine parameters including pH, arsenic, chloride, manganese, and TDS exceeded the Class I Groundwater Standards. Historically, these compounds have exceeded the Class I Groundwater Standards and the source of the elevated concentrations has been attributed to historic coal mining activities prior to use of the property as a landfill.

Three of the 31 additional compounds were detected in 4<sup>th</sup> Quarter Samples. Detected parameters include perchlorate, 1,4-dioxane, and MCPP. Perchlorate and 1,4-dioxane were present in two or more wells and MCPP was solely detected in the duplicate sample collected from MW-1. Concentrations of perchlorate and MCPP exceeded the Class 1 Groundwater Standard. The three compounds are strongly hydrophilic and perchlorate and 1,4-dioxane are persistent in the environment.

Based on the occurrence and historic use of the compounds, perchlorate is most likely associated with use of black powder, ammonia dynamite, and other explosives and blasting agents during the 50 year operation of the Lumaghi Canteen Mine #2 Mine. The dynamite was packaged in paraffin wax-covered paper with paraffin wax plugs and both may have contained 1,4-dioxane. However, the most likely source of the 1,4-dioxane is the use of herbicides that contain surfactants with 1,4-dioxane as an impurity.

The presence and the source of MCPP are less certain, but are most likely associated with current use of herbicides. However, samples of the leachate are currently being collected for inclusion in the Completion Report for construction and operation of a new French drain. Analytical results for the leachate and additional monitoring for MCPP will provide critical information to clarify whether the compound is actually present and, if present, the most likely source.

During the 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> Quarterly sampling events of 2014, samples will be collected for the routine parameters in accordance with Supplemental Permit No. 2013-373-SP and perchlorate, 1,4-dioxane, and MCP. The purpose of the additional monitoring of every well for the detected compounds is to establish a baseline for the current Petition for Adjusted Standards and identify a realistic standard for the three compounds for inclusion in the petition. Results of the monitoring and determination of background UCLs will be incorporated in a report and submitted as a supplemental permit application.

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USGS, 2004. *Effects of Abandoned Coal-Mine Drainage on Streamflow and Water Quality in the Shamokin Creek Basin, Northumberland and Columbia Counties, Pennsylvania, 1999-2001*, Water Resources Investigation Report 03-4311.

<http://www.naturescountrystore.com/roundup/page2.html>, 2014. Quoted an October 16, 1989 Letter from David H. Monroe, an Industrial and Environmental Toxicologist, to the National Campaign Against the Misuse of Pesticide.



# Appendix A

## Figures and Tables

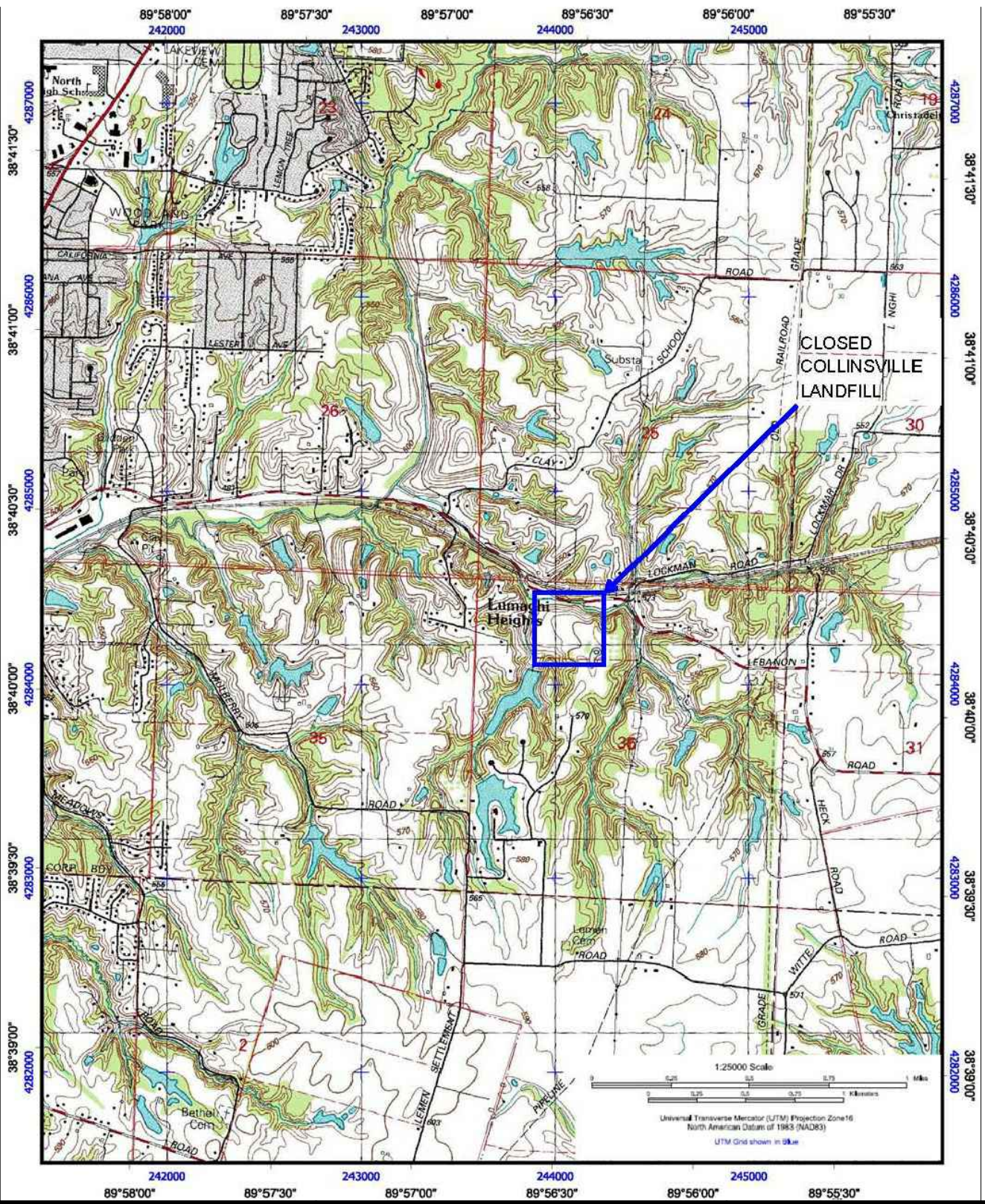
### FIGURES


- Figure 1 Topographic Map  
Figure 2 1998 Aerial Photograph, Sample Locations

### TABLES

- Table 1 4<sup>th</sup> Quarter Monitoring Results, List 1, List 2 and 31 Additional Parameters under 35 IAC 620.410 a), b), and e)

DRAWING: P:\SubwayCollinsville\T31891\7.0 Reports\Supplemental Permit Applications\Additional parameters and 4th Quarter\FIG 1 Location of Closed Collinsville landfill .DWG



 <p><b>TETRA TECH</b></p> <p>www.tetrattech.com</p> <p>1634 Eastport Drive Collinsville, IL 62234 PHONE: 618-345-0669 FAX: 618-345-1281</p>	Drawing Description	Project No.: 100-AMC-T28878
	Location of Closed Collinsville Landfill	Date: February 2014
<p><b>Collinsville Landfill</b> <b>Collinsville, Illinois</b></p>	Drawn By: DEF	Figure Number

Copyright: Tetra Tech

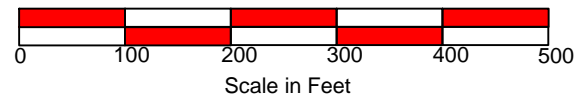
Closed Collinsville Landfill  
Petition for Adjusted Standards





### Legend

- Boundary of Waste
- Southern/Eastern Landfill Property Boundary
- Former Coal/Gob Storage
- Current Pond
- Creeks/Tributary
- Former Location of Mine Entrance
- Additional 2006-2008 Assessment Monitoring Sample Locations
- Current Sample Locations
- S - Surface Sample
- P - Piezometer
- MW - Monitoring Well
- SB - Soil Boring



[www.tetrattech.com](http://www.tetrattech.com)

1634 Eastport Plaza Drive  
Collinsville, IL 62234  
PHONE: 618-343-2300 FAX: 618-345-1281

Drawing Description  
1998 Aerial Photograph  
Sample Locations

Collinsville Landfill  
Collinsville, Illinois

Project No.: 31891

Date: February 2014

Drawn By: DWC/REB/RMN

Figure Number

2

Table 1  
4th Quarter Groundwater Monitoring Results - List 1, List 2 and 31 Additional Parameters under 35 IAC 620.410 a), b) and e)  
Closed Collinsville Landfill

**Comparison to Class 1 Groundwater Standards**

Compound	MW1	MW1 (DUP)	MW2	MW4	MW6	Class I
<b>List 1</b>						
Temperature of Water (unfiltered F)	56.16	56.16	54.5	56.19	54.84	NA
Spec Cond. (Unfiltered)	2.500	2.500	0.862	2.562	1.478	NA
pH (Unfiltered units)	<b>6.44</b>	<b>6.44</b>	6.65	6.5	6.65	6.5-9.0
Elev of GW Surf (ft ref MSL)	488.29	488.29	485.28	487.67	531.85	NA
Depth of Water (ft below LS)	7.89	7.89	9.8	7.76	29.96	NA
BTM Well Elev (ft ref MSL)	472.2	472.2	480.3	472	521.77	NA
Depth to Water Fr Mea Pt (ft)	10.61	10.61	11.02	10.73	31.85	NA
<b>List 2 Filtered</b>						
Ammonia as N Diss (mg/L)	0.11	0.10	<0.10	<0.10	<0.10	NA
Arsenic AS, Diss (ug/L)	<3.0	<3.0	<3.0	<b>10.90</b>	<3.0	10.0
Cadmium Cd, Diss (ug/L)	<2.0	<2.0	<2.0	<2.0	<2.0	5.0
Chloride Diss (mg/L)	<b>365.0</b>	<b>355.0</b>	31.0	<b>403.0</b>	81.0	200.0
Iron Fe, Diss (ug/L)	1,460.0	1,730.0	<40.0	4,930.0	<40.0	5,000.0
Lead Pb, Diss (ug/L)	<5.0	<5.0	<5.0	<5.0	<5.0	8.0
Manganese Mn, Diss (ug/L)	<b>3,120.0</b>	<b>3,290.0</b>	<15.0	<b>7,340.0</b>	<b>224.0</b>	150.0
Mercury Hg, Diss (ug/L)	<0.20	<0.20	<0.20	<0.20	<0.20	2.0
Sulfate SO4, Diss (mg/L)	82.0	83.0	121.0	91.0	54.0	400.0
Total Dissolved Solids (TDS, mg/L)	<b>1,400.0</b>	<b>1,410.0</b>	524.0	<b>1,430.0</b>	868.0	1,200.0
<b>List 2 Unfiltered</b>						
Cyanide CN, Total (mg/L)	<0.10	<0.10	<0.10	<0.10	<0.104	0.20
Phenols (Total Recoverable) (ug/L)	<15	<15.0	<15.0	<15.0	<15.0	100.0
Total Organic Carbon (TOC) (mg/L)	1.9	2.0	1.4	1.8	3.4	NA
Total Organic Halogens (TOX) (ug/L)	47.3	116.7	<20	97.4	59.9	NA
<b>Additional Parameters Part 620.410 a), b) and e)</b>						
Perchlorate (ug/L)	<b>40</b>	<b>36</b>	<4	<b>51</b>	<b>7.8</b>	4.90
Vanadium (ug/L)	<10	<10	<10	<10	<10	49.0
Acenaphthene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	420.0
Acetone (ug/L)	<5	<5	<5	<5	<5	6,300.0
Anthracene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	2,100.0
Benzo(a)anthracene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	0.13
Benzo(b)fluoranthene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	0.18
Benzo(k)fluoranthene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	0.17
Benzoic acid (ug/L)	<50	<50	<50	<50	<50	28,000.0
2-Butanone (MEK) (ug/L)	<5	<5	<5	<5	<5	4,200.0
Carbon disulfide (ug/L)	<2	<2	<2	<2	<2	700.0
Chloroform (ug/L)	<2	<2	<2	<2	<2	70.0
Chrysene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	12.0

Table 1  
4th Quarter Groundwater Monitoring Results - List 1, List 2 and 31 Additional Parameters under 35 IAC 620.410 a), b) and e)  
Closed Collinsville Landfill

**Comparison to Class 1 Groundwater Standards**

Compound	MW1	MW1 (DUP)	MW2	MW4	MW6	Class I
<b>Additional Parameters Part 620.410 a), b) and e) Continued</b>						
Dibenzo(a,h)anthracene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	0.30
Dicamba (ug/L)	<0.2	<0.2	<0.2	<0.2	<0.2	210.0
Dichlorodifluoromethane (ug/L)	<2	<2	<2	<2	<2	1,400.0
1,1-Dichloroethane (ug/L)	<2	<2	<2	<2	<2	1,400.0
Diethyl phthalate (ug/L)	<1	<1	<1	<1	<1	5,600.0
Di-n-butyl phthalate (ug/L)	<10	<10	<10	<10	<10	700.0
Fluoranthene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	280.0
Fluorene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	280.0
Indeno(1,2,3-cd)pyrene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	0.430
Isopropylbenzene (Cumene) (ug/L)	<2	<2	<2	<2	<2	700.0
MCPP (Mecoprop) (ug/L)	<7	<b>9.72</b>	<7	<7	<7	7.0
2-Methylnaphthalene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	28.0
2-Methylphenol (o-cresol) (ug/L)	<10	<10	<10	<10	<10	350.0
Naphthalene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	140.0
P-Dioxane (1,4-Dioxane) (ug/L)	5.15	4.3	<1	6.12	<1	7.70
Pyrene (ug/L)	<0.1	<0.1	<0.1	<0.1	<0.1	210.0
alpha-BHC (Alpha-Benzene) (ug/L)	<0.05	<0.05	<0.05	<0.05	<0.05	0.110
Trichlorofluoromethane (ug/L)	<2	<2	<2	<2	<2	2100.0

NOTES:

All units are as noted

**Highlighted and Bolded where the concentration exceeds Class I groundwater quality standards**

<: Compound not detected at or above detection limit. Value shown is the detection limit of the compound for the analytical process.

S: Spike Recovery outside accepted recovery limits

ref: reference

MSL: Mean Sea Level

LS: Land Surface

Fr Meas Pt: From Measuring Point

# **Appendix E**

## **Historical Leachate Sampling Results**



February 13, 2009

Mr. Stephen Nightingale, P.E.  
Manager, Permit Section  
Bureau of Land  
Illinois Environmental Protection Agency  
1021 North Grand Avenue East  
Springfield, Illinois 62794-9276

**Subject:** Closed Collinsville Landfill, 1194280002, Madison County,  
Collinsville, Illinois, Supplemental Permit No. 2008-019-SP,  
Request to reduce the number of List 3 organic compounds

Dear Mr. Nightingale:

Tetra Tech, Inc. (Tetra Tech), on behalf of the City of Collinsville, is submitting this letter to request a reduction in the number of List 3 organic compounds identified in Supplemental Permit No. 2008-019-SP, Attachment A, Condition 18. Tetra Tech requests, for future monitoring and re-establishment of background concentrations at MW-06 (Attachment A, Condition 25 of the permit), that the List 3 organic parameters be limited to the five compounds previously detected in leachate samples collected at the landfill. The List 3 organic compounds previously detected in leachate include: pentachlorophenol, picloram, 1,4-dichlorobenzene, benzene and chlorobenzene. Background and supporting information is provided below and in Appendices A and B.

During the past 10 years of monitoring performed at the Closed Collinsville Landfill, leachate samples were collected from the following locations:

- Monitoring well G103 (MW-3), installed as a background well in 2001, was sampled annually for List 3 inorganic and organic compounds. Results from the 2006-2007 assessment monitoring revealed the well was located inside the landfill and water collected from the well is considered leachate. Picloram and pentachlorophenol were detected in samples collected from MW-3.
- Temporary well point TWP-L04 was installed on November 25, 2008 and leachate sampled near in the center of the landfill where trash and leachate are thickest (Appendix A). Benzene, 1,4-dichlorobenzene, and chlorobenzene were detected in the leachate sample.
- Leachate Extraction Building 01 was sampled for List 3 organic and inorganic parameters in 2005 to expedite renewal of the Leachate Haul Permit 2001-EP-3642 (Appendix B). The permit was reissued as 2006-EP-0488 on March 20, 2006. Additional samples for one List 3 organic parameter, picloram, were collected at Building 01 on a quarterly basis in 2006 and 2007 for groundwater

Tetra Tech, Inc.

1634 Eastport Plaza Drive, Collinsville, Illinois 62234

Tel 618.345.0669 Fax 618.345.1281 www.tetratech.com

assessment monitoring activities. Organic parameters were not detected in leachate samples collected from this location.

Detected List 3 organic compounds are summarized in the table below. Boring logs, field notes, analytical data and the rationale for the location of TWP-L04 are presented in Appendix A and analytical data for the sample collected from the Leachate Extraction Building 01 in 2005 is presented in Appendix B. Analytical data from 2001 – 2008 associated with MW-3 was previously submitted to IEPA as part of the permit requirements.

SUMMARY OF LIST 3 ORGANIC COMPOUNDS DETECTED IN LEACHATE AT THE CLOSED COLLINSVILLE LANDFILL COLLINSVILLE, ILLINOIS				
Compound	Results (ug/L)	Location	Date	Class I Standards (ug/L)
Pentachlorophenol	0.399	MW-3	5-03	1.00
	0.653	MW-3	7-05	1.00
	0.324	MW-3	11-05	1.00
	0.130	MW-3	2-06	1.00
	0.223	MW-3	5-06	1.00
	0.326	MW-3	4-07	1.00
	0.135	MW-3	5-08	1.00
Picloram	0.234	MW-3	4-05	500
1,4-Dichlorobenzene	7.63	TWP-L04	11-08	75
Benzene	12.3	TWP-L04	11-08	5
Chlorobenzene	14.0	TWP-L04	11-08	100

Based on the information provided above and in the enclosed appendices, Tetra Tech requests reduction of the List 3 organic parameters identified in Supplemental Permit No. 2008-019, Attachment A, Condition 18 to the previously detected organic compounds pentachlorophenol, picloram, 1,4-dichlorobenzene (para-dichlorobenzene), benzene and chlorobenzene. Tetra Tech requests the reduction in the List 3 organic parameters be applied to the monitoring program (annual collection of List 3 organic parameters – Attachment A, Condition 18 of the permit) and to the reestablishment of the background as specified in Attachment A, Condition 25 of the permit.



Mr. Stephen Nightingale, P.E.

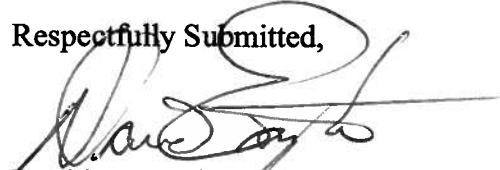
IEPA

February 13, 2009

Page 3

If you have any questions or comments concerning the above responses, please call me or Danielle Schmieg at (618) 345-0669.

Respectfully Submitted,

A handwritten signature in black ink, appearing to read "David W. Eagleton". The signature is written in a cursive style with a large, looped initial "D".

David W. Eagleton, PE  
Project Manager

**APPENDIX A**

**INSTALLATION AND SAMPLE COLLECTION OF LEACHATE**

**FROM A TEMPORARY WELL POINT INSTALLED IN THE LANDFILL**

**AT THE CLOSED COLLINSVILLE LANDFILL**

**COLLINSVILLE, ILLINOIS**

**APPENDIX A**  
**INSTALLATION AND SAMPLE COLLECTION OF LEACHATE**  
**FROM A TEMPORARY WELL POINT INSTALLED IN THE LANDFILL**  
**AT THE CLOSED COLLINSVILLE LANDFILL**  
**COLLINSVILLE, ILLINOIS**

Tetra Tech, performed additional field work at the Collinsville Landfill, Collinsville, Illinois on November 25, 2008. The objective of this work was to reduce the number of List 3 organic parameters identified in Supplemental Permit No 2008-019-SP, Attachment A, Condition 18 and thereby lower analytical costs.

Tetra Tech's activities included the following:

- Installation of one temporary well point (TWP) at a location where the trash and leachate was believed to be thickest;
- Collection of one leachate sample from the TWP for analysis of List 3 organic parameters;
- Abandonment of the TWP in accordance with Illinois requirements as soon as the sample was collected;
- Evaluation of the analytical data listing and summarizing parameters detected; and
- Submittal of the results to the Illinois Environmental Protection Agency (IEPA) along with a request to limit the List 3 organic parameters to those parameters detected in the leachate sample.

The selection of the TWP location was based on a review of the document: *Limited Site Investigation and Recommendation for Development of a Leachate Management System for the Closed Collinsville Landfill, Collinsville, Illinois, September 1991 (John Mathes & Associates, Inc.)*. According to the text of the document, a cross-section C-C,' and Plate 4 (Attachment A1), the trash and leachate were thickest near leachate well MW-1 (not the same as monitoring well MW-1 currently sampled). Leachate well MW-1 was located near the center of the landfill. Landfill characteristics at this well location included:

- Static water level for the leachate: 6.13 feet below ground surface (bgs);
- Estimated thickness of cover: six feet;
- Approximate thickness of trash: greater than 18 feet;
- Total saturated thickness: 17.87 feet; and
- Estimated depth to natural material: greater than 24 feet.

The location of leachate well MW-1, based on Plate 4, is 550 feet northeast of the small pump house located at the southern end of the gravel road.

Tetra Tech performed the work on November 25, 2008. Plate 4 was used in the field to find the approximate former location of leachate well MW-1. The boring was drilled near this location using direct push technology and the borehole was logged in accordance with IEPA protocols (see Attachment A2, boring log and field notes). A one-inch

piezometer was installed in the borehole. The PVC riser and screen were factory manufactured and the screen length was five feet. The depth of the boring was 16 feet. Leachate was extracted with a disposable bailer and pump and poured into laboratory-supplied containers, logged on a chain of custody form and submitted to TekLab for analysis of List 3 organic parameters. Sampling and analysis were performed in accordance with Supplemental Permit No. 2008-019-SP, Attachment A. Immediately following sample collection, the boring was filled with bentonite chips to the surface.

Analytical results are presented in Attachment A3 and the detected results are summarized below.

<b>Detected Organic List 3 Compounds Closed Collinsville Landfill Collinsville, Illinois</b>	
<b>Parameter</b>	<b>Result (ug/L)</b>
1,4-Dichlorobenzene	7.63
Benzene	12.3
Chlorobenzene	14.0

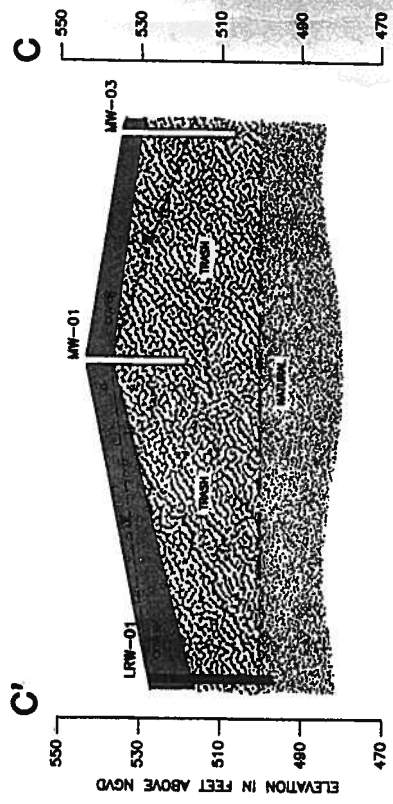
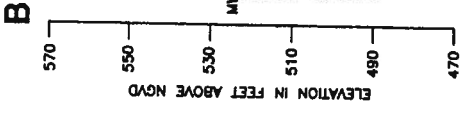
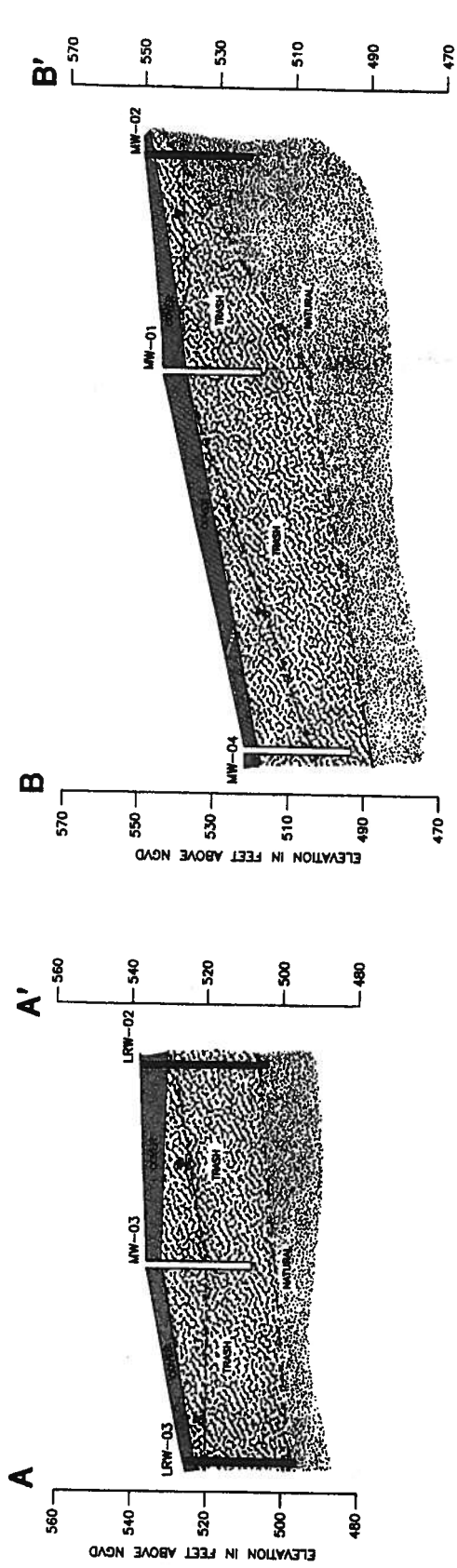
Tetra Tech would like to request that future organic List 3 parameters include 1,4-dichlorobenzene, benzene, chlorobenzene, pentachlorophenol and picloram only. The parameters listed in the table above were found in the leachate sample recently collected from temporary well described above. Picloram and pentachlorophenol were detected in MW-3. Based on information provided in the Assessment Monitoring Report (January 2008), MW-3, monitored for nine years, is installed within the landfill. Water collected from MW-3 is actually leachate.

**ATTACHMENT A1**

**CROSS-SECTION C-C AND PLATE 4 FROM**

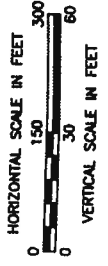
***LIMITED SITE INVESTIGATION AND RECOMMENDATION FOR DEVELOPMENT OF A LEACHATE  
MANAGEMENT SYSTEM FOR THE CLOSED COLLINSVILLE LANDFILL, COLLINSVILLE, ILLINOIS,***

***SEPTEMBER 1991, JOHN MATHES & ASSOCIATES, INC.***



- EXPLANATION**
- COVER MATERIAL (PRIMARILY SILTY CLAY)
  - TRASH MATERIAL (SLUDGE AND DEBRIS)
  - NATURAL MATERIAL (PRIMARILY CLAY)
  - PEIZOMETRIC SURFACE OF LEACHATE ON JUNE 21, 1991
  - MW-03
- BOREHOLE NUMBER AND APPROXIMATE LENGTH OF BOREHOLE. A SOLID LINE INDICATES THE BOREHOLE EXTENDED TO NATURAL MATERIAL.

**DRAFT**



John Mathes & Associates, Inc.  
CROSS SECTIONS  
A-A', B-B', AND C-C'  
COLLINSVILLE LANDFILL  
COLLINSVILLE, ILLINOIS  
123744

**General Note:**  
This profile was developed by interpolation between widely spaced boreholes. Only at the borehole locations should it be considered as an approximately accurate representation and then only to the degree implied by the notes on the borehole logs.

**FIGURE 2**

PROJECT	MANAGER	CHECKED	BY	DOCUMENT	DRAWN	BY	DATE
							9/20/81



**ATTACHMENT A2**  
**BORING LOG AND FIELD NOTES FOR**  
**INSTALLATION OF TWP-L04,**  
**NOVEMBER 25, 2008**



11/25/08 Mileage 33630.4 ~~STARS~~  
33647.8 17.4 Miles

Weather Clear, 31°F Winds NW 3-5 mph

ARRIVE 0830 Decker Harris (Chris Volde)

Set up near former location of MW-

TWP - L04

0850 Begin drilling TWP-L04

	PWD
0-6' Br silty clay, very hard	0-0.2'
6-7.3' GRAY silty clay	1.7'
7.3-16' TRASH	

Complete at 0915

Install TWP to 16' BGL (15.8')

15' PVC - 1"

5' Screen - Factory slotted 0.010

4.2' Stack up

WL = 11.38' TOC or 7.18' BGL

Sampled TWP-L04 at 0930 for  
last 3 organic parameters

DONE at 1000 Pull up PVCs <sup>Ben</sup> Fill up Ch.

1040 DEPART site

1200 Samples to LAB

Nancy M. Decker



**Illinois Environmental Protection Agency**

Site ID No. 1194280002 Federal ID No. \_\_\_\_\_

Site Name: Closed Collinsville Landfill

Quadrangle: Collinsville Sec. 36 T. 3N R. 8W

UTM (or State Plane) Coord. N. (X) \_\_\_\_\_ E. (Y) \_\_\_\_\_

Latitude: \_\_\_\_\_ Longitude: \_\_\_\_\_

Boring Location: Approx 300' SW of LRW-02 shed and 300' NE of LRW-01 near former

Drilling Equipment: TRUCK-MOUNTED Direct MW-1 Push Probing Unit

County: Madison

Boring No. TWP-LO4 Monitoring Well No. TWP-LO4 *Temp Well*

Surface Elevation: Approx 542' Completion Depth: 16' BGL

Direct Probe 16' BGL Auger Depth: \_\_\_\_\_ Rotary Depth: \_\_\_\_\_

Date: Start: 11/25/08 0850 Finish: 11/25/08 0915

Elev.	Description of Material	Graphic Log	Depth In Feet	SAMPLES					Personnel	REMARKS
				Sample No.	Sample Type	Sample Recovery (X)	Penetrometer	N Values (Blow Counts)	OVA or HNU Readings	
542	Br, v. stiff to hard silty clay, highly mottled DRY (CL)	[Vertical scale]	1				745	0		
540			2				745	0		
538	[Vertical arrow pointing down]	[Vertical scale]	3							
536			4				34/40	0		
534	GRAY soft to stiff silty clay slight mottling, moist (CL)	[Vertical scale]	5							
532			6				745	0.2		
530	TRASH and wood w/ some clay (FILL)	[Vertical scale]	7				1.0			
528			8				29/40	1.7	slight odor	
526		[Vertical scale]	9						SATURATED AT 7.3' BGL	
524		[Vertical scale]	10							



**EXHIBIT 3-2**

**Selected Reference Material Used for the Evaluation of Sources of the New Parameters**

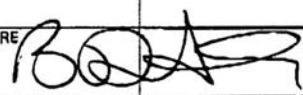
*Perchlorate*

**ALTERNATIVE CAUSES OF WIDE-  
SPREAD, LOW CONCENTRATION  
PERCHLORATE IMPACTS TO  
GROUNDWATER**

**FINAL**

**Prepared by:  
GeoSyntec Consultants  
for the  
Strategic Environmental Research and  
Development Program (SERDP)  
Arlington, Virginia**

May 5, 2005

<b>CLEARANCE REQUEST FOR PUBLIC RELEASE OF DEPARTMENT OF DEFENSE INFORMATION</b> <i>(See Instructions on back.)</i> <i>(This form is to be used in requesting review and clearance of DoD Information proposed for public release in accordance with DoDD 5230.9.)</i>			
<b>TO: Director, Freedom of Information &amp; Security Review, Rm. 2C757, Pentagon</b>			
<b>1. DOCUMENT DESCRIPTION</b>			
a. TYPE White Paper	b. TITLE Alternative Causes of Wide-Spread Low Concentration Perchlorate Impacts to Groundwater (CP-1429)		
c. PAGE COUNT 52	d. SUBJECT AREA Strategic Environmental Research & Development Program (SERDP)		
<b>2. AUTHOR/SPEAKER</b>			
a. NAME (Last, First, Middle Initial) SERDP	b. RANK	c. TITLE	
d. OFFICE Strategic Environmental Research & Development Program	e. AGENCY SERDP, Arlington, VA		
<b>3. PRESENTATION/PUBLICATION DATA (Date, Place, Event)</b> Posting on the SERDP web site. <div style="text-align: right;"> <b>CLEARED</b>  <b>For Open Publication</b>  <b>JUL 22 2005 3</b>  <b>Office of Freedom of Information and Security Review</b>  <b>Department of Defense</b> </div>			
<b>4. POINT OF CONTACT</b>			
a. NAME (Last, First, Middle Initial) Rice, Veronica		b. TELEPHONE NO. (Include Area Code) 703-326-7816	
<b>5. PRIOR COORDINATION</b>			
a. NAME (Last, First, Middle Initial) Smith, Bradley Holst, Robert	b. OFFICE/AGENCY SERDP Executive Director SERDP Compliance Program Manager		c. TELEPHONE NO. (Include Area Code) 703-696-2121 703-696-2125
<b>6. REMARKS</b>			
THE INFORMATION CONTAINED IN THIS REPORT FALLS UNDER THE PURVIEW OF THIS OFFICE.  WHEN CLEARED, PLEASE FAX DD-1910 TO 703-478-0526. ATTN: Veronica Rice (phone: 703-326-7816)  if mailed: ATTN: Veronica Rice, 1155 Herndon Parkway, Suite 900, Herndon, VA 20170			
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## EXECUTIVE SUMMARY

The frequency of detection of perchlorate in groundwater and drinking water supplies has been steadily increasing since its initial identification as a chemical of concern in 1997. It is currently estimated that perchlorate is present in groundwater in at least 30 states and affects the drinking water supplies of more than 20 million people in the southwestern United States (U.S.). The source of perchlorate in water supplies has typically been attributed to U.S. Department of Defense (DOD), National Aeronautics & Space Administration (NASA) and/or defense contractor facilities that have used ammonium perchlorate (AP) in rocket and missile propellants. Perchlorate impacts to groundwater and surface waters in southern Nevada and southern California have also been attributed to the historic production and release of perchlorate from a former chemical manufacturing facility in the Las Vegas, Nevada area (Hogue, 2003), which has impacted the surface waters of Lake Mead and the Colorado River.

As a result of its high profile and its addition to the Unregulated Contaminant Monitoring Rule (UCMR List 1), which requires perchlorate analysis by large public water suppliers and selected small water utilities, most public water supplies are now being routinely analyzed for perchlorate. Through monitoring activities, perchlorate has been detected at low levels (typically less than 50 µg/L) in a significant number of areas without apparent military sources. Investigation activities have linked these perchlorate impacts to various non-military sources, including use of perchlorate-containing blasting agents for quarrying and construction, manufacture of road flares, manufacture and use of fireworks and pyrotechnics, use of perchloric acid in industrial manufacturing, and use of Chilean nitrate fertilizers.

Perchlorate is known to be present in a significant number of products and processes. Unfortunately, it has proven exceedingly difficult to obtain records of perchlorate handling related to production and use of many of these products and processes. As such, this review focuses on five major perchlorate-containing products for which significant quantity and use information is available: Chilean nitrate fertilizers; fireworks; safety flares; blasting explosives; and electrochemically-prepared (ECP) chlorine products. The key findings of this review for each of these major perchlorate-containing products can be summarized as follows:

**Chilean Nitrate Fertilizer:** Between 1909 and 1929 (the period for which detailed information could be obtained), the U.S. imported an estimated 19 million tons of Chilean nitrate (Goldenwieser, 1919; Howard, 1931), of which an average of 65% was used as fertilizer (Brand, 1930). Assuming an average perchlorate content of about 0.2% in Chilean nitrate (based on U.S. Environmental Protection Agency research results), approximately 49 million pounds of perchlorate may have been unknowingly applied to

agricultural soils during this time period, for fertilization of crops such as cotton, tobacco, fruits and vegetables. While the use of Chilean nitrate fertilizers has steadily declined since about the 1930s, there is evidence of continued use through the present day. Additional evaluation of soils and groundwater in agricultural areas that have used (and may still be using) Chilean nitrate fertilizers seems warranted to evaluate whether past and/or present fertilizer practices can be expected to be the cause of long-term, low concentration perchlorate impacts to groundwater in some agricultural areas and watersheds.

**Fireworks:** In 2003, 221 million pounds of fireworks were consumed in the U.S., with an estimated 3% produced domestically and the remainder imported from China (APA, 2004a). Although perchlorate is widely used as an oxidizer in firework formulations, there is little information related to the amount of perchlorate residue remaining after burning of fireworks and/or statistics on dud rates and blind stars that occur during fireworks displays. As such, it is difficult to estimate potential perchlorate inputs from fireworks to the environment. Recent studies have detected perchlorate in soils, groundwater and/or surface water following fireworks displays, and therefore, the potential environmental impact of perchlorate from fireworks displays warrants further scientific study.

**Safety Flares:** Preliminary research by Silva (2003a, 2003b) of the Santa Clara Valley Water District in California indicates that 3.6 grams of perchlorate can potentially leach from an unburned, damaged (i.e., run over by a motor vehicle) 20-minute road flare. While numbers are not available for total domestic flare production, assuming an average cost per flare of \$0.50 to \$1.00 per flare and annual sales of \$20 million by the largest domestic manufacturer, some 20 to 40 million flares may be sold annually. Given this estimate, up to 237,600 pounds of perchlorate could leach from road flares annually. Surface runoff from highways and roads represents a potentially significant and largely uninvestigated impact to surface water and groundwater quality. Additional evaluation of the potential for perchlorate impacts to surface waters and groundwater from safety flare use appears warranted.

**Blasting Explosives:** Some water gels, emulsions, and non-electric detonators can contain substantial amounts of perchlorate (e.g., up to 30% by weight). While, most of the perchlorate in the explosives is expected to be consumed in the detonation, poor housekeeping practices (i.e., spillage), improper use, or misfires can potentially result in perchlorate contamination of surface and ground waters, as has been reported for multiple sites in Massachusetts. Given that the U.S produces approximately 2.5 million tons of explosives annually, perchlorate could potentially be released into the environment nationwide in substantial amounts. Currently, no publicly-available data exist to quantify

potential perchlorate impacts from blasting. More studies are required to assess and quantify the potential impact of blasting explosives on perchlorate contamination of surface and ground waters.

**ECP Chlorine Chemicals:** During the electrochemical manufacture of chlorine products, such as chlorate, from chloride brine feedstocks, perchlorate may be formed as an impurity at concentrations of 50 to 500 mg/kg. The estimated North American annual chlorate manufacturing capacity is 2.4 million tons, whereas the total annual consumption of sodium chlorate in the U.S. is approximately 1.2 million tons. The pulp and paper industry uses approximately 94% of all sodium chlorate consumed in the U.S. for on-site production of chlorine dioxide to bleach cellulose fibers. Effluents from pulp mills have been reported to contain chlorate (1 to 70 mg/L) but there is little information available as to the potential for perchlorate release from these facilities. Sodium chlorate is also used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, sundangrass, safflower, rice, and chili peppers. The use of sodium chlorate in the pulp and paper industry and as a defoliant has the potential to contribute perchlorate to the environment and needs to be better understood.

The United States DoD, NASA and related defense contractors are likely to be the most significant domestic users of perchlorate, and as such, a significant percentage of identified groundwater perchlorate impacts are likely to be attributable to DoD, NASA, and related defense contractor facilities. However, cases exist, and many more are likely to surface, where perchlorate impacts result from combinations of military, non-military, and/or natural inputs. The ability of DoD, NASA, and defense contractors to accurately apportion the relative contributions from these varying sources, and hence to properly determine liability and control cleanup cost, lies in having a good understanding of the wide variety of products and processes that may contribute perchlorate to the environment and through the development and validation of appropriate forensic tools. This review is intended to assist DOD, NASA, and defense contractors in identifying the significant number of industrial and commercial processes and products that contain perchlorate and to estimate the potential contribution of perchlorate to the environment (past and/or present) from non-military products or processes.

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## 1. INTRODUCTION

The frequency of detection of perchlorate in groundwater and drinking water supplies has been steadily increasing since its initial identification as a chemical of concern in 1997. It is currently estimated that perchlorate is present in groundwater in at least 30 states and affects the drinking water supplies of more than 20 million people in the southwestern United States (U.S.). The source of perchlorate in water supplies has typically been attributed to U.S. Department of Defense (DOD), National Aeronautics & Space Administration (NASA) and/or defense contractor facilities that have used ammonium perchlorate (AP) in rocket and missile propellants. Perchlorate impacts to groundwater and surface waters in southern Nevada and southern California have also been attributed to the historic production and release of perchlorate from a former chemical manufacturing facility in the Las Vegas, Nevada area (Hogue, 2003), which has impacted the surface waters of Lake Mead and the Colorado River.

As a result of its high profile and its addition to the Unregulated Contaminant Monitoring Rule (UCMR List 1), which requires perchlorate analysis by large public water suppliers and selected small water utilities, most public water supplies are now being routinely analyzed for perchlorate. Through monitoring activities, perchlorate has been detected at low levels (typically less than 50 µg/L) in a significant number of areas without apparent military sources. As examples:

- Researchers at Texas Tech University have detected perchlorate in groundwater over a contiguous area of some 30,000 square miles in the High Plains region of West Texas (Cristen, 2003). Of 217 public drinking wells tested in the study area, 73% contained detectable perchlorate concentrations of more than 0.5 µg/L, while 35% had perchlorate concentrations equal to or greater than 4 µg/L. Potential sources for perchlorate in groundwater over this large area were speculated to include leaching from evaporite deposits and/or in situ generation of perchlorate by an electrochemical reaction, possibly related to cathodic protection of water systems and/or oil wells.
- Perchlorate has been detected in more than 400 private water supply wells (domestic, industrial, agricultural) in the Santa Clara Valley in California near the cities of Morgan Hill and Gilroy (Ruby, 2004). The distribution of perchlorate, generally ranging between 4 and 10 µg/L, extends for approximately 9 miles. Perchlorate impacts have been attributed to a former road flare manufacturing facility.

- Perchlorate has been detected in more than 148 wells in the small town of Hills, Iowa (Bello, 2004) at concentrations in the range of 4 to 52 µg/L. According to the U.S. Environmental Protection Agency (EPA), the source of these impacts is unknown, although Chilean nitrate is suspected.
- Perchlorate has been detected in water supply wells in at least four towns in Massachusetts (Westford, Millbury, Boxborough, and Dracut). These impacts are suspected to be related to the use of explosives for rock blasting for development and/or quarrying.
- Perchlorate (related to the use of perchloric acid) was detected at elevated concentrations (2,000 mg/L) in the effluent (sewer discharge) from a medical device manufacturer in Billerica, Massachusetts. The discharge was processed through the Billerica wastewater treatment facility and was subsequently discharged to the Concord and Merrimack Rivers, causing impacts to downgradient water suppliers in Tewksbury, Massachusetts (Hughes & Murphy, 2004).

While natural sources or formation mechanisms for perchlorate may explain its presence in several of the aforementioned cases (Jackson et al., 2004; Dasgupta et al., 2005), widespread, low concentration perchlorate impacts in groundwater can apparently also result from a variety of non-military-based inputs as well, potentially including:

- i) storage, handling and use of Chilean nitrate-based fertilizers containing perchlorate;
- ii) manufacturing, storage, handling, use and/or disposal of fireworks containing perchlorate;
- iii) manufacturing, storage, handling, use and/or disposal of road flares containing perchlorate;
- iv) manufacturing, storage, handling, use and/or disposal of explosives or pyrotechnics containing perchlorate; and/or
- v) manufacture, storage, handling and use of electrochemically-prepared (ECP) chlorine products, primarily those that contain chlorate or were manufactured from chlorate feedstocks.



While various research organizations are evaluating potential natural sources of perchlorate (e.g., Orris et al. 2003; Jackson et al., 2004), few organizations are generating quantitative evidence of the potential impacts of perchlorate-containing products on wide-spread, low-level perchlorate detections in groundwater. Releases of perchlorate from these products/processes may be responsible for causing a raised baseline perchlorate concentration in some areas or watersheds.

The objective of this review is to identify the significant number of industrial and commercial processes and products that contain perchlorate, so as to understand the potential prevalence of perchlorate in the environment. Where sufficient information exists, this review attempts to estimate the potential contribution of perchlorate to the environment (past and/or present) from industrial, agricultural, commercial and/or consumer use of perchlorate-containing products or processes.

## 1.1 Perchlorate Properties and Uses

Perchlorate is an inorganic anion and oxidant consisting of chlorine bonded to four oxygen atoms ( $\text{ClO}_4^-$ ). It is typically found in association with ammonium, sodium, or potassium cations as a salt. Hydrogen perchlorate (or perchloric acid) is another commonly used form of perchlorate. Perchlorate exhibits high solubility and mobility in water and is very stable, being degraded only under anaerobic conditions (Coates et al., 1999). Consequently, perchlorate releases can result in long, persistent contaminant plumes in groundwater, as has been observed at many sites.

Perchlorate is known to be present in a significant number of products and processes, as listed in Table 1-1. While it is anticipated that DOD and NASA propulsion products represent the most significant percentage of domestic perchlorate use, the consumption of perchlorate-containing industrial, agricultural, commercial and consumer products is likely to be significant. Unfortunately, it is exceedingly difficult to obtain records of perchlorate handling related to production and use of many of the products and processes listed in Table 1-1, and therefore this review will focus on five major perchlorate-containing products for which significant quantity and use information is available: Chilean nitrate fertilizers (Section 2); fireworks (Section 3); safety flares (Section 4); blasting explosives (Section 5); and ECP chlorine products (Section 6).

**Table 1-1: Current and Historical Uses of Perchlorate**

<b>Raw Product</b>	<b>Product/Process</b>	<b>Role of Perchlorate in the Product/Process</b>
Perchlorate Salts	Ammonia production	Ingredient of catalytic mixtures used in making ammonia
	Detonating compositions	Oxidizing agent
	Matches	Oxidizing agent
	Pyrotechnic compositions	Oxidizing agent
	Railroad signal (fuse) compositions	Oxidizing agent
	Smoke-producing compounds	Oxidizing agent
	Metallurgical	Constituent of brazing fluxes, welding fluxes
	Pharmaceutical	Used in compounding and dispensing practice
	Air bag for vehicles	Initiators
	Paints and enamels	Curing/Drying Agent
	Photography	Flash powder/ oxidizing agent
	Oxygen generators	Burn Rate Modifier
	Road flares	Oxidizing agent
	Ejection seats	Propellant
	Model rocket engines	Propellant
	Rockets used for research, satellite launches, and Space Shuttle	Propellant
	Some explosives in construction, mining and other uses	Oxidizing agent
	Fireworks	Oxidizing agent
	Voltaic cells and batteries involving lithium or lithiated anodes, non-aqueous solvents or polymeric films, and manganese dioxide or other transition metal oxides	Electrolyte (Lithium perchlorate)
	Zinc and magnesium batteries	Electrolytes (zinc perchlorate and magnesium perchlorate)
	Electropolymerization reactions involving monomers such as aniline, benzidine, biphenyl, divinylbenzene, and indole	Electrolyte
	Polyvinyl chloride (PVC)	Dopants to improve heat stability and fire retardation characteristics
	Thin film polymers such as polyethylene oxide (PEO), polyethylene glycol, or poly(vinylpyridine)	Dopant to impart conductive properties in various electrochemical devices
Drying agent for industrial gases and other similar applications	Desiccant (Anhydrous magnesium perchlorate)	
Plastics and polymers	Dopants to impart antistatic and conductive properties	

**Table 1-1: Current and Historical Uses of Perchlorate (continued)**

Perchloric Acid	Nitrogen measurement	Used for Kjeldahl digestions
	Leather tanning	Extraction of chromium
	Potash measurement	Used to form insoluble potassium perchlorate
	Manufacture of inorganic chemicals, intermediates, organic chemicals, pharmaceuticals, synthetic aromatics	Oxidizing agent
	Manufacture of explosive compounds, such as the perchlorated esters of monochlorohydrin.	Reagent
	Ingredient of lead-plating baths	Facilitates the deposition of lead from baths containing lead perchlorate
	Electropolishing operations	Electrolyte in anodization of metals to produce non-corroding surfaces
	Metallurgy	Extraction of rare earth metals
	Etching brass and copper	Acid
	Acetylations, alkylations, chlorinations, polymerizations, esterifications, and hydrolyses	Catalyst
	Cellulose acetate production	Esterification of cellulose
	Destruction of organic matter, especially in preparation for the determination of calcium, arsenic, iron, copper, and other metals	Acid digestion, in combination with nitric acid
	Determination of copper and other metals in sulfide ores	Acid digestion
	Dissolving refractory substances such as titanium slags	Acid digestion
	Ammonium perchlorate, high purity metal perchlorates	Starting material for the manufacture of pure ammonium perchlorate and in the production of high purity metal perchlorates
	Pickling and passivation of iron and steels	Oxidant
	Determination of silica in iron and steel and in cement and other silicate materials	Dehydrating agent
	Determination of chromium in steel, ferrochrome, chromite, leather, and chromatized catgut	Oxidizing agent
	Separation of chromium from other metals by distillation of chromyl chloride	Used in combination with hydrochloric acid
	As a primary standard acid	Perchloric acid, when distilled in a vacuum at a carefully regulated pressure, has exactly the composition of the dihydrate, 73.6% HClO <sub>4</sub>

**Table 1-1: Current and Historical Uses of Perchlorate (continued)**

Perchloric Acid (Cont'd)	Indirectly in the manufacture of anhydrous magnesium perchlorate	Dehydrating agent
	Titration of bases in non-aqueous solvents	As the strongest of the strong acids dissolved in anhydrous acetic acid
	Analytical procedures for the destruction of organic matter prior to the determination of metallic and non-metallic ingredients such as: Determination of sulfur in coal, coke, and oils; Determination of iron in wine, beer, and whiskey; Determination of chromium and of iron in leather and tanning liquors; Determination of phosphorus, alkali metals, lead, and other ingredients; and Analysis of blood for calcium and of urine for lead.	Destruction of organic matter (mixtures of perchloric acid dihydrate with nitric acid or sulfuric acid, or of these three acids together)
Chilean Sodium Nitrate	Fertilizers	Incidental ingredient in fertilizers (largely historical, but soils previously treated may still contain perchlorate)
	Charcoal briquettes	Naturally occurring by-product
	Meat tenderizers	Naturally occurring by-product

## 2. CHILEAN NITRATE FERTILIZERS

Research by the U.S. Environmental Protection Agency (EPA) has confirmed that perchlorate is present in nitrate-based fertilizers manufactured from naturally-occurring caliche deposits mined from the Atacama Desert region of Chile (Urbansky et al., 2001a; Urbansky et al., 2001b). Historical agronomic literature indicates that Chilean nitrate fertilizers were widely used in specific agricultural practices in the early to mid 1900s, (Howard, 1931; Goldenwieser, 1919; Mehring, 1943). Past import statistics for Chilean nitrate (see Section 2.2) and historical agronomic guidelines for sodium nitrate application for various crops (see Section 2.3) indicate that significant quantities of perchlorate may have been unknowingly applied to agricultural soils over many decades from the early to mid 1900s. While the use of Chilean nitrate fertilizers steadily declined since about the 1930s, there is evidence of continued use through to the present day. For example, imports of fertilizer grade sodium nitrate supplied 27% and 6% of the total nitrogen used as fertilizer in 1939 and 1954, respectively. Since 2002, it is estimated that some 75,000 tons of Chilean nitrate fertilizer have been used annually in the U.S.

The application of these perchlorate-containing fertilizers over many decades through to the present day (albeit in much lower amounts) may explain the continued presence of low concentrations of perchlorate in soil and groundwater in some agricultural areas and watersheds. The continuing impacts of nitrate to groundwater in former agricultural areas urbanized since the 1940s is clear evidence of the potential for long lasting impacts of past fertilization practices on some regional watersheds (Fogg et al., 1998).

This chapter summarizes pertinent information related to the import and use of Chilean nitrate fertilizers and explores the potential for present-day perchlorate impacts to groundwater from historical and on-going Chilean nitrate fertilizer uses for specific agricultural practices.

### 2.1 Perchlorate Concentrations in Chilean Nitrate Fertilizer

Chilean nitrate fertilizers are derived from naturally-occurring caliche deposits that are mined from the Atacama Desert region of Chile (Urbansky et al., 2001a). The raw product used in the production of nitrate fertilizers was commonly called Chilean nitrate, nitrate of soda, sodium nitrate, Chilean saltpeter, and/or soda nitre. Chilean nitrate fertilizers are still sold commercially as “Bulldog Soda” in the U.S. The presence of perchlorate in the caliche deposits mined for Chilean nitrate fertilizer has been documented for over 100 years. Schilt (1979) briefly summarizes the early history of the

discovery of naturally-occurring perchlorate in Chilean caliche and Chilean nitrate fertilizer. He records that perchlorate was first discovered in the caliche deposits in 1886. This discovery was followed in 1896 by the confirmation of perchlorate in “Chile saltpeter” (sodium nitrate) over the widely varying concentration range of 0 to 6.79%. Schilt (1979) reports that a 1914 study determined that the maximum perchlorate concentration in refined sodium nitrate was about 1%. More recently, Ericksen (1983) provided production chemical data for caliche ores from 1932 to 1967 for the two largest production plants in Chile. Over this 35-year period, the ores contained about 30% soluble salts and averaged 6.3% nitrate and 0.03% perchlorate. The refining process for the caliche ore takes advantage of the high solubility of nitrate relative to the other anions, but perchlorate, which is even more soluble than nitrate, was not substantially separated from the nitrate. Assuming that the ratio of nitrate to perchlorate in the ore is preserved in the refined product, then the average perchlorate concentration in Chilean nitrate fertilizer would have been approximately 3,500 mg perchlorate/kg sodium nitrate or 0.35%.

Little attention was subsequently paid to the natural occurrence of perchlorate in Chilean nitrate, except as a geological curiosity, until the emergence of perchlorate as a chemical of concern at military sites. The U.S. Air Force Research Laboratories (AFRL) conducted a study in which multiple laboratories analyzed samples of a variety of lawn and garden fertilizers for perchlorate (Eldridge et al., 2000). The data from this inter-laboratory comparison study suggested the widespread presence of perchlorate in consumer fertilizers. The current definitive study of perchlorate in agricultural fertilizers was conducted in 2000 by a separate U.S. EPA laboratory (EPA-ORD-NRML-WSWRD) and is summarized in Urbansky et al. (2001a; 2001b). This study concluded that the occurrence of perchlorate in fertilizer was restricted to fertilizer products derived from Chilean nitrate produced by SQM Corporation and that all fertilizers derived partially or completely from Chilean nitrates contain appreciable perchlorate.

Today, SQM Corporation produces several nitrate products. The mined product consists predominantly of sodium nitrate (approximately 98%), with a minor component of other types of soluble salts, including perchlorate. Other current SQM products include potassium nitrate, which is produced by a chemical reaction between sodium nitrate and potassium chloride, and mixtures of sodium and potassium nitrate. Accordingly, potassium nitrate products may also contain appreciable levels of perchlorate according to the EPA-ORD-NRML-WSWRD and AFRL studies.

Data for two samples of Chilean sodium nitrate were analyzed in the EPA-ORD-NRML-WSWRD study. The inter-laboratory average of these two samples was 1,917 mg/kg and 1,590 mg/kg, for an average of 1,750 mg/kg. The AFRL study analyzed one sample consisting entirely of sodium nitrate, as indicated by the lack of P (phosphorous)

and K (potassium) in the manufacturer’s information (sodium nitrate fertilizer is listed as 16-0-0). This sample had an inter-laboratory average perchlorate concentration of 7,687 mg/kg when analyzed by ion chromatography (IC) using the AS 16 column, the preferred IC method for analyzing perchlorate. These two studies yielded a range of perchlorate concentrations in Chilean sodium nitrate fertilizer of approximately 1,750 to 7,700 mg/kg, spanning the 3,500 mg/kg average (derived from the ratio of nitrate to perchlorate) in the original caliche ore. The average perchlorate concentration obtained by the EPA-ORD-NRML-WSWRD of 1,750 mg/kg or approximately 0.2% is a reasonably conservative estimate of the average perchlorate concentration of Chilean nitrate fertilizer and will be used in the subsequent calculations in this section.

## 2.2 Chilean Nitrate Imports

Between 1909 to 1918 and 1925 to 1929, the U.S. imported approximately 7,500,000 and 5,300,000 tons of Chilean nitrate (Goldenwieser, 1919; Howard, 1931), respectively, for a total of approximately 13,000,000 tons of Chilean nitrate (Table 2-1). If we assume that approximately 1 million tons of Chilean nitrate were imported annually during 1919 through 1924, then approximately 19 millions tons of Chilean nitrate fertilizer were likely imported into the U.S. between 1909 and 1929.

**Table 2-1: Chilean Nitrate Imports**

Year	Chilean Nitrate import to US (tons)
1909	329,124
1910	538,119
1911	528,435
1912	475,560
1913	573,773
1914	561,209
1915	577,120
1916	1,067,005
1917	1,264,659
1918	1,606,498
1925	1,245,693
1926	1,024,010
1927	838,635
1928	1,156,860
1929	1,042,113

During this period, it is estimated that between 49 and 70% of the imported Chilean nitrate was used as fertilizer, with an average of approximately 65% (Brand, 1930). The percentage of Chilean nitrate used for fertilizer reportedly fluctuated based on its demand for use in explosives manufacturing. Assuming an average perchlorate concentration of about 0.2% in the Chilean nitrate and that 65% of the imported Chilean nitrate (about 12 million tons) was used as fertilizer, then approximately 49 million pounds of perchlorate is likely to have been applied to agricultural soils during this time period.

Chilean nitrate fertilizer is still produced by SQM Corporation and makes up 0.14% of the total annual U.S. fertilizer application (Urbansky et al., 2001a). It is sold commercially as Bulldog soda and is primarily used in a few niche markets and specialty products. Currently, world production is 900,000 tons/year of which 75,000 tons are sold to U.S. farmers for use on cotton, tobacco, and fruit crops (Urbansky et al, 2001a; Renner, 1999). SQM reports that the perchlorate concentration in Chilean nitrate fertilizer has been reduced through changes in the refinement processes since 2002. The current perchlorate concentration is reported as 0.01% (Urbansky et al., 2001b), which is more than an order of magnitude improvement compared to historic perchlorate contents. However, this amount still represents the potential introduction of more than 15,000 pounds of perchlorate annually to agricultural soils, the fate of which is not well understood.

### **2.3 Use of Chilean Nitrate Fertilizers**

A wide variety of agricultural publications document that Chilean nitrate was a common nitrate fertilizer in the U.S. during the first half of the 20<sup>th</sup> century. For example, in its 1938 Yearbook, the U.S. Department of Agriculture (USDA) stated that “sodium nitrate and ammonium sulfate are undoubtedly the most widely used nitrogen fertilizers at the present time”. Similarly, the USDA Fertilizer Consumption and Trends in Usage report (Mehring, 1943) identified Nitrate of Soda as the second most consumed fertilizer during its reporting period. While the use of Chilean nitrate fertilizers steadily declined since about the 1930s, there is evidence of continued use through to the present day. The following section discusses the use of Chilean nitrate fertilizer specifically related to the production of cotton, tobacco, and fruit, three crops for which Chilean nitrate use has been documented.

#### Cotton

Chilean nitrate fertilizer was often used to fertilize cotton and provided the necessary nitrogen for high yield crops (Skinner, 1932). It was typically used in delayed



applications (side dressings). The application of nitrate of soda to cotton is dependant on soil quality and the corresponding amount of nitrogen available for plant uptake. Typical delayed application rates of nitrogen for cotton were 18 to 30 pounds per acre (Skinner, 1932). This application rate is equivalent to 110 to 190 pounds per acre of nitrate of soda, which is approximately 16% nitrogen (Nelson et al, 1925), or approximately 0.2-0.3 lb of perchlorate per acre.

Between 1909 and 1929, Texas was the largest cotton producing state, harvesting approximately 283 million acres of cotton over a twenty year period. However, only 7% of the acreage in Texas required fertilizer application (Skinner, 1932). By comparison, southeastern states such as North Carolina, South Carolina, Georgia, and Alabama harvested lower quantities of cotton, but the fertilizer requirement for these soils was much greater (Skinner, 1932). For example, during this time period, Georgia, Alabama, South Carolina and North Carolina typically fertilized 91 to 97% of the total cotton acreage (Table 2-2). While the contribution of Chilean nitrate to fertilization of the cotton acreage is not clearly defined, data available in Howard (1931) suggest that in 1928 Chilean nitrate accounted for approximately 35% of total nitrogen fertilizer used that year on a nitrogen basis.

**Table 2-2: Acres Fertilized for Cotton Production from 1909 to 1929, Top 4 States**

<b>State</b>	<b>Acres Harvested (1909-1929)<sup>1</sup></b>	<b>% of Acres Fertilized<sup>1</sup></b>	<b>Total Acres Fertilized</b>
Georgia	87,242,000	95.9	83,665,078
Alabama	65,957,000	91.9	60,614,483
South Carolina	48,926,000	90.9	44,473,734
North Carolina	31,224,000	97.0	30,287,280
			219,040,575

References:

1 - Skinner, 1932

Mehring (1943) indicated that Georgia, Alabama, South Carolina, and North Carolina were heavily dependent on the use of Chilean Nitrate fertilizer, consuming between 63% to 75% of the total Chilean nitrate used domestically. Based on the 1909 to 1929 import statistics (about 12 million tons of Chilean nitrate as fertilizer), a consumption rate of 63% to 75% for these states would represent the use of 7.6 to 9.0 million tons of Chilean nitrate, which in turn would represent the potential application of 30 to 36 million pounds of perchlorate to agricultural soils (all crops) in these states over the 1909 to 1929 time frame.

## Tobacco

Chilean nitrate fertilizer was commonly used in the U.S. as a source of nitrogen for tobacco plants. In a 1927 test of fertilizers on flue-cured tobacco, “nitrate of soda showed average yields and values which were considerably better than were obtained with ammonium sulphate” (Moss, 1927). From 1909 to 1929, Kentucky was the largest producer of tobacco and harvested 10,000,000 acres. North Carolina was the second highest producer of tobacco, harvesting over 9,000,000 acres ([www.nass.usda.gov:81/ipedb/tobacco.htm](http://www.nass.usda.gov:81/ipedb/tobacco.htm)).

Fertilizer application rates for tobacco vary with the season and soil quality; however, application rates of 30 to 40 pounds of nitrogen per acre were typically recommended (Bennett et al, 1953). To obtain this amount of nitrogen from nitrate of soda (16% nitrogen), approximately 185 to 250 pounds of nitrate of soda would have been applied per acre of tobacco. This range of application rates is similar to the application rates of nitrate of soda used today for certain tobacco crops (i.e., 3-5 lb/100 yd<sup>2</sup> or 195-325 lb/acre, [www.ncagr.com/agronomi/stnote2.htm](http://www.ncagr.com/agronomi/stnote2.htm)). Prior to 2002, this Chilean nitrate fertilizer application rate would correspond to a perchlorate application rate of approximately 0.4 to 0.5 lb per acre.

## Fruit

The historic use of Chilean nitrate fertilizers has been reported for fruit trees in California, with an accepted fertilization rate between 100 and 200 pounds per acre as nitrogen. This translates to application rates ranging between 625 and 1250 pounds per acre of sodium nitrate (16% nitrogen). For simplicity, if the average application rate is assumed to be 1000 pounds per acre per year of Chilean nitrate as suggested by Collings (1949) in the textbook *Commercial Fertilizers*, then 2 pounds of perchlorate per acre per year may have potentially been applied to fruit orchard soils in some parts of California. Furthermore, between 1923 and 1960, 305,614 tons of Chilean Sodium Nitrate fertilizer were reported to have been used in California, according to data compiled by the California Department of Food and Agriculture. Assuming a perchlorate concentration of 0.2%, application of this mass of Chilean nitrate fertilizer would have resulted in the application of over 1.2 million pounds of perchlorate to agricultural soils/crops in California during this timeframe.

## 2.4 Potential to Impact Groundwater

While data summarized in the previous sections suggest that significant quantities of Chilean nitrate have historically been used to fertilize various crops, it is difficult to predict the fate and persistence of the applied perchlorate. The behavior of perchlorate in agricultural settings has not been investigated in detail, and several crucial aspects of perchlorate behavior in such settings (e.g., plant uptake, biodegradation, mobility in relation to soil factors, etc) are not well documented. However, nitrate (the principal component of the Chilean nitrate fertilizer) and perchlorate share important chemical features, and many aspects of the large body of literature concerning nitrate contamination of groundwater due to fertilizer use can be applied directly to understanding the potential for perchlorate contamination of groundwater through the same mechanism. The important aspects of the relationship between nitrate and perchlorate are summarized as follows:

- Nitrate and perchlorate are present in the potential source material, Chilean nitrate fertilizer.
- Nitrate ( $\text{NO}_3^-$ ) and perchlorate ( $\text{ClO}_4^-$ ) are both negatively charged ions and, as such, are highly mobile in soils. Soil particles are predominately negatively charged, and, therefore, electrostatic repulsion prevents adsorption.
- Sodium nitrate and sodium perchlorate, the predominant forms of these constituents in Chilean nitrate fertilizer, are both highly soluble in water (1.8 and 4.4 pounds per gallon, respectively), and thus there are no solubility constraints on the flushing of these compounds from soil into groundwater.
- Once in the vadose zone and groundwater, both nitrate and perchlorate are environmentally persistent and are not subject to chemical or biological breakdown under common groundwater conditions. The biological reduction of both nitrate and perchlorate requires the presence of organic matter, which can serve as electron donors, and anoxic conditions.

While the use of Chilean nitrate fertilizers containing perchlorate was most intense prior to 1950, the potential exists that impacts from these practices are only now being discovered in public water supplies. For example, Hudson *et al.* (2002) determined that water produced from 59 of 176 public water supply wells in the Los Angeles Basin was in excess of 50 years old. Of the remaining wells, only a small number of wells situated adjacent to large scale artificial recharge projects produce recent water, while the remainder produce mixed aged water of which at least 50% was recharged more than 50

years ago. Bohlke (2001) presents data for four representative surficial aquifers in the eastern U.S. with mean ages of 27-50 years. Note that these are mean ages and that some component of the groundwater must be older. Similarly, Crandall (2000) presents age data for a surficial aquifer in Florida where wells produce water with a spread in ages of from 3-50 years. Fogg *et al.* (1998) and Weissman *et al.* (2002) discuss the significance of the dispersion of groundwater ages with regard to breakthrough time and persistence of agricultural pollutants, noting that in areas with deep alluvial aquifers the observed nitrate pollution may be the result of agricultural practices more than 50 years previously. Given that perchlorate was a component of Chilean nitrate-based fertilizers, the hypothesis may be true for perchlorate.

The available nitrate literature reviewed for this paper indicates that it is possible that low level perchlorate impacts to groundwater in some areas may be the result of historic use of Chilean nitrate fertilizers. Additional evaluation of soils and groundwater in common crop areas discussed in this section seems warranted to evaluate whether historical fertilizer practices can be expected to be the cause of low concentration perchlorate impacts to groundwater in some agricultural areas and watersheds.

## 2.5 Summary

Between 1909 and 1929, the U.S. imported approximately 19 million tons of Chilean nitrate (Goldenwieser, 1919; Howard, 1931), of which an average of 65% was used as fertilizer (Brand, 1930). Assuming an average perchlorate content of about 0.2% in Chilean nitrate, approximately 49 million pounds of perchlorate may have been unknowingly applied to agricultural soils/crops during this time period for fertilization of crops such as cotton, tobacco and fruits. Since 2002, it is estimated that some 75,000 tons of Chilean nitrate fertilizer containing 0.01% perchlorate have been used annually in the U.S., suggesting that 15,000 pounds of perchlorate continue to be applied to agricultural soils on an annual basis. While the behavior of perchlorate in agricultural settings has not been investigated in detail, nitrate (the main component of Chilean nitrate fertilizer) and perchlorate share important chemical and transport characteristics, and many aspects of the large body of literature concerning nitrate contamination of groundwater due to historical fertilizer use may be applied directly to understanding the potential for perchlorate contamination of groundwater through the same mechanism. Clearly, additional evaluation of soils and groundwater in agricultural areas that used Chilean nitrate fertilizers seems warranted to evaluate whether historical fertilizer practices can be expected to be the cause of long-term, low concentration perchlorate impacts to groundwater.

### 3. FIREWORKS

Fireworks are widely used by both pyrotechnic professionals and individual consumers for celebratory displays. Perchlorate is known to be a component of many pyrotechnics, and as such, the manufacturing, storage, handling, use and disposal of these products have the potential for introduction of perchlorate into the environment. Many pyrotechnic displays are launched near or over surface waters, presumably for visual impact and safety reasons, increasing the potential for perchlorate impacts to water sources. The following sections describe the main components of commercial pyrotechnics and assess the potential for perchlorate to impact the environment.

#### 3.1 Components of Fireworks

A display firework consists of multiple components, including one or several “breaks”, a time-delay fuse, stars, black powder, a launch tube, main fuse and a lift charge, as shown in Figure 3-1. The break or breaks house the stars in cardboard compartments within the shell. Each compartment has its own bursting charge, which ignites and throws out the stars. The breaks in a firework may also contain sound charges. To make these loud explosions, which are often accompanied by a bright white flash, perchlorate is often used.



**Figure 3-1: Display Firework Schematic**  
(from [www.pbs.org/wgbh/nova/fireworks/anat\\_flash.html](http://www.pbs.org/wgbh/nova/fireworks/anat_flash.html))

The stars, contained in the breaks, produce the bright colored firework displays. To produce different colors, perchlorate and black powder are typically blended with binding and coloring agents such as: magnesium or aluminum for white; sodium salts for yellow; strontium nitrate or carbonate for red; barium nitrate for green; copper salts for blue; and charcoal/carbon for orange ([www.pbs.org/wgbh/nova/fireworks/anat\\_flash.html](http://www.pbs.org/wgbh/nova/fireworks/anat_flash.html)). Black powder is composed of 75% saltpeter (potassium nitrate), 15% charcoal, and 10 percent sulfur. The particle size of the black powder controls the burn rate, with finer particles burning faster than coarser ones. The lift charge consists of black powder in a pouch at the bottom of the firework cylinder. As the black powder burns, the heat and gas push at the inside of the launch tube until an explosion results, which propels the firework shell as high as 1,000 feet in the air.

### **3.2 Perchlorate in Fireworks**

Perchlorate is a major component of fireworks and is used primarily as an oxidizing agent. It decomposes at moderate-to-high temperatures, liberating oxygen gas. Because oxidizers must be low in hygroscopicity, potassium salts are preferred over sodium salts. Potassium perchlorate has gradually replaced potassium chlorate as the principal oxidizer in civilian pyrotechnics because of its superior safety record. Potassium perchlorate produces mixtures that are less sensitive to heat, friction, and impact than those made with potassium chlorate, because of its higher melting point and less-exothermic decomposition (Conkling, 1985). Potassium perchlorate can be used to produce colored flames, noise, and light as summarized in Table 3-1. Ammonium perchlorate is also used in some fireworks formulations.

**Table 3-1: Perchlorate Content and Effects in Fireworks**

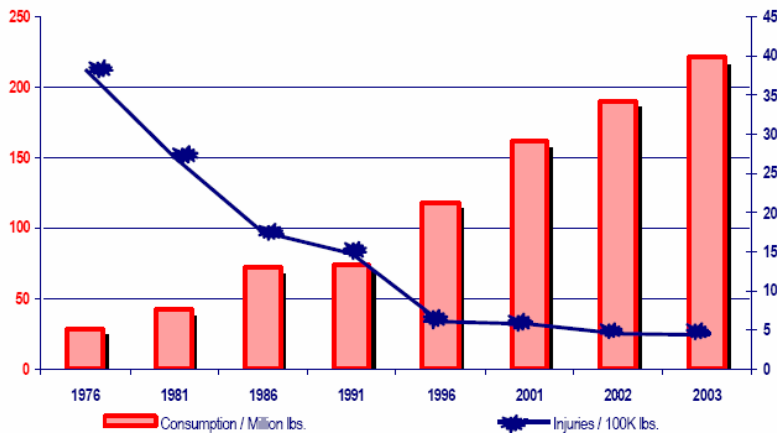
<b>Purpose/Effect</b>	<b>Composition (% by Wt)</b>	
White Light	Potassium Perchlorate	64
	Antimony, Sb	13
	Gum	10
	Potassium Nitrate	13
White Sparks	Potassium Perchlorate	42.1
	Titanium	42.1
	Dextrine	15.8
White Sparks “water fall”	Potassium Perchlorate	50
	“Bright” Aluminum Powder	25
	“Flutter” Aluminum, 30-80 mesh	12.5
	“Flutter” 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 ( <i>additional %</i> )
Blue Flame	Ammonium Perchlorate	70
	Red Gum	10
	Copper Carbonate	10
	Charcol	10
	Dextrine	5 ( <i>additional %</i> )
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.

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 well documented for sodium nitrate fertilizers.

### 3.3 Fireworks Consumption/Market

In 2003, 221 million pounds of fireworks were consumed in the U.S. This represents almost a 10-fold increase in consumption since 1976, as shown in Figure 3-2. The demand for fireworks is expected to increase, due to an upsurge of patriotism and an increase in the number of states permitting consumer fireworks. It is now legal to sell consumer fireworks in 43 states plus the District of Columbia (APA, 2004a.). Although the consumer fireworks industry is having record-breaking sales and profits, the public display industry has suffered as a result of the additional regulations following the events of 9/11. Additional security concerns have resulted in increased insurance costs, increased transportation and fuel fees, and criminal background checks for pyrotechnic professionals and large quantity users (APA, 2004b).



**Figure 3-2: Fireworks Consumption in the United States from 1976-2003**  
(from [www.americanpyro.com](http://www.americanpyro.com))

Import and export data for consumer and display fireworks in 2003 (the most recent census with data in all categories) is summarized in Table 3-2. Production statistics were estimated by taking the fireworks consumption data in Figure 3-2 and subtracting the imports and adding the exports. Import and export statistics categorized the type of firework to some degree. Import statistics were obtained for consumer, display, and other



fireworks, while export statistics were only collected for consumer and other firework category types, with the other category capturing display fireworks.

From Table 3-2, it is clear that most of the fireworks consumed in the U.S. are imported. Only approximately 3% of the total mass of fireworks is produced in the U.S. Most of the consumer fireworks are made in China (APA, 2004a). In 2003, 87.5 million kilograms (192 million lbs) of the 89.2 million kilograms (196 million lbs) of imported consumer fireworks or 98% and 7.5 million kilograms (16.5 million lbs) of the 8.1 million kilograms (17.8 million lbs) or 93% of imported display fireworks were from China ([www.ita.doc.gov/td/industry/otea/Trade-Detail/Latest-December/Imports/36/360410](http://www.ita.doc.gov/td/industry/otea/Trade-Detail/Latest-December/Imports/36/360410)).

**Table 3-2: Production, Import, and Export Data For Fireworks - 2003**

	Display Fireworks (Class 1.3G)		Consumer Fireworks (Class 1.4G)		Other Classes (NESOI) <sup>1</sup>		All Classes	
	<i>Mass (kg)</i>	<i>Value (\$)</i>	<i>Mass (kg)</i>	<i>Value (\$)</i>	<i>Mass (kg)</i>	<i>Value (\$)</i>	<i>Mass (kg)</i>	<i>Value (\$)</i>
<b>Production<sup>2</sup></b>	--	--	--	--	--	--	3,486,384	--
<b>Import<sup>3</sup></b>	8,101,763	27,273,000	89,153,821	135,561,000	90,989	233,000	97,346,573	163,067,000
<b>Export<sup>4</sup></b>	167,796	5,728,000	--	--	210,616	8,032,000	378,412	13,760,000
<b>Net Consumption</b>							100,454,545	--

Notes:

1. NESOI = Not elsewhere specified or included; for Imports this classes includes fireworks not in Class 1.3G and 1.4G. For Exports Other Classes includes fireworks not in Class 1.3G
2. Production Statistics were obtained by subtracting Import data and adding export data from the net consumption of fireworks reported by the APA in Figure 3-2
3. U.S. Census Bureau, Foreign Trade Division, "U.S. Imports of Merchandise, December 2003"
4. U.S. Census Bureau, "U.S. Exports of Merchandise, December 2003"

### **3.4 Potential to Impact Groundwater**

Raw perchlorate from fireworks manufacturing facilities and perchlorate residue from detonated fireworks both have the potential to contaminate surface and groundwater. Although fireworks contain high percentages of perchlorate, it is not currently known how much of the perchlorate finds its way into the environment. If we assume that most of the perchlorate present in the firework is ultimately decomposed with the burning of the firework, it seems necessary to consider only the perchlorate from blind stars, un-ignited display shells, and residues from the fireworks or lift charges (Schneider et al., 2001). However, statistics on dud rates (fireworks that are launched but not burned) do not exist (R. Schneider, personal communication). To date, housekeeping (i.e., post-event cleanup) related to fireworks displays has been done for safety purposes with the main aim being removal of unexploded fireworks. Typically, dud display shells are removed, but blind stars (which contain perchlorate) are typically not collected. Blind stars are often released at high altitudes and can therefore travel great distances from the launch site. Blind stars can also be released as a result of the breakage of dud shells.

As previously indicated, many fireworks displays occur at the water's edge or on barges, presumably for safety reasons and/or to enhance visual impact. Post-display clean-up becomes more difficult as duds and blind stars can be submerged. The advantage is that there is likely to be less dud breakage. However, perchlorate may leach out of the shell either through the fuse or as the result of de-lamination of the shell casing. The latter is more likely to result in perchlorate releases when the shell casing is comprised of paper/cardboard, as is often the case with fireworks produced in China.

### **3.5 Past and Current Environmental Studies**

The number of case studies in the literature discussing extent of soil and water contamination at firework discharge sites is limited. More controlled studies are currently being conducted, which should shed more light on the extent of perchlorate contamination associated with fireworks.

A limited test to determine whether perchlorate contamination resulted as a consequence of fireworks displays was conducted at Harbor Island, in Milwaukee, Wisconsin. The island had been used since 1991 by the Bartolotta Fireworks Company to conduct public fireworks displays, using both domestic and imported fireworks (Schneider et al., 2001). Ten soil samples were collected for perchlorate analysis, 5 before a fireworks display and 5 after the display. The soil samples were extracted and the aqueous extract was analyzed using a rapid, field colorimetric method. No perchlorate

was detected above the 1 ug/mL detection limit in the extract of any of the samples. However, this detection limit corresponds to a detection limit in soil of 1 ppm (Phil Thorpe, personal communication), which is relatively high.

A study was conducted to evaluate the impact of more than 2000 fireworks displays over a small lake located at EPCOT Center in Lake Buena Vista, Florida (DeBusk, et al, 1992). Water chemistry data were collected from 1982 to 1992 and sediment data were collected in 1992. As this study pre-dated interest in perchlorate, perchlorate analysis was not conducted. However, detectable amounts of barium, strontium, and antimony were detected in the water and sediments. Gradual increases in water column concentrations of antimony paralleled the cumulative number of fireworks displays at the site, indicating that antimony may prove to be a good “marker” for detecting fireworks activity (DeBusk, et al, 1992). Antimony has a very low crustal abundance and, therefore, is not expected to be present in uncontaminated sediments (Riley and Chester, 1981).

Perchlorate contamination linked to fireworks displays is currently being examined by the Massachusetts Department of Environmental Protection (MADEP) at the University of Massachusetts at Dartmouth. Eight monitoring wells have been installed at a site where fireworks were launched/displayed over the Labor Day weekend of 2004 (Berckshire Eagle Online, Sept. 2, 2004). The campus has been the site of summertime fireworks for more than 10 years. Prior to the 2004 display, soil samples had no detectable levels of perchlorate, while groundwater samples had perchlorate concentrations ranging from 0 to 36 µg/L (Cape Cod Times, Sept. 4, 2004). Soil samples were collected the day following the display, while groundwater samples were collected periodically throughout the fall. Modeling will be conducted by MADEP to estimate the fate and transport of any perchlorate released by the fireworks display (R. Knox, Mass. DEP, personal communication, Sept., 7, 2004). The results of this study are not yet publicly available.

There is speculation that some of the perchlorate detected in groundwater at Camp Edwards on Cape Cod may be due to fireworks displays conducted at the Upper Cape Cod Regional Technical School. Soil samples taken by the Army after the 2003 Independence Day fireworks display contained 7500 µg/kg perchlorate. Regulators are not yet convinced that fireworks are the only cause of perchlorate in groundwater at this site, given the proximity of the site to the Massachusetts Military Reservation (Cape Cod Times, Sept. 4, 2004).

Perchlorate contamination may also originate from fireworks manufacturing facilities, given that perchlorate is handled on site. For example, perchlorate was detected at a concentration of 270 µg/L in an inactive well near a defunct fireworks site in Rialto,

California (<http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/earlyfindings.htm>). Perchlorate has also been detected at a concentration of 24 µg/L in groundwater from a well near a fireworks manufacturing facility in Mead, NE (<https://www.denix.osd.mil/denix/Public/Library/Water/Perchlorate/releases.html>).

### **3.6 Summary**

In 2003, 221 million pounds of fireworks were consumed in the U.S., with an estimated 3% produced domestically and the remainder imported from China (APA, 2004a). Although perchlorate is widely used as an oxidizer in firework formulations, there is currently little information related to the amount of perchlorate residue remaining after burning of fireworks and/or statistics on dud rates and the fraction of blind stars that occur during fireworks displays. As such, it is difficult to estimate potential perchlorate inputs from fireworks to the environment. Several recent studies have detected perchlorate in soils, groundwater and/or surface water following fireworks displays, and therefore, the potential environmental impact of perchlorate from fireworks displays warrants further scientific study.

## **4. SAFETY FLARES**

Safety flares (or fusees) are used in emergency situations for road-side accidents and rail and marine emergencies. Road flares typically come in 15 minute, 20 minute, and 30 minute burn times. The average burn time for an automotive emergency flare is a function of its length and, to some degree, minor variations in flare composition. The use of 2 road flares per event is recommended by most flare manufacturers for most automotive emergencies. The following sections describe the main components of commercial safety flares and assess the potential for perchlorate to impact the environment.

### **4.1 Perchlorate Content in Safety Flares**

A flare generally consists of a waxed cardboard tube casing filled with a burn mixture and a cap at the end to ignite the flare. Based on Material Safety Data Sheets (MSDS), the burn mixture contains primarily strontium nitrate (75% by weight), potassium perchlorate (<10% by weight), sulfur (<10% by weight) and sawdust/soil (<10% by weight). Other ingredients present in lesser amounts can include: synthetic rubber, aromatic polycarboxylic anhydride fuel, benzene tetracarboxylic acid (dianhydride and metallic dianhydride), sodium nitrate, polyvinyl chloride case binder, dextrin, magnesium, cellulose nitrate, black powder, wax, and red phosphorus (Silva, 2003b). The ignition mix is liquid and is heated and dried into a black button on the end of the flare and is used for igniting the flare by using the striking pad on the cap.

Through experiments conducted by the Santa Clara Valley Water District in California, Silva (2003a) analyzed the contents of an unburned road flare and detected 50,000 mg/kg of perchlorate and 450,000 mg/kg nitrate in a single flare. Comparison of perchlorate leaching from unburned flares that had been damaged (i.e., sliced open) to completely burned flares indicated that the unburned damaged flares leached 2000 times more perchlorate than damaged road flares that were completely burned (3,645 mg versus 1.95 mg).

### **4.2 Production/Use Statistics**

In 1997, approximately \$101.5 million dollars worth of pyrotechnics (NAICS product code of 325998H107) were produced in the U.S. (U.S. Census Bureau, 2001). This classification includes road flares, jet fuel igniters, railroad torpedoes, and toy pistol

caps, but not fireworks. Production and trade statistics for road flares alone are not available. In 2003, 7.0 million lbs or \$10.6 million dollars worth of pyrotechnics were imported ([www.ita.doc.gov/td/industry/otea/trade-detail/latest-december/imports](http://www.ita.doc.gov/td/industry/otea/trade-detail/latest-december/imports)), with 92% from China. Only 0.57 million pounds of pyrotechnics were exported in 2003 ([www.ita.doc.gov/td/industry/otea/trade-detail/latest-december/exports](http://www.ita.doc.gov/td/industry/otea/trade-detail/latest-december/exports)). The world's largest manufacturer of emergency flares is located in the U.S. and has annual sales of \$20,000,000, based on available data.

Annual flare consumption data are not available; however, annual purchase records by state and federal agencies provide some insight into the volume of flares that may be purchased annually across the nation. Table 4-1 provides a summary of the number of flares procured by some large urban centers in the U.S.

**Table 4-1: Summary of Flares Procured in Selected Urban Centers**

Purchasing Entity	Total Number of Flares Procured	Comments
New York, NY	93,816	2 contracts (initiated in 2004, assumed to be annual), both through the NY statewide procurement. Total contract cost and per dozen unit price given - total number of flares based on these numbers.
Los Angeles, CA	576,000	Documentation for contract initiated in 2003 (assumed to be annual) for 4000 gross.
Chicago, IL	3,600	Documentation for single purchase (in 4/2002) for 50 cases of flares from local all-purpose supplier. A request for detailed flare procurement information submitted on 10/21/04.
Houston, TX	115,000	Bid tabulation for two year contract (FY2001-2003) for two types of flares. Total is for combined flare purchase.
San Antonio, TX	216,000	FY2003 bid tabulation for 1500 gross.
Milwaukee, WI	25,200	Contract initiated in 2004 (assumed to be annual).
Miami, FL	204,000	A 2-year contract beginning 5/04. Only the total price is given - total number of flares based on estimated cost per-flare of \$0.85.
Florida Hwy Dept	293,760	FY2005 award. Total contract cost and per gross unit price given - total number of flares based on these numbers.
Pennsylvania Turnpike	500,000	FY2005 RFQ. Total number of flares requested.
Michigan State Police	298,080	A 3-yr contract beginning 7/04. Total contract cost and per gross price given - total number of flares based on these numbers.
Illinois Toll way	10,588	FY2004 contract list (assumed to be annual). Only total price is given - total number of flares based on estimated cost per-flare of \$0.85.

While numbers are not available for total flare production, assuming an average cost per flare of \$0.50 to \$1.00 per flare and annual sales of \$20 million by the largest manufacturer, then between 20 to 40 million flares may be sold annually. The fate of these flares is largely unknown. For example, it is unlikely that all flares procured on an annual or contract basis are burned through the course of the contract, and it's therefore assumed that disposal or controlled burn of some portion of the unused flares may periodically occur.

### **4.3 Potential to Impact Groundwater**

Preliminary research by Silva (2003a, 2003b) of the Santa Clara Valley Water District (SCVWD) indicates that 3.6 g of perchlorate can potentially leach from an unburned, damaged (i.e., run over by a motor vehicle) 20-minute road flare. According to Silva (2003a), this amount of perchlorate can potentially contaminate 2.2 acre-feet of drinking water above 4 µg/L (the standard EPA Method 314.0 quantitation limit). Interestingly, even fully burned flares leached 1.9 mg perchlorate/flare (Silva, 2003a). More than 40 metric tons of flares were reported to be used/burned in 2002 in Santa Clara County, California alone (Silva, 2003a). Given this estimate, 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.

Road flare manufacturing has also been implicated in perchlorate contamination at a site in Morgan Hill, California ([www.valleywater.org](http://www.valleywater.org)). From 1956 to 1996, highway flares were manufactured at this location ([www.valleywater.org](http://www.valleywater.org)). Perchlorate was detected at one on-site monitoring well in 2001 and was detected in a municipal well in March 2002. The perchlorate plume is estimated to be 9 miles long (The Mercury News, Sept. 10, 2003). It is important to note that this site is located in an area that was historically used for fruit and nut production, and perchlorate impacts to soil and groundwater in some areas may also be the result of past fertilizer practices, as discussed in Section 2).

### **4.4 Summary**

Preliminary research by Silva (2003a, 2003b) of the Santa Clara Valley Water District (SCVWD) indicates that 3.6 g of perchlorate can potentially leach from an unburned, damaged (i.e., run over by a motor vehicle) 20-minute road flare. Even fully burned flares leached 1.9 mg perchlorate per flare (Silva, 2003a). While numbers are not



available for total domestic flare production, assuming an average cost per flare of \$0.50 to \$1.00 per flare and annual sales of \$20 million by the largest manufacturer, then at least 20 to 40 million flares may be sold annually. Given this estimate, up to 237,600 pounds of perchlorate could leach from road flares annually. Surface runoff from highways and roads represents a potentially significant and largely uninvestigated impact to surface water and groundwater quality. Additional evaluation of the potential for perchlorate impacts to surface waters and groundwater from safety flare use appears warranted.

## 5. BLASTING EXPLOSIVES

Blasting agents are non-cap sensitive explosives. Generally, they are intimate mixtures of inorganic oxidizers and fuels, rather than the organic explosives commonly used in military applications (e.g., RDX, TNT, HMX). While the main oxidizer employed is usually ammonium nitrate (AN), ammonium perchlorate and other perchlorates (sodium or potassium perchlorate) are compatible with the AN mixtures and can be employed for special applications and to take advantage of perchlorate available from DOD demilitarization activities. Furthermore, sodium nitrate (Chilean origin) historically used in commercial explosives may contain perchlorate as an impurity. Review of MSDS information identifies perchlorate as a common component of many slurry gel explosives (Table 5-1). The following sections discuss the composition of various commercial blasting agents based on review of MSDS information and examine the potential for perchlorate impacts to soil and groundwater from blasting operations.

### 5.1 Common Blasting Agents, Explosives & Detonators

Blasting agents, as opposed to explosives, require a booster, in addition to a detonator, to initiate. This is a significant advantage in terms of less stringent and more economical storage and transport considerations. The most common and simplest blasting agent is ammonium nitrate fuel oil (ANFO), which consists of ammonium nitrate prills soaked with fuel oil (about 5 to 6 wt%). ANFO accounts for a large share of the domestic commercial explosives market (about 80% in 1998) (ISEE, 1998) and is available in bulk form for on-site mixing or in premixed bags. The hydrophilicity of AN precludes its use in wet conditions without special precautions (ISEE, 1998), and a number of products have been developed to address this issue.

AN remains the key oxidizer in commercial explosives. The problem of its high hydrophilicity is addressed by gelling the AN in an aqueous matrix (slurries or water gels) or encapsulating it in a water-in-oil emulsion. Both types of products are sold in bulk or prepackaged chubbs. Slurries, also referred to as water gels, contain AN in aqueous solution. To aid water resistance and handling, they are thickened and gelled with a gum, such as guar gum. Depending on the remainder of the ingredients, slurries can be classified as either blasting agents (not cap-sensitive) or explosives. Slurry blasting agents contain non-explosive sensitizers or fuels such as carbon, sulfur, or aluminum; whereas slurry explosives contain cap-sensitive ingredients such as PETN. As shown in Table 5-1, several water gels contain sodium perchlorate.

As emulsion technology advanced over the years, AN in emulsion, rather than in slurries, became popular. Emulsions generally contain AN dissolved in water, but it is

possible to prepare waterless emulsions where an AN/salt eutectic serves alone as the discontinuous phase. Emulsions have made it possible to shoot small diameter and wet boreholes. A typical formulation would be 80-90% AN, 4-6% hydrocarbon, 10-15% water, and 1-2% emulsifier (Oxley, 1989, 1992). Unlike slurries, emulsions are generally sensitized with a gassing agent or micro-balloons rather than a sensitizing chemical.

Another popular blasting product consists of a blend of prilled ANFO or AN with AN emulsion in various ratios. Blends containing less than 50% emulsion are sometimes referred to as “heavy ANFO.” Their benefits include reduced mining costs, increased water resistance and increased density/strength (ISEE, 1998). MSDS sheets for some heavy ANFOs list “inorganic oxidizers”. Further testing is required to determine if these products contain perchlorate.

A number of AN products include sodium perchlorate to increase shock initiation sensitivity (Table 5-1). Furthermore, some list sodium nitrate as a constituent. Since sodium nitrate of Chilean origin is known to contain perchlorate, these blasting agents are likely to contain perchlorate.

**Table 5-1: Blasting Agents and Explosives Containing Perchlorate  
(% Composition)**

Type Product	Blasting Agent (1.5) or Explosive (1.1)	NH <sub>4</sub> NO <sub>3</sub>	NaNO <sub>3</sub>	NaClO <sub>4</sub>	Al	hexamine dinitrate	PETN	other energetic fuel	fuel oil	stabilizer
gel bulk or packaged	blasting agent	55-85	--	0-4	0-10	0-15	--	--	0-5	--
packaged gel	blasting agent	33-40	10-15	--	0-9	--	--	25 - 51	--	1-3
package emulsion	explosive	60-70	0-5	0-15	0-5	--	0.5 - 3	--	--	--
package emulsion	explosive	60-80	0-12	--	0-10	--	--	--	0-12	--
packaged gel	explosive	<65	<20	<7	<7	<20	--	--	--	--
ANFO	blasting agent	94.5	--	--	--	--	--	--	5.5	--
water gel	blasting agent	<80	--	<5	--	<15	--	--	--	--
water gel	blasting agent	< 75	<5	<5	<3	< 23	--	--	--	--
water gel	explosive	<65	<20	<7	<7	<20	--	--	--	--
water gel	explosive	<65	<20	<7	<7	<20	--	--	--	--
water gel, presplit	explosive	<65	<20	<7	<7	< 20	< 2	--	--	--
water gel	blasting agent	10-20	10-20	20-30*	--	10-15	--	--	--	--

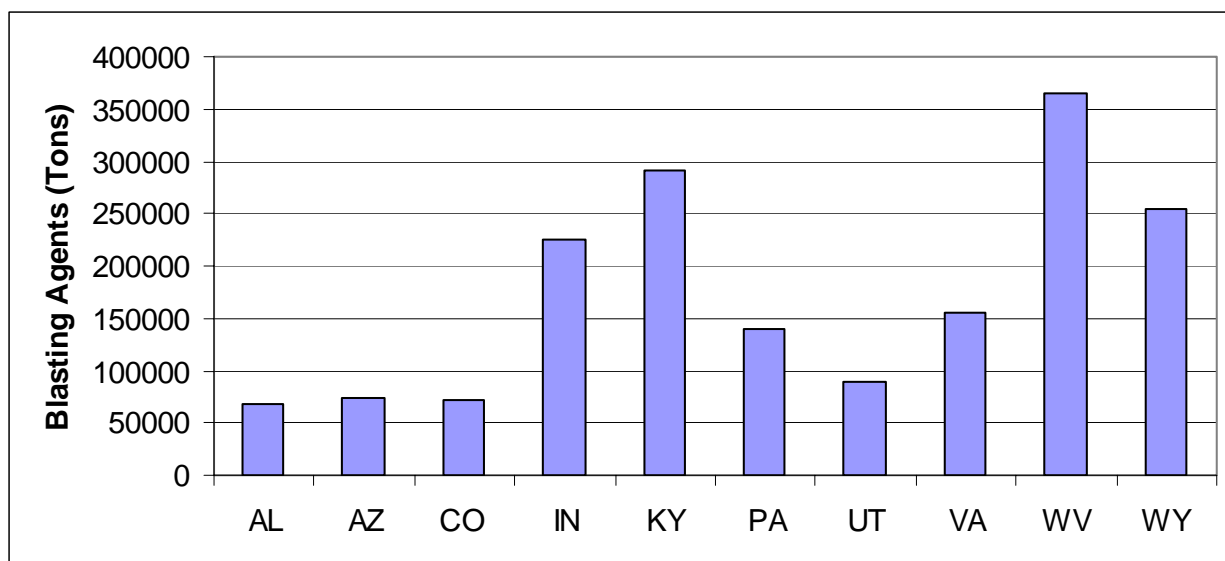
\* ammonium perchlorate

Detonators initiate a shock wave in a primary explosive and amplify it to a secondary explosive. Detonators may be electric or non-electric. Some non-electric detonators can contain up to 10% potassium perchlorate.

## 5.2 Consumption/Market

In 2003, the U.S. production of explosives, reported by 23 commercial explosive manufacturers, was 2,525,000 tons (Kramer, 2003). This amount of explosives is typical of the annual U.S. production in the last decade. Of the total U.S. commercial production, 2,723,000 tons were classed as blasting agents. Sales of blasting agents were reported in all states with West Virginia, Kentucky, Wyoming and Indiana consuming the highest quantities (Figure 5-1). Sixty seven percent of the blasting agents were used in coal mining. Quarrying and nonmetal mining, the second-largest consuming industry, accounted for 14% of total explosives sales. Construction, metal mining and miscellaneous uses accounted for 8%, 8%, and 3% of explosives sales, respectively (Kramer, 2003).

**Figure 5-1: Blasting Agents and Oxidizers – Usage by Top Ten States (2003)**



## 5.3 Potential to Impact Groundwater

Although most perchlorate should be consumed during detonation of blasting agents, there are instances where groundwater contamination related to perchlorate in blasting agents may occur. The following are examples of practices that could lead to perchlorate contamination:

- Poor housekeeping of perchlorate-containing explosives (i.e., spillage on-site);
- Exceeding the sleep time of the explosive. Sleep time is the length of time that an explosive can remain in the ground after charging and still detonate with full energy. Blast hole conditions have a large impact on the sleep time of explosives in wet conditions;
- Poorly designed initiation of the charge, permitting small pockets of undetonated material after the blast; and
- Blasting misfires, where a loaded hole(s) fails to detonate or partially explodes. If the blaster follows proper methods of priming, loading, stemming, hooking up the shot and firing it, the likelihood of a misfire is small (ISEE, 1998).

To our knowledge, no detailed studies are publicly available that quantify the amount of perchlorate originating from blasting agents and explosives. There have been several newspaper and internet reports that attempt to link blasting operations to high perchlorate concentrations in groundwater and surface water, particularly in Massachusetts (Ward, 2004; Wims, 2004; Town of Tewksbury, 2004). Perchlorate concentrations as high as several hundred parts per billion have been measured in close proximity to blasting sites. In response to perchlorate contamination in the Boxborough, Massachusetts area, the Fire Chief has issued a ban on the use of perchlorate-based agents for all blasting activities in Boxborough ([town.boxborough.ma.us](http://town.boxborough.ma.us)). In addition, the State of Massachusetts is prohibiting its own contractors from using blasting agents that contain perchlorate (Hughes, 2004).

## 5.4 Summary

Some water gels, emulsions, and non-electric detonators can contain substantial amounts of perchlorate (e.g., up to 30%). While, most of the perchlorate is expected to be consumed in the detonation, poor housekeeping practices (i.e., spillage), improper use, or misfires can potentially result in perchlorate contamination of surface and ground waters. Given that the U.S produces approximately 2.5 million tons of explosives annually, perchlorate could potentially be released into the environment in relevant amounts. Currently, no publicly-available data exist that indicate what amount of perchlorate might impact the environment from blasting. More studies are required to assess and quantify the potential impact of blasting explosives on perchlorate contamination of surface and ground waters.

## 6. ELECTROCHEMICALLY-PRODUCED CHLORINE PRODUCTS

During the electrochemical manufacture of chlorine products, such as chlorate, from chloride brine feedstocks, small amounts of perchlorate may be formed as an impurity (Wanngard, 1991; Betts et al., 1997). Because perchlorate was not known to be a chemical of environmental concern until quite recently (1997), and because the impurity level was considered small relative to the primary chemical being produced (e.g., chlorate), little attention has been paid to its presence. Therefore, little publicly-available information regarding perchlorate contamination in ECP chlorine products exists. Recent analysis of several sodium chlorate feedstocks being used for large-scale commercial perchlorate manufacturing suggest that perchlorate is present in the chlorate products at concentrations ranging from 50 to 230 mg/kg chlorate, and therefore, potential exists for release of perchlorate to the environment through chlorate manufacture, storage, handling, and use. The following sections provide information related to chlorate manufacturing and use and discuss the potential for impacts to soil and groundwater.

### 6.1 Manufacture of Chlorate

Sodium chlorate is produced electrochemically by the electrolysis of aqueous sodium chloride, and its production is governed by the following equation (Betts, 1997):



During the production of sodium chlorate, sodium perchlorate is often produced as an impurity in the electrolytic cell. Concentrations of up to 500 mg of sodium perchlorate per kg sodium chlorate are not uncommon (Wanngard, 1991). Accumulation of sodium perchlorate decreases the solubility of sodium chlorate and is actually undesirable to the manufacturer of the chlorate product. As such, several processes have been developed and patented to improve the efficiency of the electrolytic cell, prevent perchlorate formation, and/or remove the perchlorate from the chlorate (Wanngard, 1991; Betts et al., 1997). The formation of perchlorate stems from anodic oxidation of chlorate during the electrochemical reaction in accordance with the following reaction (Betts, 1997):



Significant amounts of ECP chlorine chemicals such as sodium chlorate are produced in the U.S. on an annual basis. The majority of sodium chlorate produced in the U.S. is used domestically, with only 3% of the annual domestic production exported. To satisfy demand for use, it is estimated that an additional 40% is imported for domestic

consumption. Table 6-1 lists the total domestic production and consumption rates of sodium chlorate. The total annual consumption of sodium chlorate is approximately 1.2 million tons (U.S. Department of Commerce, 2003).

**Table 6-1: U.S. Production and Consumption of Sodium Chlorate**

	<b>Production (tons)</b>	<b>Exports (tons)</b>	<b>Imports for Consumption</b>	<b>Apparent Consumption (tons)</b>
1991 <sup>a</sup>	448,908	n/a	n/a	n/a
1992 <sup>a</sup>	554,564	n/a	n/a	n/a
1993 <sup>a</sup>	539,259	n/a	n/a	n/a
1994 <sup>a</sup>	559,015	n/a	n/a	n/a
1995 <sup>a</sup>	614,536	n/a	n/a	n/a
1996 <sup>b</sup>	600,890	54,375	395,199	941,714
1997 <sup>b</sup>	567,797	65,680	411,687	913,804
1998 <sup>c</sup>	706,909	49,425	430,384	1,087,868
1999 <sup>c</sup>	742,476	57,543	439,567	1,124,500
2000 <sup>d</sup>	852,756	48,983	440,461	1,244,234
2001 <sup>e</sup>	792,167	32,834	495,379	1,254,712
2002 <sup>e</sup>	721,086	39,828	528,239	1,209,497

**Notes:**

- a - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: Fourth Quarter 1996, February 27, 1997
- b - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: 1997, September 29, 1998
- c - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: 1999, September 28, 2000
- d - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: 2001, August 2002
- e - U.S. Department of Commerce, Economics and Statistics Administration, US Census Bureau, Inorganic chemicals: 2002, August 2003

In North America, chlorate production is dominated by a relatively small number of companies. Due to anticipated differences in the manufacturing process/technology employed by these various companies, significant differences in perchlorate levels in chlorate may exist. Table 6-2 provides a summary of estimated North American annual chlorate manufacturing capacity for the five major chlorate producers.

**Table 6-2: Summary of North American Annual Chlorate Manufacturing Capacity**

<b>Chlorate Producer</b>	<b>State/Province</b>	<b>Capacity (tons)</b>
Company 1	MS	225,000
	WA	65,000
	QB	165,000
Company 2	QB	125,000
	GA	150,000
	SC	90,000
Company 3	MS	150,000
Company 4	GA	115,000
	AB	83,000
	MAN	44,000
	QB	132,000
	AB	55,000
	BC	101,000
	SK	55,000
	ON	55,000
Company 5	ON	55,000
	QB	48,000
	MAN	190,000
	AB	75,000
	BC	20,000
Total Capacity - USA		1,022,000
Total Capacity - Canada		1,323,000
Total Capacity - North America		2,460,000

## 6.2 Chlorate Use

Historic and current uses for chlorate include pulp and paper bleaching, non-selective contact herbicide application, and plant defoliation (OMRI, 2000). Sodium chlorate is also used in limited capacities for water treatment, mining, and in the production of other chemicals such as sodium perchlorate and other metallic perchlorates.

The pulp and paper industry uses approximately 94% of all sodium chlorate consumed in the U.S. (OMRI, 2000). In this industry, it is primarily used for the on-site production of chlorine dioxide to bleach cellulose fibers. In 1998, the U.S. EPA ruled that, by April 2001, pulp and paper mills in the U.S. would have to use elemental chlorine free (ECF) bleaching instead of the traditional chlorine bleaching, which has the potential to produce organic halides. Chlorine dioxide produced from sodium chlorate meets this requirement. As a result, the sodium chlorate industry has grown annually at about 3%, similar to that of the paper industry (TIG, 2004). If perchlorate is indeed a chemical of concern in chlorate materials, then the potential for perchlorate impacts from chlorate use are likely to increase with increased demand for paper products.



In addition to pulp and paper bleaching, sodium chlorate is used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, sundangrass, safflower, rice, and chili peppers (Table 6-3; OMRI, 2000). As a defoliant, approximately 99% of sodium chlorate application is used on cotton plants (PAN Pesticide Database, 2002). By removing the foliage, a better yield is obtained during harvest and the cotton does not become stained. The application of chlorate defoliants is generally unique to Arizona and California because of their warm climates. Elsewhere, early frost causes foliage to drop from cotton plants naturally. In California and Arizona, the frost typically occurs too late, if at all, and the leaves remain on the plants during harvesting, requiring the use of defoliants. Depending on the yearly weather conditions, other states including Mississippi, Texas, Alabama, Arkansas, Georgia, Louisiana, Tennessee and North Carolina may use sodium chlorate as a defoliant for cotton.

**Table 6-3: National Totals for Sodium Chlorate Use for Defoliation**

<b>Crop</b>	<b>Pounds Active Ingredient</b>	<b>Acres Treated</b>
Cotton	4,581,793	1,507,850
Sunflower	10,091	1,771
Safflower	29,856	5,043
Rice	19,606	4,005

Source : <http://ca.water.usgs.gov/pnsp/crop/index.html>

In terms of quantity of use, California used more than 24 million pounds of sodium chlorate on cotton between 1991 and 2003, with an average application rate of 4.6 lbs/acre (Table 6-4). By comparison, Arizona, Mississippi, and Texas had total application rates of 6.3, 4.5, and 1.7 million pounds, respectively, between 1991 and 2003 (Table 6-4).

**Table 6-4: Sodium Chlorate Application to Cotton Crops by State,  
1991-2003**

State	1991		1992		1993		1994	
	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)
Alabama	-	-	-	-	-	-	-	-
Arizona	1,231,000	6.29	709,000	4.56	644,000	4.31	773,000	5.73
Arkansas	-	-	-	-	337,000	2.77	152,000	2.08
California	2,448,000	4.98	3,326,000	5.13	3,072,000	5.47	1,924,000	2.86
Georgia	-	-	-	-	-	-	-	-
Louisiana	-	-	138,000	1.17	-	-	70,000	0.84
Mississippi	696,000	2.16	256,000	2.08	-	-	489,000	3.32
North Carolina	-	-	-	-	-	-	-	-
Tennessee	-	-	-	-	-	-	-	-
Texas	185,000	1.10	-	-	116,000	1.03	330,000	2.12

State	1995		1996		1997		1998	
	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)
Alabama	-	-	-	-	42,000	0.88	36,000	0.6
Arizona	769,000	5.77	456,000	4.43	450,000	4.29	550,000	5.24
Arkansas	251,000	2.55	-	-	-	-	208,000	2.53
California	4,624,000	5.79	2,317,000	4.93	1,123,000	3.79	499,000	4.13
Georgia	-	-	-	-	113,000	1.21	150,000	1.03
Louisiana	321,000	1.25	-	-	181,000	2.89	106,000	2.28
Mississippi	305,000	2.10	973,000	2.64	262,000	1.29	-	-
North Carolina	-	-	-	-	-	-	-	-
Tennessee	-	-	-	-	19,000	0.8	-	-
Texas	343,000	1.66	-	-	482,000	1.35	-	-

State	1999		2000		2001		2002	
	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Application Rate (lbs/acre)
Alabama	-	-	-	-	-	-	-	-
Arizona	372,000	4.81	155,000	2.98	-	-	-	-
Arkansas	429,000	4.25	62,000	1.01	-	-	-	-
California	1,106,000	4.89	815,000	4.82	-	-	2,379,994	6.05
Georgia	72,000	0.95	-	-	-	-	-	-
Louisiana	70,000	2.57	16,000	1.13	-	-	-	-
Mississippi	324,000	3.53	199,000	1.29	819,000	3.73	-	-
North Carolina	14,000	0.57	21,000	0.57	-	-	-	-
Tennessee	-	-	-	-	-	-	-	-
Texas	-	-	141,000	0.66	76,000	0.71	-	-

State	2003		1991 to 2003			
	Total Applied (lbs)	Application Rate (lbs/acre)	Total Applied (lbs)	Average Application Rate (lbs/acre)	Total Potential Perchlorate Applied (lbs)	Average Potential Perchlorate Application Rate *
Alabama	15,000	0.62	93,000	0.70	47	0.00035
Arizona	172,000	4.98	6,281,000	4.85	3,141	0.00243
Arkansas	24,000	0.86	1,463,000	2.29	732	0.00115
California	680,000	2.73	24,313,994	4.63	12,157	0.00232
Georgia	-	-	335,000	1.06	168	0.00053
Louisiana	-	-	902,000	1.73	451	0.00087
Mississippi	192,000	1.85	4,515,000	2.40	2,258	0.00120
North Carolina	-	-	35,000	0.57	18	0.00029
Tennessee	11,000	0.35	30,000	0.58	15	0.00029
Texas	-	-	1,673,000	1.23	837	0.00062

Note: "-" usage data are not published.

\* These values assume that the sodium chlorate is contaminated with 0.05% sodium perchlorate

Source: Agricultural Statistics Board, NASS, USDA Agricultural Chemical Usage Field Crop Summary.(1991 to 2003)

Sodium hypochlorite has also been used as an herbicide and may contain trace amounts of perchlorate. However, application quantities for sodium hypochlorite are substantially lower than sodium chlorate (35,414 lbs applied to crops in California in 2002; PAN Pesticide Database, Sodium Hypochlorite, 2002), and therefore sodium hypochlorite is unlikely to represent a major source of perchlorate contamination relative to defoliant use.

### **6.3 Potential to Impact Surface Water and Groundwater**

Based on the documented occurrence of perchlorate in sodium chlorate and available use statistics, it appears that chlorate use by the pulp and paper industry and as a defoliant has the potential to introduce perchlorate to the environment. For example, assuming 1.2 million tons of sodium chlorate are consumed annually in the U.S. (U.S. Department of Commerce, 2003), and that sodium chlorate may contain perchlorate at concentrations ranging from 50 to 500 mg/kg, this represents the potential handling of 120,000 to 1,200,000 lbs of perchlorate annually, the fate of which is largely unknown.

Chlorine dioxide production for pulp and paper bleaching involves the addition of a sodium chlorate solution and a reducing agent to produce chlorine dioxide. Reducing agents include sulfur dioxide, methanol, chloride ion, and hydrogen peroxide (Dence and Reeve, 1996). Chlorine dioxide is produced as a gas and later absorbed into water prior to being used as a bleaching agent. As such, perchlorate originating in the sodium chlorate would not be expected to be present in the gas stream because of its non-volatility. However, perchlorate is likely to end up in the by-product salt-cake from the chlorine dioxide generator, which is generally added back to the kraft liquor cycle, where it may undergo reduction. On occasion, excess salt-cake is sewerred. The fate of perchlorate in this process is unknown, but low ppb levels of perchlorate in mill effluents are possible if the perchlorate is not significantly treated by the plant's effluent treatment system. Further study of the fate of perchlorate in pulp and paper mills is warranted.

With respect to sodium chlorate use as a defoliant, the average yearly application of sodium chlorate in California is nearly 2 million pounds, applied directly to agricultural lands. Assuming a perchlorate impurity level of between 0.05 to 0.5% sodium perchlorate, the use of sodium chlorate as a defoliant may result in the application of 1,000 to 10,000 pounds of sodium perchlorate to agricultural lands in California per year. While this annual application appears to be relatively small, repeated application over many years to decades may result in an accumulation of perchlorate in soils because of its recalcitrance in most soil environments. Over time, perchlorate in soils could impact

surface waters due to overland flow during rainfall events or groundwater through longer term infiltration.

## **6.4 Summary**

During the electrochemical manufacture of chlorine products, such as chlorate, from chloride brine feedstocks, perchlorate may be formed as an impurity at concentrations of 50 to 500 mg/kg. The estimated North American annual chlorate manufacturing capacity is 2.4 million tons, whereas the total annual consumption of sodium chlorate in the U.S. is approximately 1.2 million tons. The pulp and paper industry uses approximately 94% of all sodium chlorate consumed in the U.S. for on-site production of chlorine dioxide to bleach cellulose fibers. Effluents from pulp mills have been reported to contain chlorate (1 to 70 mg/L; Warrington, 2002), but there is little information available as to the potential for perchlorate release from these facilities. Sodium chlorate is also used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, sundangrass, safflower, rice, and chili peppers. The use of sodium chlorate in the pulp and paper industry and as a defoliant has the potential to contribute perchlorate to the environment.

## 7. CONCLUSIONS

The frequency of detection of perchlorate impacts to soil, groundwater and surface water, unrelated to military activities, is likely to increase as water utilities analyze for this constituent as part of their UCMR monitoring programs. Based on emerging product and process information, perchlorate is present (intentionally or not) in many more products and processes than initially understood.

The U.S. DOD, NASA and related defense contractors are likely to be the most significant domestic users of perchlorate in North America, and as such, a significant percentage of identified groundwater perchlorate impacts are attributable to DOD, NASA, and related defense contractor facilities. However, cases exist, and many more are likely to surface, where perchlorate impacts result from combinations of military, non-military, and/or natural inputs. The ability of DoD, NASA, and defense contractors to accurately apportion the relative contributions from these varying sources, and hence to properly determine liability and control cleanup cost, lies in having a good understanding of the wide variety of products and processes that may contribute perchlorate to the environment, and through the development and validation of forensic tools, such as chlorine isotope analyses.

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*Mecoprop (MCP)*

# Herbicides for Weed Control in Turfgrass

James McAfee, Ph.D.,  
Extension Turfgrass Specialist, Dallas, Texas  
and  
Paul A. Baumann, Ph.D.,  
Professor and Extension Weed Specialist, College Station, Texas

## Herbicides for Weed Management in Turf

Integrated weed management (IWM) is a component of integrated pest management (IPM). Homeowners and turf grass professionals alike can benefit by employing an integrated approach to weed management. These approaches should consider; 1) Preventative, 2) Biological, 3) Cultural, 4) Mechanical and 5) Chemical control measures. Chemical weed control demands precision and judicious use of herbicides. This publication provides information to make an informed decision regarding the use of herbicides but is not a substitute for a product label. Herbicides can injure or kill weeds **and** turf grass. Therefore, the individual product label should be consulted prior to use, especially regarding weeds controlled, application timing, and tolerant turf species.

## Preemergence & Postemergence Herbicides

**Preemergence** herbicides are applied before the weeds sprout through the soil surface. Generally speaking, to control warm-season annual weeds, apply a pre-emergence herbicide in early spring (January to March) before the soil temperature has warmed to 55 degrees F. For weeds that tend to sprout throughout the summer, a second application may be required in June or July. To control cool-season annual weeds, apply a pre-emergence herbicide in early fall (August to September). It is difficult to target a particular calendar date for preemergence applications due to variable soil temperature and moisture conditions from year to year.

**Postemergence** herbicides are applied after weeds have sprouted. They are most effective when weeds are still small: less than 4 inches high. Some herbicides (ex.; atrazine, simazine, dithiopyr) have both postemergence and preemergence activity if they reach the soil through direct contact or by washing off the foliage.

## Contact and Systemic Herbicides

**Contact herbicides** (ex.; paraquat, diquat) cause damage wherever they touch a plant. To work well, a contact herbicide should thoroughly cover the leaves and stems. Contact herbicides work best on small annual weeds. They have little effect on perennial weeds unless applications are repeated. Most contact herbicides work very quickly (1-3 days).

**Systemic herbicides** (ex.; 2,4-D, glyphosate) are absorbed and moved throughout the plant. They are sometimes applied to the foliage and sometimes to the soil although some systemic herbicides such as glyphosate are inactivated by contact with clay particles in the soil. They can be absorbed and translocated (moved) from the foliage, roots or stems to other parts of the plant. Systemic herbicides work well on perennial weeds because the herbicide is moved to parts of the plant other than where it was applied. This feature is particularly valuable for killing root, tuber and rhizome growth on perennial weeds.

## Selective and Non-Selective Herbicides

**Selective herbicides** kill one type of plant but not another—for example, grass weeds but not broad-leaved weeds. This selectivity may be due to differences in herbicide absorption, translocation or physiological differences between weeds and the turfgrass.

**Nonselective herbicides** kill almost all kinds of plants. Use them very carefully in lawns, and be sure to keep them away from shrubs and bedding plants. Some of these (ex.; glyphosate and paraquat) are “inactivated” once they come in contact with the soil and are therefore useful when applied prior to establishing a new turf stand.

## Broadleaf Weeds, Grasses and Sedges

**Broadleaf weeds** have two seed leaves (first leaves) as they emerge through the soil. Their leaves are generally wider than those of grass weeds. Veins on the leaves are branched or net-like. Their stems are oval, round or square and are often branched. They may have showy flowers.

**Grass weeds** have only one seed leaf. Their leaf blades are narrow and have parallel veins. Stems are round or oval. They may develop seed heads at the ends of the stems, but if they have flowers they will be inconspicuous.

**Sedges** look a lot like grasses but their stems are triangular. Their leaves are usually shiny and smooth. Sedges often have “nuts” or tubers attached to their roots. In purple nutsedge, several tubers can be connected in a “chain”.

## Annual, Biennial and Perennial Weeds

**Annual** weeds germinate from seed each year and live for one growing season. Summer annuals germinate in the spring and die back in the fall. Winter annuals germinate in late summer or early fall and die the following spring or summer. Annual weeds can produce thousands of seeds per plant which can germinate for many years after the seed has been shed by lying “dormant” in the soil until light, temperature and moisture conditions are adequate for germination. Most annual weeds will not germinate below a 1 inch soil depth unless they are large-seeded (>1/8” in diameter).

**Biennials** have a 2-year life cycle. They germinate, emerge, and usually form a rosette (radial cluster of leaves close to the ground) in the first year. The second year, the plant bolts (produces a flower stalk), flowers, sets seed, matures, then dies.

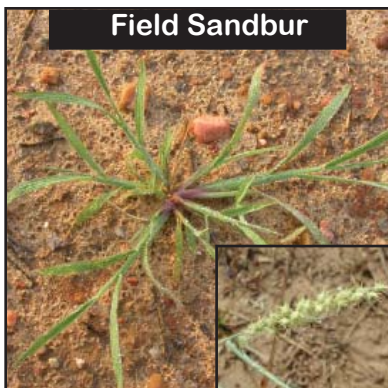
**Perennials** live 3 years or more. Some reproduce by seed, and some reproduce by creeping stems that can be either above-ground (stolons) or below-ground (rhizomes). Sometimes, as in nutsedges, the rhizomes produce tubers from which new plants grow. Many a homeowner has discovered that what appeared to be individual nutsedge plants in the flower bed were actually a series of plants that have sprouted from these connected tubers. If the stolons, rhizomes, or tubers are broken or separated into pieces, new plants can form from these pieces and spread the weed. Therefore, tillage or hand pulling is discouraged when trying to eradicate most perennial weeds.

## Herbicide Names

Individual herbicide products have what would be considered three names; trade, common, and chemical. Examples of these names for one product are as follows; *Roundup* (trade name), *glyphosate*

(common name) and *N-(phosponomethyl) glycine* (chemical name). This publication will focus on the common name, often referred to as the active ingredient on the label. This name could be the same across a number of different trade named products but still perform the same.

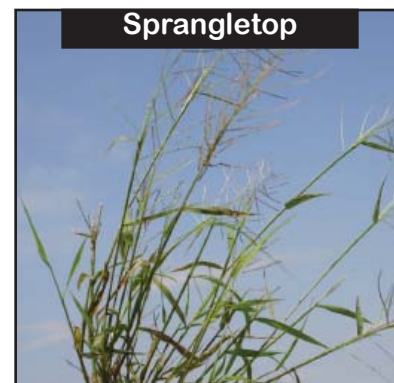
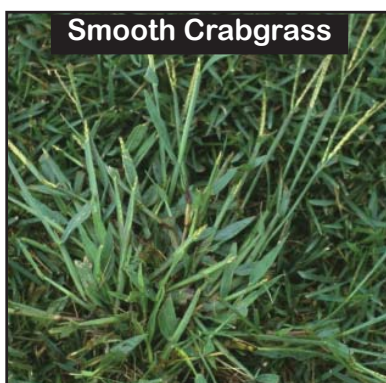
### Annual Grass Weeds



PREEMERGENCE HERBICIDES	
Annual Grass Weed Control	
Common Name	Trade Name(s)
atrazine	Atrazine 4L, Aatrex 4L, Purge 4L
benefin	Balan 2.5G, Balan 60 DF, 2.5 Benefin Granules
benefin + oryzalin	XL 2G, Excel-5 Plus
benefin + oxadiazon	Regal Star
benefin + trifluralin	Team 2G, Team Pro
bensulide	Betasan, Bensumec, PreSan, Weedgrass Preventor
bensulide + oxadiazon	Goose/Crab Control
dithiopyr	Dimension, Ultra WSP
ethofumesate	Prograss 1.5 EC
metolachlor	Pennant Magnum 7.62 EC
oryzalin	Surflan 4 AS
oxadiazon	Ronstar <sup>1</sup>
pendimethalin	Pendulum (several), Pre-M
prodiamine	Barricade, Endurance, Factor, RegalKade G
pronamide	Kerb
simazine	Princep 4L, Simazine 4L, Simtrol 4L
1. Not for use in residential lawns.	

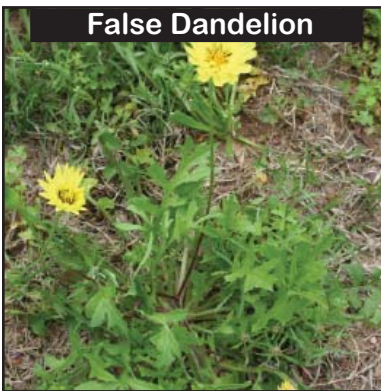
Annual Broadleaf Weed Control	
Common Name	Trade Name(s)
isoxaben	Gallery
ethofumesate	Prograss 1.5 EC

Sedge Control or Suppression	
metolachlor	Pennant Magnum 7.62 EC





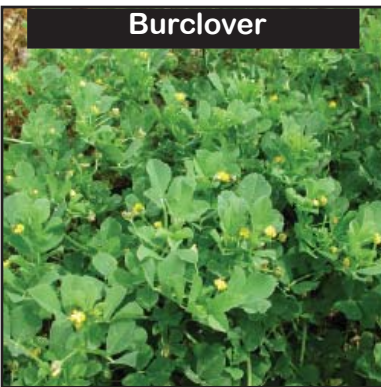
## Annual Broadleaf Weeds



**False Dandelion**



**Bracted Plantain**



**Burclover**



**Carolina Geranium**



**Carpetweed**

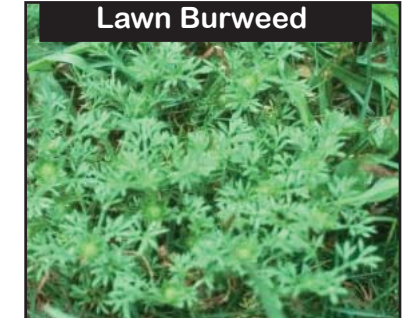
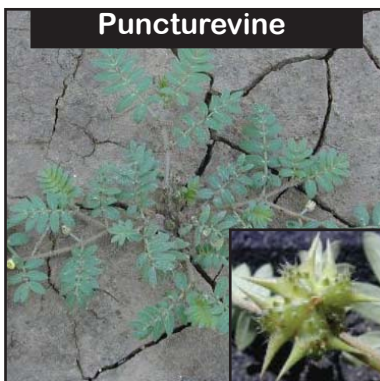
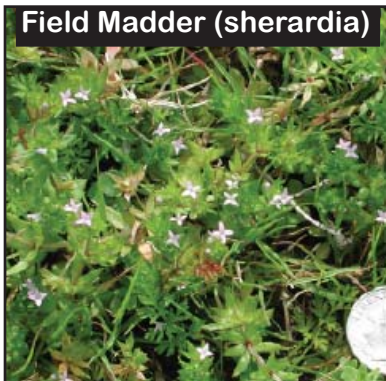
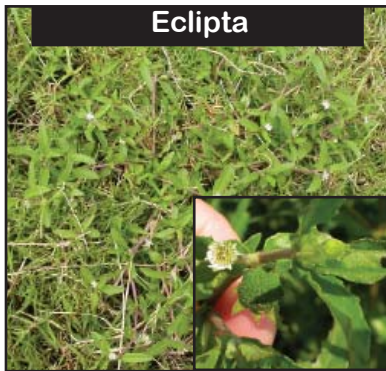
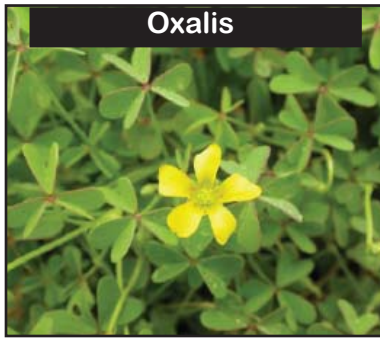
## POSTEMERGENCE HERBICIDES

### Broadleaf Weed Control

Common Name	Trade Name(s)
atrazine	Atrazine, Aatrex 4L, Purge 4L
carfentrazone	Quicksilver
chlorosulfuron	Corsair
clopyralid	Lontrel <sup>1</sup>
diquat	Reward Landscape & Aquatic Herbicide
ethofumesate	Prograss 1.5 EC
fluroxypyr	Spotlight
foramsulfuron	Revolver
imazaquin	Image
MCPA	MCPA L.V. 4 Ester
MCPA, MCPP, dicamba	TriPower Selective, Encore
MCPA, MCPP, dicamba, carfentrazone	Powerzone
MCPA, triclopyr, dicamba	TruPower
MCPA, fluroxypyr, dicamba	TruPower 2
Mecroprop (MCPP)	MCPP-4 amine, Mecomec 2.5 EC
MCPP, 2,4-D, dicamba	Trimec Southern, Lesco Three Way Selective, Bentgrass Selective, Triplet SF
MCPA, triclopyr, dicamba	Cool Power Ester, Lesco Eliminate, Three Way Ester II Sensitive, Horsepower
metsulfuron-methyl	Blade, Manor
pyraflufen ethyl	Octane <sup>1</sup>
quinclorac	Drive
triclopyr	Turflon Ester
triclopyr, clopyralid	Confront <sup>1</sup>
2,4-D	Dymec, WEEDestroy AM-40 Amine, Hardball, Lesco A-4D
2,4-D, 2,4-DP	Patron 170 Ester
2,4-D, clopyralid, dicamba	Millennium Ultra
2,4-D, clopyralid, dicamba, MSMA	Millennium Ultra Plus
2,4-D, dicamba	Lesco Eight-One
2,4-D, MCPP, dicamba	Three-Way Selective, Trimec Southern, Trimec Bentgrass, Trimec Classic, Trimec Turf Herbicide
2,4-D, MCPP-p, dicamba	Triplet HI-D, Triplet Selective
2,4-D, MCPP, dicamba, carfentrazone	Speedzone, Speedzone Southern
2,4-D, MCPP, dicamba, sulfentrazone	Surge
2,4-D, MCPP, 2,4-DP	Dissolve, Triamine
2,4-D, triclopyr, clopyralid	Momentum
2,4-D, triclopyr	Chaser
MSMA, 2,4-D, MCPP, dicamba	Trimec Plus
trifloxysulfuron	Monument
1. Not for use in residential lawns.	



**Annual Broadleaf Weeds**





## Perennial Grass Weeds



Grass Weed Control	
Common Name	Trade Name(s)
chlorsulfuron	Corsair
diquat	Reward Landscape & Aquatic Herbicide
ethofumesate	Prograss 1.5 EC
fenoxaprop	Acclaim <sup>1</sup>
flazasulfuron	Katana
foramsulfuron	Revolver <sup>3</sup>
fluazifop-p-butyl	Fusilade II <sup>2</sup>
metribuzin	Sencor 75W
metsulfuron-methyl	Blade, Manor
MSMA	MSMA 6 Plus, Bueno 6, Target 6.6, MSMA Plus HC, TurfMax 6 Plus, MSMA Turf Herbicide, Lesco Soluble MSMA Granules
MSMA, 2,4-D, MCPP, dicamba	Trimec Plus
rimsulfuron	TranXit <sup>3</sup>
trifloxysulfuron	Monument <sup>3</sup>

1. For grassy weed control in cool season turfgrasses.  
 2. For control of grassy weeds in zoysiagrasses.  
 3. Primarily used for poa annua control and as ryegrass transition aid.

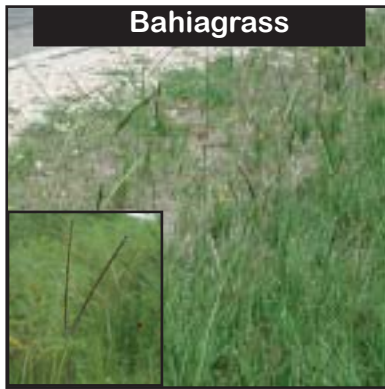
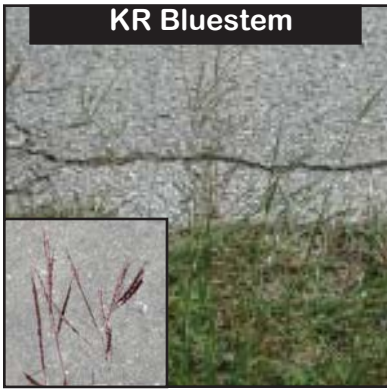
Nutsedge Control	
Common Name	Trade Name(s)
bentazon	Basagran T/O, Lescogran
flazasulfuron	Katana
halosulfuron	Sedgehammer
imazaquin	Image
sulfosulfuron	Certainty
trifloxysulfuron	Monument

NON-SELECTIVE HERBICIDES	
Common Name	Trade Name(s)
glufosinate	Finale
glyphosate	Glypro Plus, Roundup, Roundup Pro, Roundup Pro Dry, Roundup Quick Pro, AquaMaster, Prosecutor, Touchdown Pro

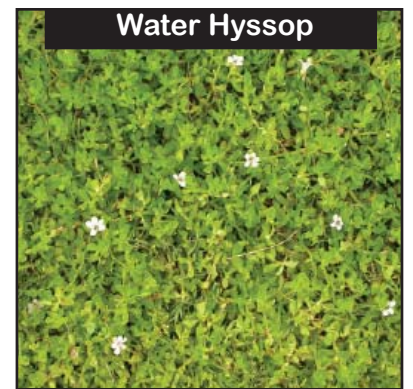
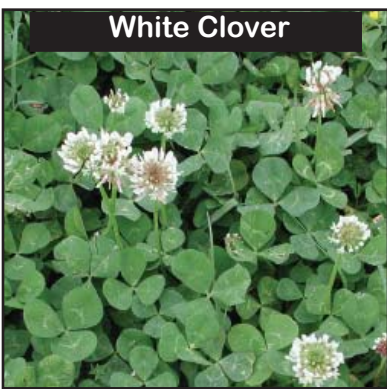
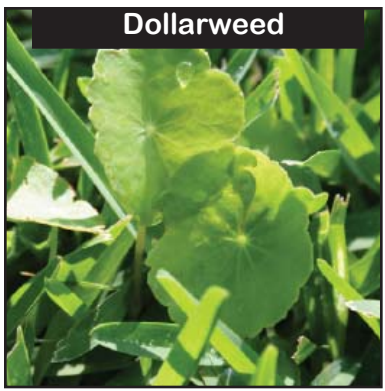
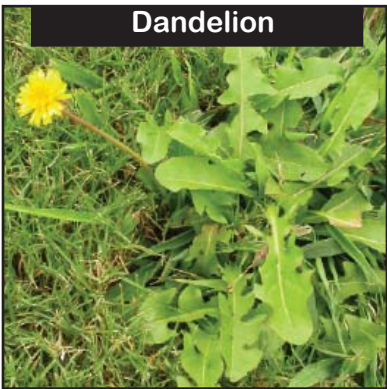
While this is not a complete list of herbicides for weed control in turfgrasses, it does contain the majority of commonly used or found herbicides. This is a working list and will be updated on a regular basis as more herbicides become registered for use in turfgrasses.

Always advise individuals to read the label carefully before purchasing and before using to make sure the herbicide is labeled for the weeds needing controlled and that the herbicide is labeled for the turfgrass species the weeds are found. Also, registration for these different herbicides could change over time.

**Perennial Grass Weeds**

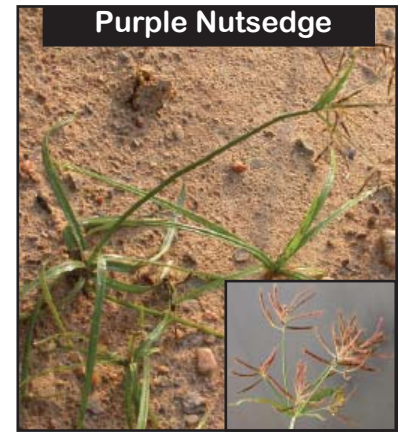


**Perennial Broadleaf Weeds**

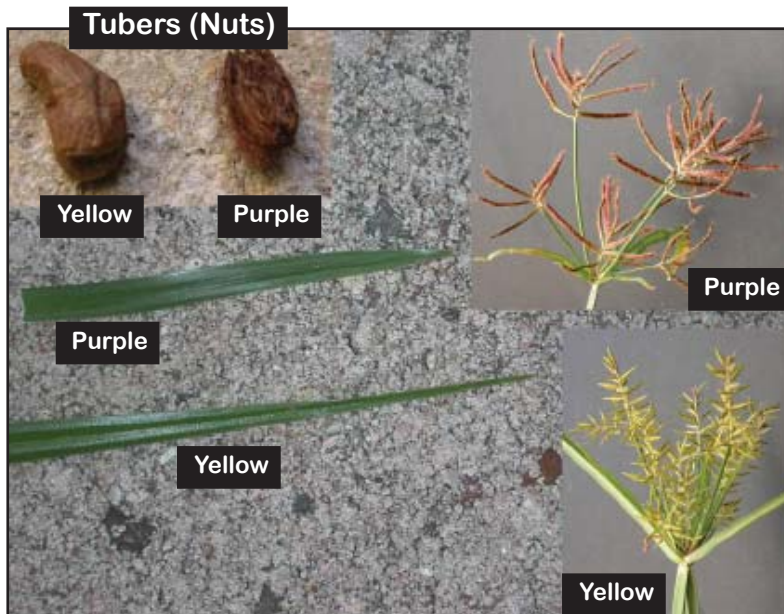




## Sedges



### Distinguishing Features of Yellow and Purple Nutsedge



Yellow and purple nutsedge can often appear indistinguishable from each other, however, it is important to recognize them in order to choose the appropriate herbicide for control. The flowering parts (seedheads) are often quite different in appearance. Yellow nutsedge flower spikes exhibit an overall yellow appearance and “bottlebrush” look. Purple nutsedge has distinct purple colored flower spikes with more loosely arranged spikelets. The leaves of yellow nutsedge have a gradual, narrow taper to the leaf tip while the leaves on purple nutsedge taper much more abruptly. The tubers (nuts) on yellow nutsedge are usually without hairs while the tubers of purple nutsedge are most often covered with them. In addition, purple nutsedge can have “chains” several tubers long. Yellow nutsedge will only have one tuber connected to a rhizome (thickened root) coming off the parent plant.

Produced by the Department of Soil and Crop Sciences, Texas A&M University, College Station, Texas. For further information go to [www.soilcrop.tamu.edu](http://www.soilcrop.tamu.edu). The authors may be contacted at [JMcafee@ag.tamu.edu](mailto:JMcafee@ag.tamu.edu) or [PBaumann@ag.tamu.edu](mailto:PBaumann@ag.tamu.edu).

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CMG GardenNotes #552

# Broadleaf Weed Control in Lawns

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- Outline: Where do lawn weeds come from?, page 1  
Using herbicides on manage lawn weeds, page 2  
Summer broadleaf weed management page 2  
Difficult-to-control weeds, page 3  
Post emergence weed control products for home lawns, page 4
- 

Dandelion, clover, plantain and other broadleaf weeds are among the most common and troublesome turf pest problems in lawns. Even though most broadleaf weeds can be easily controlled with herbicides, a completely weed-free lawn is neither practical nor environmentally sensible. A safe and sound approach to lawn weed control is to grow a healthy lawn, spot-treat weeds with the correct weed control product as they appear, and avoid the temptation to have a 100% weed-free lawn.

The best way to minimize weed problems in your lawn is through the use of good cultural practices: proper mowing height and frequency, sensible fertilization, and adequate irrigation. On the other hand, lawn weeds are encouraged by: mowing your lawn too short or not often enough; fertilizing too much, not enough, or at the wrong time of the year; and over- or under-watering.

## Where Do Lawn Weeds Come From?

- Seeds of broadleaf weeds occur naturally in all soils, and can persist for 30 or more years. They will germinate when a lawn is thin and not healthy, when the seeds are brought to the surface by human or pet traffic, or when the turf is damaged or killed by drought, heavy traffic, insect feeding, or disease activity.
- Cheap, low-quality grass seed often contain unwanted weed seed. If the seed label lists ANY weed seed as a component, DON'T buy it! The best quality grass seed (sold by professional seed suppliers) will almost always be 100% weed-free, and will often cost nearly the same as poor quality products which contains weed seed. READ THE SEED LABEL! The Weed Content of any grass seed you buy (expressed as a %) should be 0%.
- Weed seeds are often brought to a landscape in topsoil or low quality compost. Make sure that all soil or compost comes from a reputable supplier and is guaranteed to be weed-free.

## Using Herbicides to Manage Lawn Weeds

The most common herbicide choice is a general-purpose mixture comprised of two or three of the following individual herbicides or active ingredients: 2,4-D; MCPP (mecoprop); and dicamba (Banvel). Multiple active ingredients will control a wider spectrum of broadleaf weeds, than a single active ingredient. Read and follow all directions on the herbicide label if you choose to apply a herbicide to your lawn.

The best time to apply a general-purpose broadleaf herbicide for the control of perennial broadleaf weeds such as dandelion, plantain, and clover is early-September to early November. As winter approaches, perennial broadleaf weeds are storing energy reserves in stems and roots; a fall-applied herbicide will enter the plant and travel to these plant parts with the food reserves. The second best time is in the late spring or early summer period after the weeds have flowered. If applying in the late spring, be extremely cautious with these herbicides near ornamentals, trees, flowers, and vegetable gardens because these plants can be damaged by these herbicides through direct application, drift, and/or volatilization (the herbicide turns into a vapor). This is another reason why we prefer to apply these herbicides in the fall.

- If you only have a few weeds in your lawn, simply spot-apply a herbicide rather than applying to the entire lawn. Apply just enough to wet the leaf and do not apply to the point that the herbicide is dripping off the leaf.
- Apply to actively growing, preferably young weeds.
- Do not apply herbicides when the soil moisture is low and weeds are drought-stressed; an actively growing, healthy, non-stressed weed is the easiest one to control.
- Apply herbicides on a calm, clear day when the air temperature is between 50 and 85F; applying when temperatures exceed 90° F increases the potential for volatilization injury to other plants in the landscape.
- Don't apply if rainfall will occur within 12 hours; avoid applying irrigation for at least 12 hours following a herbicide application.
- Don't mow the lawn for 2 days before and after the herbicide application.
- Do not apply to new turfgrass seedlings until the grass has been mowed at least three times.
- Delay applying a broadleaf herbicide to new sod for 4 to 5 weeks after planting.

### Summer Broadleaf Weed Management

Summer annual broadleaf weeds (e.g., spurge, knotweed, purslane, etc.) are very difficult to control for a number of reasons. Depending on the species, these weeds germinate at different times during the summer and mature in a very short period of time. Thus, a single application of herbicide might only control a single weed species because other species have not germinated or have grown

too large to be controlled. Summer annual weeds often have a thick, waxy cuticle layer on their leaf surface to prevent water loss; this layer may also make it more difficult to get herbicide into the weed.

Some annual broadleaf weeds can be effectively controlled by preemergence herbicides. For example, summer annuals like spurge, knotweed, purslane and puncturevine can be controlled with products containing prodiamine, pendimethalin or isoxaben.

### **Difficult-to-Control Weeds**

Weeds such as bindweed, thistles, and wild violets are difficult to control because they spread by underground stems. Multiple herbicide applications may be necessary to completely control difficult perennial weeds, including dandelions. Post-emergence broadleaf herbicides containing 2,4-D, MCPP, dicamba, triclopyr or sulfentrazone should be used.

---

Author: **Tony Koski**, Ph.D., Extension Turf Specialist, Department of Horticulture & LA, Colorado State University Extension.

- For additional information on lawn care, refer to [csuturf.colostate.edu](http://csuturf.colostate.edu).
- Colorado Master Gardener *GardenNotes* are available on-line at [www.cmg.colostate.edu](http://www.cmg.colostate.edu).
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December 2010







*p-Dioxane (1,4-Dioxane)*



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**SELECTED COMMERCIAL FORMULATIONS OF  
GLYPHOSATE -  
*ACCORD, RODEO, ROUNDUP* and *ROUNDUP PRO*  
Risk Assessment  
Final Report**

Prepared for:

**USDA, Forest Service**

**Leslie Rubin, COTR  
Animal and Plant Health Inspection Service (APHIS)  
Biotechnology, Biologics and Environmental Protection  
Environmental Analysis and Documentation  
United States Department of Agriculture  
Suite 5B05  
4700 River Road  
Riverdale, MD 20737**

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Submitted by:

**Syracuse Environmental Research Associates, Inc.  
5100 Highbridge St., 42C  
Fayetteville, New York 13066-0950**

**Telephone: (315) 637-9560**

**Fax: (315) 637-0445**

**[Internet:SERA\\_INC@msn.com](mailto:SERA_INC@msn.com)**

and

**Syracuse Research Corporation  
Merrill Lane  
Syracuse, New York 13210**

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## ACRONYMS, ABBREVIATIONS, AND SYMBOLS

<b>a.e.</b>	<b>acid equivalents</b>
<b>a.i.</b>	<b>active ingredient</b>
<b>AEL</b>	<b>adverse-effect level</b>
<b>ACGIH</b>	<b>American Conference of Governmental Industrial Hygienists</b>
<b>AChE</b>	<b>acetylcholinesterase</b>
<b>AMPA</b>	<b>aminomethylphosphonate</b>
<b>ATSDR</b>	<b>Agency for Toxic Substances and Disease Registry</b>
<b>BCF</b>	<b>bioconcentration factor</b>
<b>bw</b>	<b>body weight</b>
<b>ChE</b>	<b>cholinesterase</b>
<b>cm</b>	<b>centimeter</b>
<b>2,4-D</b>	<b>dichlorophenoxyacetic acid</b>
<b>EC<sub>50</sub></b>	<b>concentration causing 50% inhibition of a process</b>
<b>EC<sub>100</sub></b>	<b>concentration causing complete inhibition of a process</b>
<b>F</b>	<b>female</b>
<b>F<sub>1</sub></b>	<b>first filial generation</b>
<b>FS</b>	<b>Forest Service</b>
<b>g</b>	<b>gram</b>
<b>GC</b>	<b>gas chromatography</b>
<b>HQ</b>	<b>hazard quotient</b>
<b>IARC</b>	<b>International Agency for Research on Cancer</b>
<b>kg</b>	<b>kilogram</b>
<b>K<sub>ok</sub></b>	<b>organic carbon partition coefficient</b>
<b>K<sub>ow</sub></b>	<b>octanol-water partition coefficient</b>
<b>K<sub>p</sub></b>	<b>skin permeability coefficient</b>
<b>L</b>	<b>liter</b>
<b>lb</b>	<b>pound</b>
<b>LC<sub>50</sub></b>	<b>lethal concentration, 50% mortality</b>
<b>LD<sub>50</sub></b>	<b>lethal dose, 50% mortality</b>
<b>LD<sub>95</sub></b>	<b>lethal dose, 95% mortality</b>
<b>LOAEL</b>	<b>lowest-observed-adverse-effect level</b>
<b>m</b>	<b>meter</b>
<b>M</b>	<b>male</b>
<b>MCS</b>	<b>multiple chemical sensitivity</b>
<b>mg</b>	<b>milligram</b>
<b>mg/kg/day</b>	<b>milligrams of agent per kilogram of body weight per day</b>
<b>mL</b>	<b>milliliter</b>
<b>MS</b>	<b>mass spectrometry</b>
<b>MW</b>	<b>molecular weight</b>
<b>MOS</b>	<b>margin of safety</b>
<b>NCI</b>	<b>National Cancer Institute</b>
<b>NNG</b>	<b>N-nitrosoglyphosate</b>
<b>NOAEL</b>	<b>no-observed-adverse-effect level</b>
<b>NOEL</b>	<b>no-observed-effect level</b>

**ACRONYMS, ABBREVIATIONS, AND SYMBOLS (continued)**

NRC	National Research Council
OPP	Office of Pesticide Programs
pKa	dissociation constant
POEA	polyoxyethyleneamine
ppm	parts per million
RBC	red blood cells
RfD	reference dose
RTU	ready to use
OF	uncertainty factor
U.S.	United States
U.S. EPA	U.S. Environmental Protection Agency
USDA	United States Department of Agriculture
	greater than
	greater than or equal to
	less than
	less than or equal to
	equal to
	approximately equal to

## COMMON UNIT CONVERSIONS AND ABBREVIATIONS

<u>To convert ...</u>	<u>Into ...</u>	<u>Multiply by ...</u>
acres	hectares (ha)	0.4047
acres	square meters (m <sup>2</sup> )	4,047
atmospheres	millimeters of mercury	760
centigrade	Fahrenheit	1.8C°+32
centimeters	inches	0.3937
cubic meters (m <sup>3</sup> )	liters (L)	1,000
Fahrenheit	centigrade	0.556F°-17.8
feet per second (ft/sec)	miles/hour (mi/hr)	0.6818
gallons (gal)	liters (L)	3.785
gallons per acre (gal/acre)	liters per hectare (L/ha)	9.34
grams (g)	ounces, (oz)	0.03527
grams (g)	pounds, (oz)	0.002205
hectares (ha) [10,000 m <sup>3</sup> ]	acres	2.471
inches (in)	centimeters (cm)	2.540
kilograms (kg)	ounces, (oz)	35.274
kilograms (kg)	pounds, (lb)	2.2046
kilograms per hectare (kg/ha)	pounds per acre (lb/acre)	0.892
kilometers (km)	miles (mi)	0.6214
liters (L)	cubic centimeters (cm <sup>3</sup> )	1,000
liters (L)	gallons (gal)	0.2642
liters (L)	ounces, fluid (oz)	33.814
miles (mi)	kilometers (kin)	1.609
miles per hour (mi/hr)	cm/sec	44.70
milligrams (mg)	ounces (oz)	0.000035
meters (m)	feet	3.281
meters/sec	miles/hour	2.237
ounces (oz)	grams (g)	28.3495
ounces per acre (oz/acre)	grams per hectare (g/ha)	70.1
ounces per acre (oz/acre)	kilograms per hectare (kg/ha)	0.0701
ounces fluid	cubic centimeters (cm <sup>3</sup> )	29.5735
pounds (lb)	grams (g)	453.6
pounds (lb)	kilograms (kg)	0.4536
pounds per acre (lb/acre)	kilograms per hectare (kg/ha)	1.121
pounds per gallon (lb/gal)	grams per liter (g/L)	119.8
square centimeters (cm <sup>2</sup> )	square inches (in <sup>2</sup> )	0.155
square centimeters (cm <sup>2</sup> )	square meters (m <sup>2</sup> )	0.0001
square meters (m <sup>2</sup> )	square centimeters (cm <sup>2</sup> )	10,000
yards	meters	0.9144

Note: All references to pounds and ounces refer to avoirdupois weights unless otherwise specified.

## CONVERSION OF SCIENTIFIC NOTATION

Scientific Notation	Decimal Equivalent	Verbal Expression
$1 \cdot 10^{-10}$	0.0000000001	One in ten billion
$1 \cdot 10^9$	0.000000001	One in one billion
$1 \cdot 10^8$	0.00000001	One in one hundred million
$1.10^7$	0.0000001	One in ten million
$1.10^6$	0.000001	One in one million
$1 \cdot 10^5$	0.00001	One in one hundred thousand
$1 \cdot 10^4$	0.0001	One in ten thousand
$1 \cdot 10^3$	0.001	<del>One in one thousand</del>
$1 \cdot 10^2$	0.01	One in one hundred
$1 \cdot 10^1$	0.1	One in ten
$1 \cdot 10^0$	1	One
$1.10^1$	10	Ten
$1.10^2$	100	One hundred
$1.10^3$	1,000	One thousand
$1.10^4$	10,000	Ten thousand
$1.10^5$	100,000	One hundred thousand
$1.10^6$	1,000,000	One million
$1 \cdot 10^7$	10,000,000	Ten million
$1.10^8$	100,000,000	One hundred million
$1.10^9$	1,000,000,000	One billion
$1 \cdot 10^{10}$	10,000,000,000	Ten billion

## EXECUTIVE SUMMARY

### BACKGROUND

Three commercial formulations of the isopropylamine salt of glyphosate are used by the USDA in vegetation management programs: Accord, Rodeo, and Roundup. This document provides risk assessments for human and health and ecological effects to support the assessment of the environmental consequences of using these products in future Forest Service programs.

Glyphosate is a broad-spectrum, non-selective, post-emergence herbicide. The compound is readily soluble in water and strongly sorbed to most types of soils. The three commercial formulations of glyphosate covered by this risk assessment—Accord, Rodeo, and Roundup—all contain the isopropylamine salt of glyphosate. Two of the formulations, Accord and Rodeo, are simply aqueous solutions of the isopropylamine salt of glyphosate and contain no inert ingredients other than water. Roundup is formulated as an aqueous solution of the isopropylamine salt of glyphosate with a polyethoxylated tallow amine surfactant. Technical grade glyphosate also contains an impurity, N-nitrosoglyphosate.

Although aerial applications may be used in some instances, backpack (selective) foliar, hack and squirt, and boom spray or roadside hydraulic spraying are the most common methods for applying glyphosate in Forest Service programs. The typical application rate used by the Forest Service is 1 lb a.i./acre, and few applications will exceed 2.5 lbs a.i./acre. The maximum allowable application rate is 7.5 lbs a.i./acre. In some instances, areas treated with glyphosate may be subject to brown-and-burn operations. In previous Forest Service vegetation management programs, glyphosate has been applied in relatively small amounts, compared with the application of other herbicides.

### HUMAN HEALTH RISK ASSESSMENT

The toxicity of glyphosate is relatively well characterized in humans and experimental mammals, although the mechanism of action is not clear. The acute toxicity of glyphosate is relatively low, with oral LD<sub>50</sub> values ranging from approximately 1,000 to 4,000 mg/kg. Most of the data regarding human exposure to glyphosate involves the consumption of large quantities of glyphosate during attempted suicides. The signs of toxicity are generally consistent with massive mucosal irritation and tissue degeneration. In addition, glyphosate may interfere with normal metabolic biochemical functions.

Glyphosate contains small amounts of a nitrosamine, N-nitrosoglyphosate (NNG), and is metabolized, to a small extent, to aminomethylphosphonate (AMPA). The potential effects of these compounds are encompassed by the available toxicity data on glyphosate and glyphosate formulations.

One formulation of glyphosate, Roundup, contains a surfactant, polyoxyethyleneamine (POEA). There is some uncertainty in the interpretation of the toxicity data on Roundup concerning the potential significance of POEA. For the assessment of toxic effects, this uncertainty is relatively

minor in that the available toxicity data on Roundup are adequate for the identification of toxic thresholds.

POEA contains a contaminant, 1,4-dioxane, that has been classified by U.S. EPA as a probable human carcinogen. The potential hazard associated with this effect must be addressed explicitly in the hazard characterization. The chronic toxicity of glyphosate has been well characterized in laboratory mammals. According to U.S. EPA's classification of carcinogens and assessment of the available data, glyphosate is not carcinogenic to humans. Thresholds for other toxic effects are relatively well defined. There is no evidence that glyphosate causes birth defects, and thresholds for potential reproductive effects have been defined. Glyphosate is a skin and eye irritant. This effect must be considered in the handling of commercial formulations. In addition, the toxicology of the combustion products of glyphosate has not been well characterized and this adds uncertainty to the risk assessment for brown-and-burn operations.

Two general exposure assessments are presented in section 3.2.2, job-specific assessments and incident assessments. Job-specific assessments estimate absorption associated with relatively complex job activities, such as mixing, loading, or applying glyphosate, in which multiple routes of exposure are likely. All of these assessments are given as a range based on the projected application rates, empirical observations of variability in exposure rates, and projected variations in herbicide usage [i.e., number of acres treated/hour].

Incident assessments are relatively easy to make. They estimate absorption from spilling glyphosate onto the skin or wearing contaminated clothing. All of these scenarios are extreme or accidental in nature, as discussed in sections 3.2.2 and 3.2.3.

Workers, compared with the general public, are exposed to greater levels of glyphosate and the other components in glyphosate. Exposure to glyphosate is greater for ground workers than for workers involved in aerial applications, in terms of exposure per amount of material handled; however, gross exposure to glyphosate is greater for workers involved in aerial applications because of the large quantity of material that they may handle. The average exposure rate for aerial workers is 0.014 mg/kg body weight with a range of 0.0016-0.16 mg/kg body weight. Boom spray workers may have comparable levels of exposure [0.013 (0.0016-0.11) mg/kg], and other ground workers are exposed to much less [0.006 (0.0005-0.072) mg/kg]. Members of the general public are usually exposed only to extremely low levels of glyphosate [0.00012-0.007 mg/kg], except for accidental exposures scenarios, when exposure levels may approach levels for occupational exposure [0.007-0.019 mg/kg].

The current RfD for glyphosate is 0.1 mg/kg/day (U.S. EPA 1993a), which is based on a NOAEL of 10 mg/kg/day with an uncertainty factor of 100 used to account for species-to-species extrapolation and sensitive subgroups. The RfD was reviewed by U.S. EPA on 9/1/90 and is not undergoing additional review. The Office of Pesticides of the U.S. EPA has recommended a higher RfD of 2 mg/kg/day for glyphosate (U.S. EPA 1993b). The proposed RfD has not been reviewed by the U.S. EPA RfD Work Group.

Quantitative considerations regarding the dose-response data from an epidemiology study and the dose-severity relationships in experimental mammals suggest that each of the RfDs is protective. The estimated threshold for lethality is 445 mg/kg, and the probability of observing a frank toxic effect at this dose level is about 0.04. The estimated LD<sub>50</sub> for humans, based on the Taiwan poisoning experience, is approximately 3,000 mg/kg, which falls in the middle range of reported LD<sub>50</sub> values for experimental mammals.

The major hazard associated with the use of glyphosate will involve accidental or incidental dermal or ocular contact. Glyphosate is an irritant to the skin and eyes. If dermal or ocular contact with undiluted or weakly diluted formulations occurs, irritation is likely to develop and will require corrective action to ameliorate the irritant effects. These irritant effects, if properly handled, will be transient.

Based on the exposure assessments discussed in section 3.2 and the dose-response assessments discussed in section 3.3, the quantitative risk assessments for workers and the general public are summarized in Tables 3-2, 3-3, and 3-4. In these tables, risk is characterized as the hazard quotient, the ratio of the anticipated level of the exposure to some index of acceptable exposure or exposure associated with a defined risk. Thus, if the hazard quotient is less than unity, concern for the exposure is minimal. As the hazard quotient increases above unity, concern also increases.

There is no substantial concern for systemic toxic effects in workers or the general public at the typical application rate of 1 lb a.i./acre or the upper range of the application rate used by the Forest Service, 2.5 lbs a.i./acre. At the maximum labelled rate of 7.5 lbs a.i./acre, there may be marginal concern for effects in some groups of workers (i.e., hazard quotients of approximately 0.6) at the upper limit of conservative exposure assumptions.

Consistent with previous assessments conducted by the Forest Service, the carcinogenic risk associated with exposure to 1,4-dioxane appears to be less than 1 in 10 million.

Given the rapid elimination of glyphosate—in the environment and from the body of mammals—as well as the very weak duration-severity relationships observed in animal studies, cumulative effects do not seem plausible. Similarly, there is no basis for identifying specific groups as being at a substantially increased risk.

#### **ECOLOGICAL RISK ASSESSMENT**

Standard toxicity bioassays have been conducted on several wildlife species, including mammals, birds, fish, and some terrestrial and aquatic invertebrates, as well as many species of aquatic and terrestrial plants. Furthermore, there are several available field studies that examine the effects of glyphosate applications comparable to those used by the Forest Service.

The toxicity studies on terrestrial animals are generally consistent with those on experimental mammals. Although the mechanism of glyphosate toxicity is unclear, glyphosate can cause toxic effects including mortality at sufficiently high dose levels. The available field studies, however, clearly

suggest that at plausible levels of ambient exposure, direct toxic effects are unlikely. The effects on terrestrial animals appear to be secondary to changes in habitat resulting from toxic effects on vegetation.

The herbicidal activity of glyphosate has been studied extensively. Glyphosate interferes with normal metabolic processes in plants, and, at sufficiently high levels of exposure, may cause cell death, tissue damage, growth inhibition, and death of the plant. The biochemical pathway that is affected is specific to plant species and does not occur in animals.

The toxicity of glyphosate to aquatic species depends on the acidity (pH) of the water. Glyphosate is more toxic in relatively highly acidic water (pH-6) by up to a factor of about 10, compared with alkaline water (pH-10). Generally, the reported LC<sub>50</sub> values for aquatic animals range from approximately 10 to 400 mg/L, depending on the species and pH of the water.

A major qualitative difference between the effect of glyphosate and glyphosate formulations on aquatic and terrestrial organisms concerns the surfactant, POEA, used in Roundup. The surfactant is much more toxic than glyphosate to aquatic organisms. Unlike glyphosate, POEA is more toxic in alkaline water than in acidic water. Thus, the relative potency of POEA with respect to glyphosate is pH dependent.

As with the human health risk assessment, there is little indication that glyphosate will cause adverse effects in the environment at anticipated levels of exposure. The small mammal is a conservative target species for characterizing risk because small organisms, in general, will receive higher doses of an agent, compared with larger organisms, at fixed levels of exposure in environmental media (e.g., contaminated food, water, or air). Moreover, the available toxicity data do not suggest any systematic differences in sensitivity to glyphosate among species. The primary route of exposure for terrestrial animals appears to be contaminated vegetation. For this source, levels of contamination remain below those of concern even at the maximum allowable application rate, 7.5 lbs a.i./acre. At application rates anticipated by the Forest Service, levels of exposure are substantially below those of concern. This analysis is consistent with the field studies on glyphosate, which indicate that direct toxic effects are unlikely.

Glyphosate is an effective herbicide, and terrestrial plants will be affected by applications of glyphosate used to control vegetation. Non-target plants could be damaged by unintentional application or drift. The extent of drift will depend on the specific conditions under which the glyphosate is applied. As would be expected, the potential hazards of drift are greater for aerial applications, compared with ground applications. The extent of damage will depend on the plant species and time of application. Field studies involving both ground and aerial applications of glyphosate suggest that the effects of drift are likely to be most evident within 50 m of the application site.

There is not much evidence that aquatic animals or plants will be affected adversely by normal applications of glyphosate. Although glyphosate is registered for use as an aquatic herbicide, it is



**only effective on aquatic plants with vegetation growing above the water level. Most species of algae and macrophytes do not appear to be more sensitive than fish or aquatic invertebrates to glyphosate. For most aquatic species, glyphosate levels of 1 mg/L are not likely to cause adverse effects. For aquatic animals, Roundup (glyphosate+POEA) is not likely to cause adverse effects at levels of 0.1 mg/L, measured as glyphosate. Furthermore, there is no evidence that Roundup is more toxic than glyphosate to aquatic plants. Some sensitive species of algae could be affected; however, the effects are likely to be transient, given the rapid dispersion and removal of glyphosate from ambient water.**

## 1. INTRODUCTION

The three commercial formulations of the isopropylamine salt of glyphosate used by the Forest Service (FS) in vegetation management programs are Accord, Rodeo, and Roundup. In 1989, the Southern Region of the Forest Service prepared a series of environmental impact statements accompanied by risk assessments covering the use of these products (USDA 1989a,b,c). The present document provides updated risk assessments for both human and health and ecological effects to support a reassessment of the environmental consequences of using these products in future Forest Service programs. An additional formulation, Roundup Pro, is being considered for use and is also included in this risk assessment.

This document has four chapters: the introduction, program description, risk assessment for human health effects, and risk assessment for ecological effects or effects on wildlife species. Each of the two risk assessment chapters has four major sections: an identification of the hazards associated with the commercial formulations of glyphosate, an assessment of potential exposure to these products, an assessment of the dose-response relationships, and a characterization of the risks associated with exposure. The sections follow the basic steps recommended by the National Research Council of the National Academy of Sciences (NRC 1983) for conducting and organizing risk assessments.

Although this is a technical support document and addresses some highly specialized technical areas, every effort has been made to ensure that the document can be understood by individuals who do not have specialized training in the chemical and biological sciences. Certain technical concepts and terms common to all parts of the risk assessment are described in as plain a language as possible in a separate document: *The Preparation of Environmental Documentation and Risk Assessments for the Forest Service* (SERA 1995a). In addition, these terms are defined in the glossary that accompanies this risk assessment. Some of the specialized terms and concepts are defined, as necessary, in the text.

This document focuses on a concise characterization of human and ecological risks associated with plausible levels of exposure to the commercial products as a result of activities contemplated by the Forest Service. Thus, the risk assessments presented in this document are not, and are not intended to be, comprehensive summaries of all of the available information.

Much of the early literature is summarized in the previously prepared chemical background statement on glyphosate (Mitre Corporation 1989), previously prepared risk assessments and environmental impact statements on glyphosate (USDA 1989a,b,c), monographs by the World Health Organization (FAO and WHO 1986), as well as a series of comprehensive reviews in *The Herbicide Glyphosate* (Grossbard and Atkinson 1985). More recently, the U.S. EPA prepared a comprehensive summary and analysis of the confidential business information (CBI) used to support the re-registration of glyphosate (U.S. EPA 1994) as well as CBI and open literature information used to support the drinking water criteria for glyphosate (U.S. EPA 1992a). Recent

reviews of the potential human health and ecological effects of glyphosate have been published by Smith and Oehme (1992) as well as WHO (1994).

Because the existing reviews provide adequate summaries of most of the available information on glyphosate, and, in the interest of economy, an updated chemical background statement was not prepared with the current risk assessment. Most of the information that would be included in an update is available in the reviews cited above. Information relevant to this risk assessment, taken from earlier reviews as well as more recent publications, is summarized in the appendices to this document.

## 2. PROGRAM DESCRIPTION

### 2.1. OVERVIEW

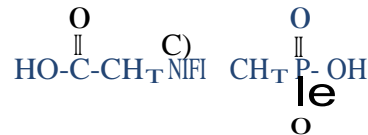
Glyphosate is a broad-spectrum, non-selective, post-emergence systemic herbicide. The compound is readily soluble in water and strongly sorbed to most types of soils. The three commercial formulations of glyphosate covered by this risk assessment—Accord, Rodeo, and Roundup—all contain the isopropylamine salt of glyphosate. Two of the formulations, Accord and Rodeo, are simply aqueous solutions of the isopropylamine salt of glyphosate and contain no inert ingredients other than water. Roundup is formulated as an aqueous solution of the isopropylamine salt of glyphosate with a polyethoxylated tallow amine surfactant. Technical grade glyphosate also contains an impurity, N-nitrosoglyphosate.

Although aerial applications may be used in some instances, backpack (selective) foliar, hack and squirt, and boom spray or roadside hydraulic spraying are the most common methods for applying glyphosate in Forest Service programs. The typical application rate used by the Forest Service is 1 lb a.i./acre and few applications will exceed 2.5 lbs a.i./acre. The maximum allowable application rate is 7.5 lbs a.i./acre. In some instances, areas treated with glyphosate may be subject to brown-and-burn operations. In previous Forest Service vegetation management programs, glyphosate has been applied in relatively small amounts, compared with the application of other herbicides.

### 2.2. GLYPHOSATE AND COMMERCIAL FORMULATIONS

Glyphosate is a broad-spectrum, non-selective, post-emergence systemic herbicide developed by Monsanto (Franz 1985). The herbicidal properties of glyphosate were first described by Baird et al. (1971). The chemical and toxicological properties of glyphosate are well studied. As of 1985, there were more than 7,000 publications on glyphosate in the literature (Franz 1985). Since 1985, more than 3,000 additional papers on glyphosate have been published.

Glyphosate is the common name for N-(phosphonomethyl)glycine:



**Table 2-1. Physical, chemical, and biochemical properties of glyphosate**

<b>CAS Number:</b>	<b>1071-83-6</b>
<b>Molecular weight:</b>	<b>169.07</b>
<b>Melting point (°C):</b>	<b>200 (Tomlin 1994)</b>
<b>Density (g/cm<sup>3</sup>):</b>	<b>0.5 (bulk density) (Tomlin 1994)</b>
<b>Density (g/ml):</b>	<b>1.74 (WSSA 1989)</b>
<b>Vapor pressure (mm Hg):</b>	<b>1.94 x 10<sup>-7</sup> mmHg (45° C) (WSSA 1989)</b> <b>&lt; 7 x 10<sup>-9</sup> mm Hg (25° C) (Weber 1991)</b> <b>2.89 x 10<sup>-7</sup> mm Hg (25° C) (SRC 1995)</b> <b>negligible (Tomlin 1994)</b> <b>practically zero (Hartley and Kidd 1985)</b>
<b>Water solubility:</b>	<b>12 g/L (25°C) (Tomlin 1994)</b> <b>1.57% (25°C) (WSSA 1989)</b>
<b>Henry's law constant:</b>	<b>insignificant (Reinert and Rodgers 1987)</b> <b>5.36 x 10<sup>-11</sup> atm-m<sup>3</sup>/mole (25°C)</b> <b>(calculated from vapor pressure and water solubility)</b>
<b>Log K<sub>ow</sub>:</b>	<b>-0.70 (pH 1) (Chamberlain et al. 1994)</b> <b>-1.15 (pH 3) (Chamberlain et al. 1994)</b> <b>-1.30 (pH 5) (Chamberlain et al. 1994)</b> <b>-2.90 (pH 7) (Chamberlain et al. 1994)</b> <b>-3.05 (pH 7.5) (Chamberlain et al. 1994)</b> <b>-1.90 (pH 9) (Chamberlain et al. 1994)</b> <b>-0.80 (pH 11) (Chamberlain et al. 1994)</b>
<b>Soil adsorption K<sub>d</sub>:</b>	<b>10,000-100,000 (Weber 1991)</b> <b>554-34,000 (Piccolo et al; 1994)</b> <b>2,600-4,900 (Glass 1987)</b>
<b>Evaporation rate:</b>	<b>low (Neary et al. 1993)</b>
<b>Foliar half-life (days):</b>	<b>-1.6 (Thompson et al. 1994)</b> <b>8-10 (Feng and Thompson 1990)</b> <b>10.6-26.6 (Newton et al. 1984)</b>
<b>Soil half-life (days):</b>	<b>20-40 (Weber 1991)</b> <b>&lt;60 (average) (WSSA 1989)</b> <b>45-60 (Feng and Thompson 1990)</b> <b>29-40 (Newton et al. 1984)</b>
<b>Water half-life (days):</b>	<b>50-70 (U.S. EPA 1992a)</b> <b>14 (minimum rate) (Reinert and Rodgers 1987)</b> <b>42-70 (Reinert and Rodgers 1987)</b> <b>3.5-11.2 days [surface water; some glyphosate in the water column was transferred to sediment and not degraded] (Goldsborough and Brown 1993)</b>
<b>Air half-life (days):</b>	<b>5 [estimated; method of Meylan and Howard (1993)]</b>

Some basic chemical and physical properties of glyphosate are summarized in Table 2-1. At ambient temperatures, glyphosate is a white crystal. In the crystalline form, glyphosate has both positive and negative regions of charge, indicated by the circled plus (+) and minus (-) signs in the schematic above. Such dipolar ion species are sometimes referred to as a *zwitterions*. In aqueous solutions, the hydrogen atoms of the carboxylic acid (COOH) and phosphate (P<sub>0</sub><sub>2</sub>H<sub>2</sub>) groups may be associated (e.g., -COOH) or dissociated (e.g., -COO<sup>-</sup> + W) depending on the pH of the solution. The dissociation constants, or pK values, for these reactions are illustrated in Figure 2-1. The pH of most biological fluids range from approximately 5 to 9. Thus, within this range of pH, glyphosate has a net negative charge and is predominantly in form of H<sub>2</sub>G<sup>-1</sup> or HG<sup>-2</sup>, as illustrated in Figure 2-1.

Because glyphosate has a relatively low solubility in water, about 12 g/L (see Table 2-1), the compound is usually formulated as a more soluble salt. As summarized in Table 2-2, the three commercial formulations of glyphosate covered by this risk assessment—Accord, Rodeo, and Roundup—all contain the isopropylamine salt of glyphosate. Table 2-2 gives the concentrations both as the isopropylamine salt of glyphosate (a.i.) as well as the acid equivalents of glyphosate (a.e.). Application rates are commonly expressed in units of active ingredient (a.i.), while monitoring studies and some toxicity studies are expressed in units of acid equivalents (a.e.). Unless otherwise specified, units of concentration or application rate are expressed as active ingredient and dose units are expressed as acid equivalents.

Technical grade glyphosate also contains an impurity, N-nitrosoglyphosate, which is sometimes abbreviated as NNG. The U.S. EPA has determined that 92% of technical grade glyphosate contains NNG at less than one part per million (<1 mg/L) and that this amount is toxicologically insignificant. Similarly, the surfactant used in Roundup contains 1,4-dioxane as an impurity. The upper limit of this compound in Roundup is about 0.03% (Monsanto 1990). In a previous review, the U.S. Forest Service determined that the amount of exposure to 1,4-dioxane is toxicologically insignificant (Borrecco and Neisess 1991). Both of these assessments are discussed further in the hazard identification (section 3.1).

Two of the formulations, Accord and Rodeo, are simply aqueous solutions of the isopropylamine salt of glyphosate and contain no inert ingredients other than water. Roundup is an aqueous solution of the isopropylamine salt of glyphosate with a polyethoxylated tallow amine surfactant. This material is referred to in the literature as MON 0139, with the MON presumably referring to Monsanto, or polyoxyethyleneamine (POEA) (Smith and Oehme 1992). The surfactant in Roundup is present at 15% (Hoogheem 1987; Sawada et al. 1988) or 150 g/L assuming that the 15% value refers to the level in terms of weight per unit volume. Presumably, the Roundup surfactant is a derivative of tallow, a complex mixture of fat from the fatty tissue of cattle or sheep. Tallow contains a variety of fatty acids including oleic (37-43%), palmitic (24-32%), stearic (20-25%), myristic (3-6%), and linoleic (2-3%) acids as well as small amounts of cholesterol, arachidonic, elaidic, and vaccenic acids (Budavari 1989). As discussed in the hazard identification for human health (section 3.1) and ecological effects (section 4.1), the presence of the surfactant must be considered in the risk assessments of Roundup. Roundup Pro is a recently



introduced formulation of glyphosate that contains a phosphate ester neutralized polyethoxylated tallowamine surfactant at a level of 14.5% (Monsanto 1995 a,b; Monsanto 1996) or 145 g/L. Other than the specification that the tallow amine surfactant in Roundup Pro is a phosphate ester of POEA, no published information is available on the chemical differences between the surfactant in Roundup and Roundup Pro. As detailed in Sections 3 and 4, there is relatively little information available on the toxicity of Roundup Pro.

**Table 2-2. Summary of commercial formulations containing glyphosate covered by this risk assessment<sup>1</sup>**

Formulation	Ingredient	Pounds (a.i.)/gallon	Pounds (a.e.)/gallon	Grams (a.e.)/L
Accord (Monsanto)	glyphosate, isopropylamine salt (41.5%)	4	3	356
	inerts (58.5%) water			
Rodeo (Monsanto) (53.8%)	glyphosate, isopropylamine salt	5.4	4	480
	inerts (46.2%) water			
Roundup (Monsanto) (41%)	glyphosate, isopropylamine salt	4	3	356
	inerts (59%)			
	ethoxylated tallow amines (CAS No. 61791-26-2), 15% <sup>b</sup> , and water			
Roundup Pro (Monsanto) (41%)	glyphosate, isopropylamine salt	4	3	356
	inerts (59%)			
	phosphate ester neutralized ethoxylated tallow amines, 14.5% <sup>c</sup> , and water			

<sup>1</sup>Taken from Monsanto (1993, 1994a,b, 1995a) (unless otherwise specified).

<sup>b</sup>Hoogheem (1987) (Letter Feb 27 to Larry Gross).

<sup>c</sup>Monsanto 1995b.

a.e. = acid equivalents; a.i. = active ingredient



### 2.3. APPLICATION METHODS

Proposed application methods and vegetation management uses for glyphosate are summarized in Table 2-3. Detailed descriptions of the silvicultural uses of herbicides and the various methods of herbicide applications are available in the general literature (e.g., Cantrell and Hyland 1985) and earlier environmental impact statements conducted by the Forest Service (USDA 1989a,b,c). The following summary focuses on those aspects of application that are most germane to the exposure assessments (sections 3.2 and 4.2).

**Table 2-3. Proposed uses and application methods for glyphosate**

Use	Application Method			
	Broadcast		Selective	
	Aerial	Boom Spray	Backpack (Selective Foliar)	Cut Surface (Hack and Squirt)
Conifer release	<b>O</b>			
General weeds			<b>M</b>	
Noxious weeds			<b>M</b>	
Rights-of-way	<b>F</b>	<b>F</b>		
Site preparation	<b>F</b>		<b>M</b>	<b>F</b>
Vegetation			<b>M</b>	<b>F</b>
Wildlife habitat improvement		<b>M</b>	<b>M</b>	

**M** = Planned Use    **F** = Potential use

**O** = Done commercially but not used by the Forest Service

The most commonly used application method is the backpack (selective) foliar application. In selective foliar applications, the herbicide sprayer or container is carried by backpack and the herbicide is applied to selected target vegetation. Application crews may treat up to shoulder high brush, and chemical contact with the arms, hands, or face is plausible. To reduce the likelihood of

significant exposure, application crews are directed not to walk through treated vegetation. Typically, a worker will treat approximately 0.5 acres/hour with a plausible range of 0.2-51.0 acres/hour.

Hack and squirt applications are a form of cut surface treatment in which the bark and cambium of a standing tree is cut with a hatchet and the herbicide is then applied to the cut using a squirt bottle. This treatment is used to eliminate large trees during site preparation, conifer release operations, or rights-of-way maintenance. As with selective foliar applications, a worker usually will treat approximately 0.5 acres/hour with a plausible range of 0.25-1.0 acres/hour.

Boom spray or roadside hydraulic broadcast spraying is used primarily in rights-of-way management. Spray equipment mounted on tractors or trucks is used to apply the herbicide on either side of the roadway. Boom spray may also be used for maintenance or rehabilitation of wildlife openings, with spray equipment mounted on or towed behind tractors. Usually, about 8 acres will be treated in a 45-minute period [approximately 11 acres/hour] with approximately 200 gallons of the herbicide mixture [270 gallons/hour]. Some special truck mounted spray systems may be used to treat up to 12 acres in a 35-minute period with approximately 300 gallons of herbicide mixture [about 21 acres/hour and 510 gallons/hour] (USDA 1989b, p 2-9 to 2-10).

Aerial applications may involve the use of fixed wing aircraft (Roundup and Rodeo) or helicopters (Accord, Rodeo, and Roundup). Liquid formulations of glyphosate are applied through specially designed spray nozzles and booms. The nozzles are designed to minimize turbulence and maintain a large droplet size, both of which contribute to a reduction in spray drift. Aerial applications may only be made under meteorological conditions that minimize the potential for spray drift. In aerial applications, approximately 40-100 acres may be treated per hour.

In some instances, areas treated with glyphosate may be subject to brown-and-burn operations. As indicated in USDA (1989b), these operations involve burning a treated area 45-180 days after treatment with the herbicide.

## **2.4. MIXING AND APPLICATION RATES**

Accord is labeled for use in forestry site preparation, utility rights-of-way maintenance, as well as conifer and hardwood release for application as a foliar spray to control or destroy most herbaceous and woody plants. For both ground and aerial applications for site preparation and rights-of-way management, the maximum labeled rate is 10 quarts/acre, which is equivalent to 7.5 lbs a.e./acre [2.5 gallons/acre • 3 lbs a.e./gallons]. The maximum amount that may be applied in a single season is 10.6 quarts/acre or approximately 8 lbs a.e./acre [10.6 quarts/acre • 0.25 gallons/quart • 3 lbs a.e./gallons]. For conifer or hardwood release, much lower application rates are used, generally 1-2 quarts/acre [0.75-1.5 lbs a.e./acre], although as many as 3 quarts/acre [2.25 lbs a.e./acre] may be used in Maine for difficult to control species. To be effective in any of these applications, Accord must be mixed with a nonionic surfactant with greater than 50% active

ingredient. The product label for Accord (Monsanto 1994a) indicates that a surfactant is required for some applications:

*In forest?), site preparation and utility rights-of-way management, this product requires use with a nonionic surfactant. Use a nonionic surfactant with greater than 50 percent active ingredient and labeled for use with herbicides. The use of this product without surfactant will result in reduced performance.*

As indicated in Table 2-2, Roundup and Roundup Pro contain the same amount of glyphosate as Accord, 3 lbs a.e./gallon. In addition, both Roundup and Roundup Pro contain a surfactant, ethoxylated tallow amine at a concentration of 15% (Roundup) or a phosphate ester neutralized polyethoxylated tallow amine (Roundup Pro). Also as with Accord, these products are applied to terrestrial vegetation for the control of undesirable plant species. Roundup, however, is registered for both crop and non-crop applications. Roundup Pro is labeled only for non-crop uses. Another Monsanto product, Roundup Ultra, appears to be identical to Roundup Pro but is labeled for agricultural uses (Matura 1996a,b). For both Roundup and Roundup Pro, the maximum labeled application rate is 5 quarts/acre or 3.75 lbs a.e./acre [1.25 gallons/acre • 3 lbs a.e./gallons]. Many weeds, however, are controlled at application rates of 1 quart/acre. As with Accord, the maximum amount of both Roundup formulations that may be applied in a single season is 10.6 quarts/acre or approximately 8 lbs a.e./acre [10.6 quarts/acre • 0.25 gallons/quart • 3 lbs a.e./gallons] (Monsanto 1994b, 1995a).

As also indicated in Table 2-2, Rodeo is essentially the same product as Accord except that glyphosate is present at a higher concentration, 4 lbs a.e./gallon in Rodeo and 3 lbs a.e./gallon in Accord. Rodeo is registered for the control of both terrestrial and aquatic plants. As with Accord, the label for Rodeo recommends the use of a nonionic surfactant. For both terrestrial and aquatic vegetation, the highest recommended application rate is 7.5 pints/acre or 3.75 lbs a.e./acre [3.75 quarts/acre • 0.25 gallons/quart • 4 lbs a.e./gallon] (Monsanto 1993). In terms of acid equivalents of glyphosate, this is the same as the maximum application rate of Roundup and 50% of the maximum application rate of Accord.

The Forest Service does not plan to use glyphosate at the highest labelled application rates. In 1995, the typical rate for glyphosate was about 1 lb a.i./acre. All but one application (2.8 lb a.i./acre) was less than 2.5 lb a.i./acre (USDA/FS 1995).

In previously conducted Forest Service vegetation management programs (USDA 1989a,b,c), glyphosate was applied in relatively small amounts, compared with the application of other herbicides. For example, in Forest Service Region 8 (comprised of Alabama, Arkansas, Florida, Georgia, Kentucky, Louisiana, Mississippi, North California, Oklahoma, South Carolina, Tennessee, Texas, Virginia, and part of West Virginia), there are approximately 12,000,000 acres

of National Forests and Grassland, of which up to 600,000 acres are treated with various herbicides each year. In the late 1980s, glyphosate was applied to 9,700 acres/year, 0.081% of the total area and 1.6% of the treated area (USDA 1989b, p.2-4). In recent years, Forest Service use of herbicides in Region 8 has been reduced to treatment of fewer than 100,000 acres/year. In 1995, only 3,704.2 acres were treated with glyphosate (USDA/FS 1995).