

**Granite City PM_{2.5} Exceptional Event
July 5th, 2008 Fireworks**

Technical Documentation of Regional Concurrence

Region 5 Air Monitoring and Analysis Section

INTRODUCTION

This document provides EPA Region 5's rationale for concurrence with the exceptional event flag on the 24-hr average PM_{2.5} concentration recorded on July 5th, 2008 at the Granite City Fire Station monitor (AQSID 17-119-1007) ambient air monitoring site operated by the Illinois Environmental Protection Agency (IEPA). According to 40 CFR 50.1(j), Exceptional event means an event that affects air quality, is not reasonably controllable or preventable, is an event caused by human activity that is unlikely to recur at a particular location or a natural event, and is determined by the Administrator in accordance with 40 CFR 50.14 to be an exceptional event.

40 CFR 50.14(b)(2) states that EPA shall exclude data from use in determinations of exceedances and National Ambient Air Quality Standard (NAAQS) violations where a State demonstrates to EPA's satisfaction that emissions from fireworks displays caused a specific air pollution concentration in excess of one or more national ambient air quality standards at a particular air quality monitoring location and otherwise satisfies the requirements of this section. Such data will be treated in the same manner as exceptional events under this rule, provided a State demonstrates that such use of fireworks is significantly integral to traditional national, ethnic, or other cultural events including, but not limited to July Fourth celebrations which satisfy the requirements of this section.

40 CFR 50.14(c)(3)(III) states that the demonstration to justify data exclusion shall provide evidence that: (A) the event satisfies the criteria set forth in 40 CFR 50.1(j); (B) there is a clear causal relationship between the measurement under consideration and the event that is claimed to have affected the air quality in the area; (C) the event is associated with a measured concentration in excess of normal historical fluctuations, including background; and, (D) there would have been no exceedance or violation but for the event.

As part of the demonstration, the state must provide documentation that public comment process was followed and the state must submit the public comments it received along with its demonstration to EPA. IEPA provided Region 5 with a copy of the exceptional event description and the public notice for comment. IEPA received two comments during the 30-day public comment period, and provided copies of these comments as well as IEPA's responses with the final demonstration to Region 5.

Region 5 has reviewed the exceptional event demonstration package submitted by IEPA's on June 12th, 2009. At the request of Region 5 on July 8th, IEPA had archived July 5th, 2008 PM_{2.5} Federal Reference Method (FRM) filters from the Granite City Fire Station monitoring site and the Granite City Gateway Medical Center monitoring site analyzed with x-ray fluorescence (XRF). At the request of Region 5 on July 14th, IEPA had four additional pairs of archived FRM filters from the two Granite City monitoring sites analyzed with XRF. The following documentation of Region 5's review follows the criteria set forth in the Exceptional Events Rule.

Meteorological data (wind speed / direction) is not collected at the Granite City Fire Station monitoring site, but the Blair Street site (Missouri, AQSID 29-510-0085), located approximately 4 miles Southwest of Granite City reported both hourly wind speed and direction data for July 5th. Hourly meteorological data from this site is generally consistent with the National Weather Service data collected at the St. Louis Airport, as reported in IEPA's demonstration. Through 6:00 am on July 5th, when the highest concentrations occurred from the various continuous PM_{2.5} monitors, the Blair Street monitoring site indicates that wind was from the West at less than 1 mile per hour, and between 273 and 288 degrees.

Comparison to Background Levels: The observed and flagged July 5th concentration is the highest 24-hr average PM_{2.5} concentration recorded at this site during calendar years 2006 through 2008. Through the first calendar quarter of 2009, IEPA has not reported any concentrations from the Granite City Fire Station monitor greater than 41.8 µg/m³. Historically, using all of the data collected at this site since it began operating in 1999, 41.8 µg/m³ is the 12th highest of 1134 observations, and only three (all in 2002) of these values occurred in June or July. This PM_{2.5} 24-hour NAAQS exceedance of 41.8 µg/m³ satisfies the criterium of being in excess of normal historical values.

Impact on Design Value: The Granite City Fire Station (17-119-1007) monitoring site has the highest three-year annual average 98th percentile (design value) for the St. Louis area for the 2006 to 2008 three-year period. During 2008, the Granite City monitoring site was required to operate every third day and reported 89 observations; therefore, the annual 98th percentile is the second highest 24-hour average concentration. The three highest 24-hour averages in 2008 are 41.8 µg/m³, 36.0 µg/m³, and 31.9 µg/m³. Since this event received concurrence by Region 5, the annual 98th percentile defaults to the next highest (third) 24-hour average concentration (31.9 µg/m³) and the three-year (2006 to 2008) design value is 34.7 µg/m³. All other monitors in the St. Louis area attain with 2006 to 2008 data.

2006 Annual 98th percentile: 36.3 µg/m³

2007 Annual 98th percentile: 36.0 µg/m³

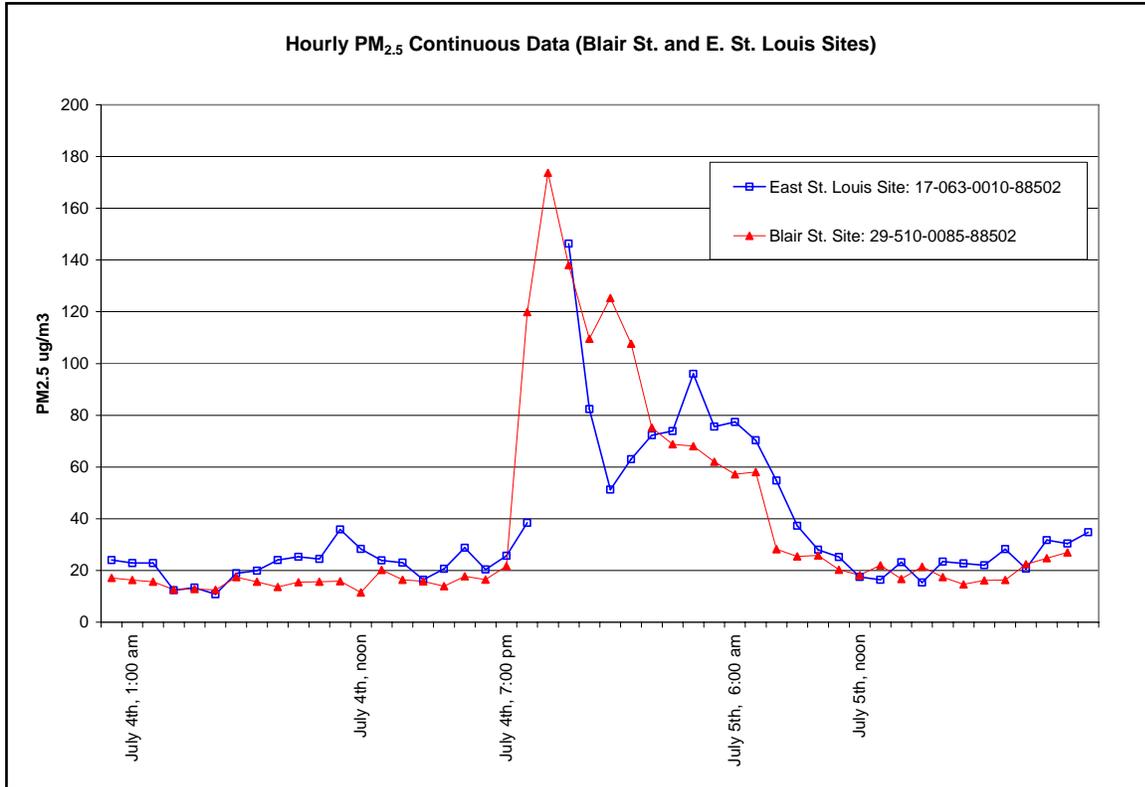
2008 Annual 98th percentile: 31.9 µg/m³

Design Value: 34.7 µg/m³ with Regional concurrence on the July 5th exceptional event

Causal Relationship:

For short-term events, hourly PM_{2.5} data from non-regulatory continuous instruments assist in determining the diurnal profile of concentrations that contribute to the 24-hr average gravimetric concentration reported by the FRM. Although many monitoring sites have continuous PM_{2.5} monitors, the Granite City Fire Station site does not. Nearby sites (Blair Street site approximately 4 miles to the southwest in Missouri and the East St. Louis site approximately 4 miles south in Illinois) reported continuous PM_{2.5} data. The following graph shows data from these two sites.

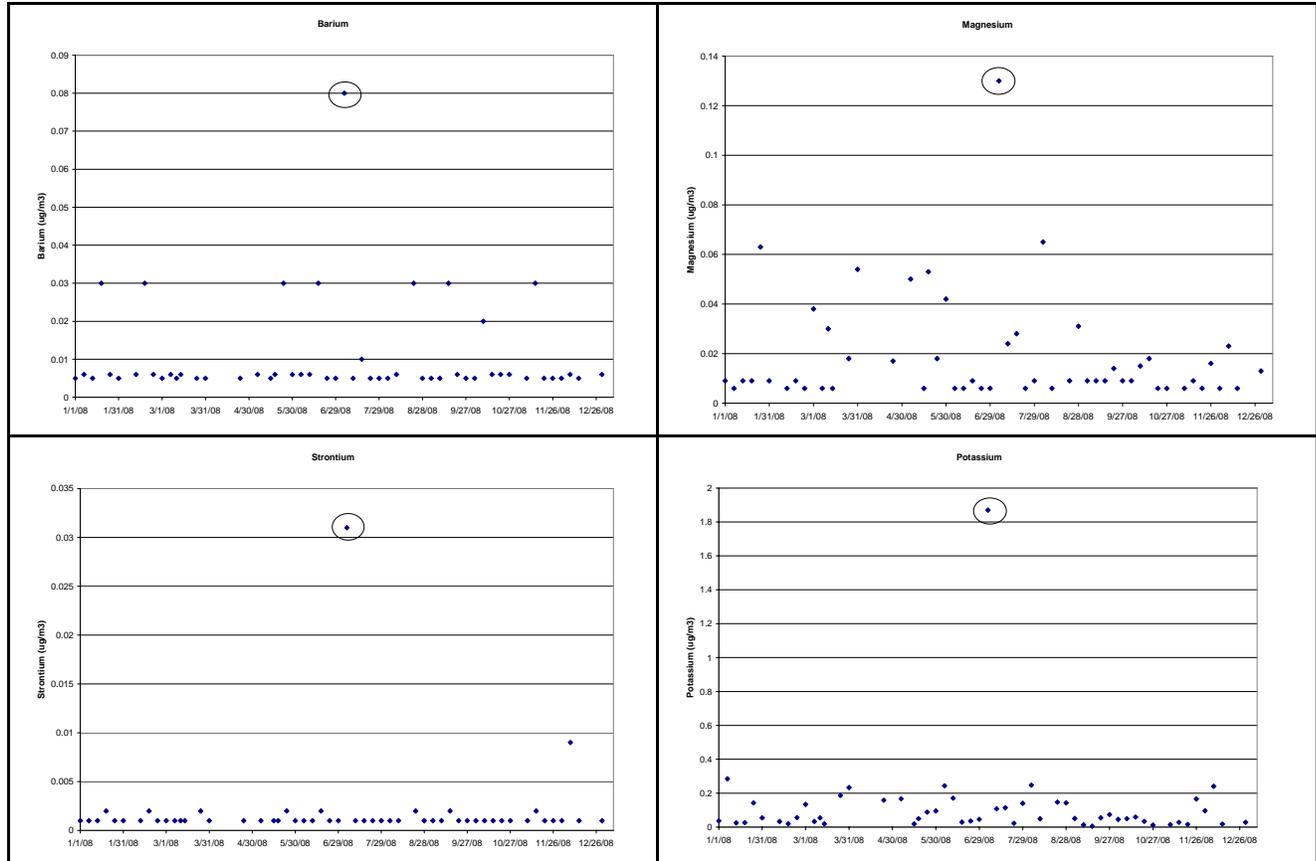
July 5th, 2008 Exceptional Event for Granite City, IL (St. Louis)



The diurnal concentration pattern depicted above is typical for a fireworks event with calm weather conditions. Concentrations spike between dusk and midnight when the fireworks emissions are occurring, then concentrations decrease throughout the night until the sun rises and vertical mixing of the air begins. Data from both stations have similar profiles, which indicate widespread impact from St. Louis area firework displays. Hourly PM₁₀ data collected at the Granite City Fire Station site, depicted on page 6 of IEPA's demonstration also follows this diurnal pattern.

Better evidence of the causal connection between the event and the observed exceedance can be obtained by assessing elemental tracers of fireworks reported by the PM_{2.5} chemical speciation network (CSN). The IEPA demonstration identifies fireworks tracers such as barium (Ba), copper (Cu), potassium (K), strontium (Sr), and magnesium (Mg). Nitrates, sulfates and organic carbon are also byproducts of fireworks displays, but these compounds can also be associated with other emission sources. The nearest PM_{2.5} speciation data to the flagged Granite City Fire Station observation is collected at the Granite City Gateway Medical (17-119-0024) monitoring site, located several blocks away. The following time series for Ba, Mg, Sr, and K clearly show unusually high levels on the July 5th, 2008.

July 5th, 2008 Exceptional Event for Granite City, IL (St. Louis)



Although this speciation data indicates the Granite City Medical Center was impacted by fireworks, more information was needed to confirm the causal connection to the Granite City Fire Station monitoring site. On July 8th, Region 5 asked IEPA to analyze archived filters from the PM_{2.5} Federal Reference Method (FRM) monitor using XRF. The archived PM_{2.5} FRM filters collected on July 5, 2008 from both the Granite City Gateway Medical Center and Fire Station sites were submitted for chemical analysis to assess the fireworks impacts at the Fire Station site. EPA’s national contract laboratory, Research Triangle Institute (RTI), performed the same XRF analyses for metals as that conducted on samples for the CSN.

Table 1: Chemical Analysis Summary for July 5, 2008 Samples (µg/m³)

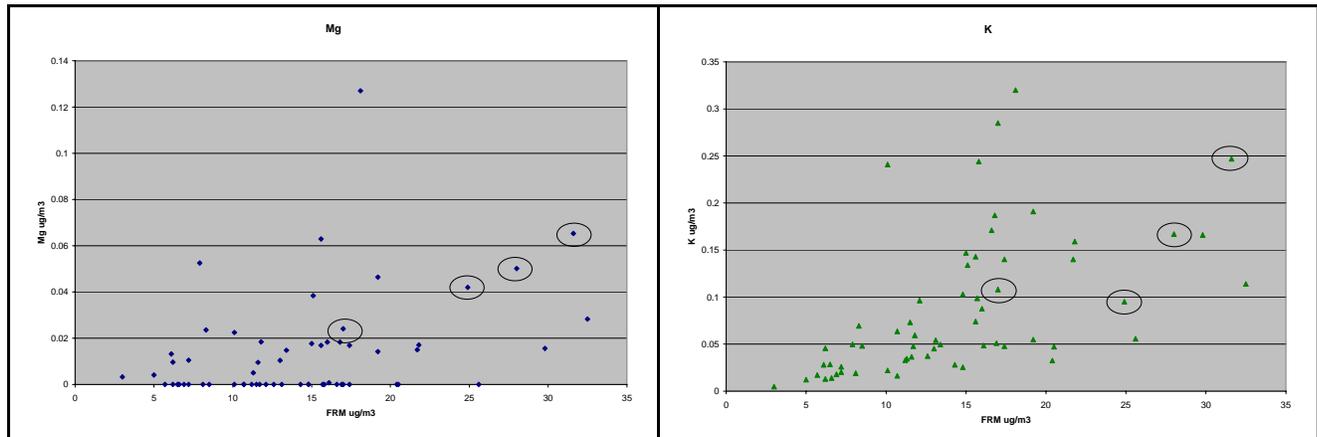
Element	GC Medical CSN	GC Medical FRM	GC Fire Station FRM
Aluminum	0.06	0.08	0.18
Barium	0.08	0.20	0.16
Copper	0.04	0.08	0.06
Magnesium	0.13	0.26	0.25
Potassium	1.87	3.12	2.56
Strontium	0.03	0.06	0.05

The table above shows that the concentrations of firework tracer elements from the archived July 5th PM_{2.5} FRM filters were higher than the species concentrations collected at the Granite City Medical Center CSN monitor. To assess whether there is a consistent difference between the

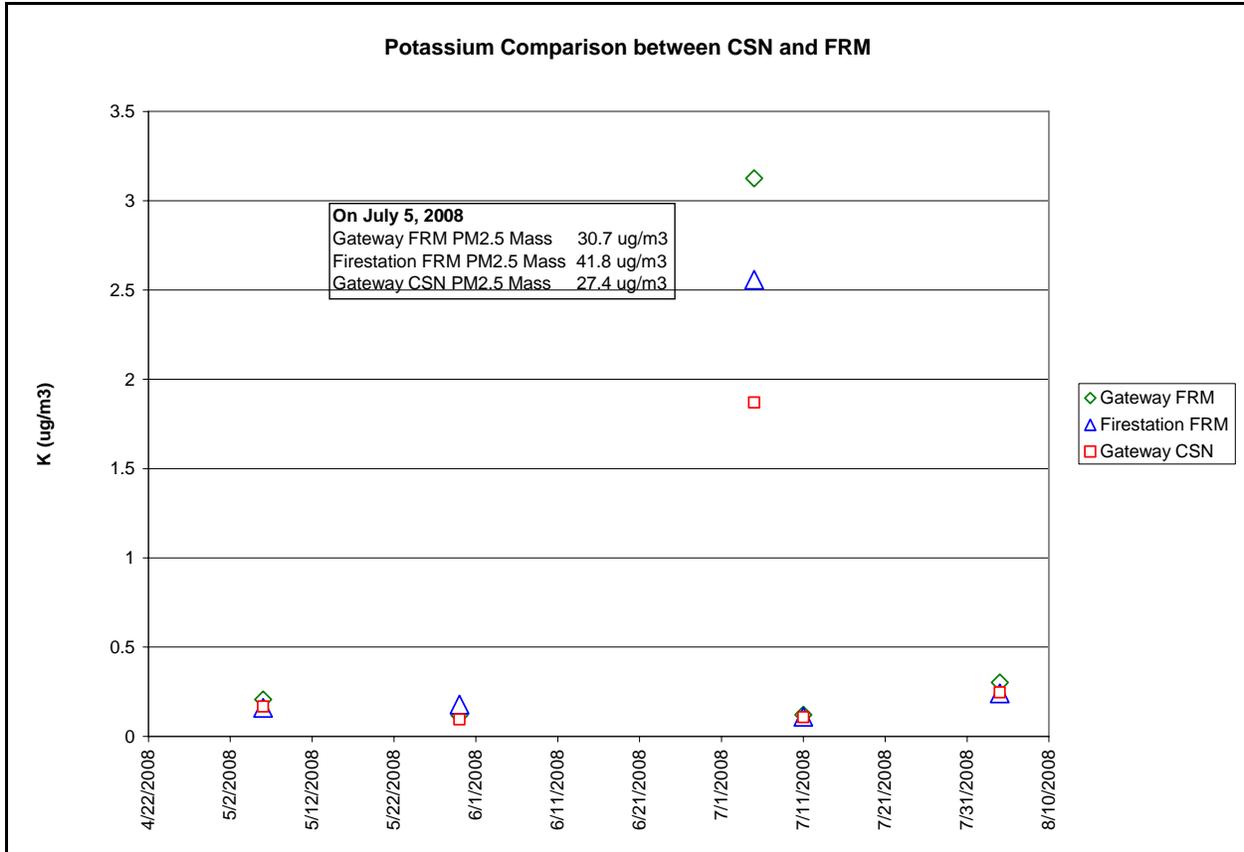
CSN and FRM speciation measurements Region 5 requested (July 14th) XRF analysis for pairs of FRM filters for an additional 4 days. Specific days were selected by Region 5 using the following criteria:

1. days with available archived FRM filters for both the Fire Station and Gateway Medical sites and available CSN data from the Gateway Medical monitoring site
2. days with PM_{2.5} concentrations in the higher range to assess potential tracer contribution of non-firework sources on high PM_{2.5} days
3. days with a range of K and Mg concentrations reported by the CSN monitor
4. days within several months of July 5th, 2008

Using these criteria, the following four dates were selected: May 6, 2008; May 30, 2008, July 11, 2008, and August 4, 2008. Although not one of the higher concentration days, July 11th (17 $\mu\text{g}/\text{m}^3$) was selected because it was the next consecutive day with CSN data available following July 5th. The following charts show the Potassium (K) and Magnesium (Mg) versus FRM concentration using the routinely collected PM_{2.5} chemical speciation data (CSN) from the Granite City Gateway Medical monitor. The 4 circled data points identify the days where Region 5 requested additional XRF chemical speciation analysis of IEPA's archived PM_{2.5} FRM filters. The July 5th concentrations are not included on the two charts below because the K concentration was so much higher (1.87 $\mu\text{g}/\text{m}^3$) than other displayed K concentrations and the effect of including it would have resulted in a y-axis scale illustrating little distinction to the four identified values.



The following chart shows the K concentration on all 5 days of PM_{2.5} FRM filters analyzed by XRF for the two Granite City monitoring sites and the routinely collected PM_{2.5} CSN data. Except for July 5th, the K concentrations from the three filters are consistent with each other within each day. For example, on July 11th, the Gateway Medical Center CSN and FRM K concentrations are 0.121 and 0.108 $\mu\text{g}/\text{m}^3$, respectively, and the Firestation FRM K concentration is 0.109 $\mu\text{g}/\text{m}^3$. In addition, except for the July 5th concentrations, the concentrations on the other 4 days are consistent in magnitude, especially given the range of observed total PM_{2.5} concentrations (28, 24.9, 17, and 31.6 $\mu\text{g}/\text{m}^3$) observed on these days. From this chart, it is evident that July 5th was unique, and because of the consistency between sites on days other than July 5th, baseline concentrations of potassium at the Granite City Fire Station monitor can be estimated from the Granite City Gateway Medical Center PM_{2.5} CSN data.



Given the continuous PM data and high concentrations of trace metal indicators identified in the Granite City Fire Station FRM filter, the July 5th PM_{2.5} observation was clearly impacted by fireworks.

Demonstration of Exceedance “But For” the Event: The final requirement of the Exceptional Events Rule is that there would have been no exceedance or violation but for the event. Region 5 applied two separate approaches, each of which resulted in an estimate at least as large as the estimate of PM_{2.5} mass from fireworks at the Granite City Fire Station monitoring site. Subtracting the estimates of firework contribution observed mass results in an adjusted PM_{2.5} concentration below the PM_{2.5} 24-hr NAAQS.

The first approach uses a previously concurred fireworks exceptional event from an Indianapolis monitor (18-097-0078) to develop a factor using potassium as the tracer element. First, excess PM_{2.5} contribution from fireworks at the Indianapolis site was estimated as 35.5 µg/m³ using the average of 15 hourly PM_{2.5} observations clearly not affected by the event (5:00 am to 7:00 pm). Next, using historical CSN data collected at that site, excess K was calculated as the K concentration on July 4th minus the baseline K. Based on a baseline K of 0.1 µg/m³ and an observed K of 11.2 µg/m³, excess K was estimated as 11.1 µg/m³. The ratio of excess K to excess mass is then 3.2 (35.5 / 11.1). This factor (3.2) derived using the Indianapolis example can then be multiplied by the excess K from the Granite City Fire Station monitor to estimate the excess mass attributed to the fireworks in Granite City. The Granite City Fire Station excess K is 2.48 µg/m³ (2.56 minus 0.08, which is the observed concentration minus annual average baseline

concentration from GC Med Center CSN without July 5th observation); therefore, the estimated PM_{2.5} mass attributed to fireworks is 7.9 µg/m³ (3.2*2.48 µg/m³). Subtracting 7.9 µg/m³ from the observed Granite City Fire Station value of 41.8 µg/m³ results in an adjusted mass of 33.9 µg/m³, which is well below the PM_{2.5} 24-hour NAAQS exceedance level of 35.5 µg/m³. Therefore, using this approach, the exceedance would not have occurred but for the event.

Although this approach relied on a single event, which may also have been affected by events other than fireworks, using the continuous PM_{2.5} data and CSN data from the Blair Street monitoring site in Missouri for July 5th, 2008, a similar factor is derived. The excess PM_{2.5} mass calculated as the difference between the total 24-hour average of the continuous data and the average of continuous data not impacted by fireworks (16 hours, 7:00 am to 11:00 pm) is 18.8 µg/m³. The excess K (observed minus baseline) on July 5th is 6.13 µg/m³, which yields a factor of 3. Using this factor, the estimated excess mass at the Granite City Fire Station site is 7.4 µg/m³ (3* 2.48 µg/m³). Subtracting 7.4 µg/m³ from the observed Granite City Fire Station value of 41.8 µg/m³ results in an adjusted mass of 34.4 µg/m³, which also supports the conclusion that the exceedance would not have occurred but for the event.

The second approach uses mass reconciliation to develop a formula to estimate firework impact from observed excess K. Black powder is a granular mixture of a nitrate, typically potassium nitrate (KNO₃), which supplies oxygen for the reaction; charcoal, which provides carbon and other fuel for the reaction, simplified as carbon (C); and sulfur (S), which, while also a fuel, lowers the temperature of ignition and increases the speed of combustion. A commonly cited chemical equation for the combustion of black powder is:



Assuming that the product of fireworks combustion is 2K₂CO₃ + 3K₂SO₄ + 6CO₂ + 5N₂ from the equation above, combustion particulate matter is proportional to K, and 40% of the combustion K is associated with carbonate and 60% with sulfate. Therefore, if all of the K is associated with the products of combustion in the equation above, then

Given: 2.48 µg/m³ excess K,
 molecular weight of K₂SO₄ = 174
 molecular weight of K₂CO₃ = 138
 molecular weight of K₂ = 78

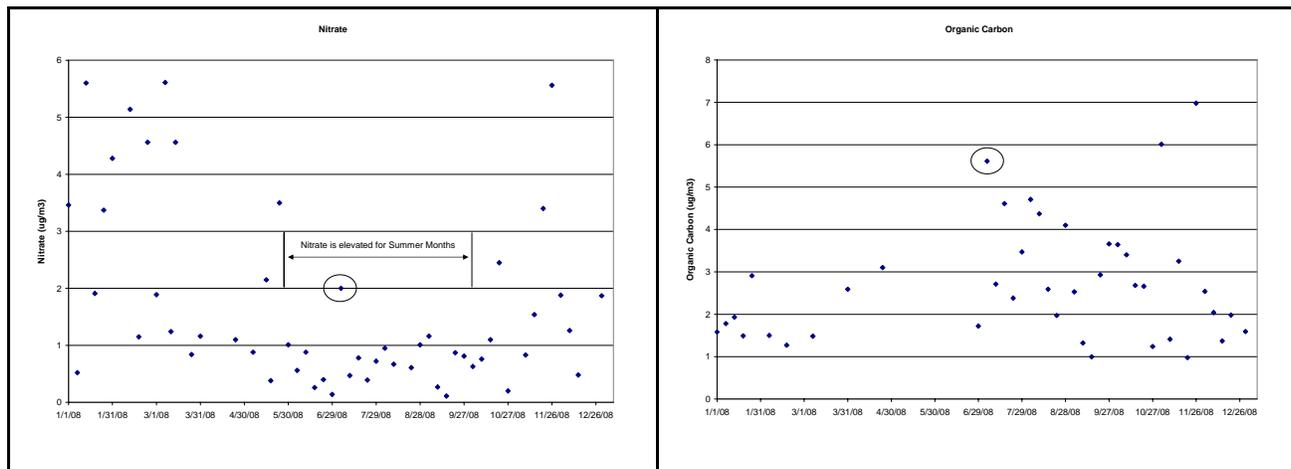
Estimated K₂SO₄ = (0.6*2.48 µg/m³)(174/78) = 3.3 µg/m³
 Estimated K₂CO₃ = (0.4*2.48 µg/m³)(138/78) = 1.8 µg/m³
 Total = 3.3+1.8 = 5.1 µg/m³

This can be simplified to: **Fireworks = 2.1*(excess K)**

Since there appears to be excess NO₃, we assume this to be K₂NO₃ from unburnt material. The 1.4 µg/m³ excess NO₃ (see nitrate chart below) was estimated from the observed NO₃ on July 5th minus the average NO₃ concentrations for summer months at the Granite City Medical Center monitoring site. The molecular weight ratio of K to NO₃ in saltpeter is 39:62, therefore the excess NO₃ (1.4 µg/m³) multiplied by this ratio yields an estimate that the unburnt K

concentration is $0.9 \mu\text{g}/\text{m}^3$. Adding the unburnt K ($0.9 \mu\text{g}/\text{m}^3$) to the excess NO_3 ($1.4 \mu\text{g}/\text{m}^3$) results in $2.3 \mu\text{g}/\text{m}^3$ associated with KNO_3 . Subtracting the product of excess nitrate times the ratio of K to NO_3 in saltpeter ($0.9 \mu\text{g}/\text{m}^3$) from the excess observed K ($2.48 \mu\text{g}/\text{m}^3$), leaves $1.58 \mu\text{g}/\text{m}^3$ K. Multiplying this remaining K times 2.1 (factor in simplified equation above) results in $3.3 \mu\text{g}/\text{m}^3$ of burnt K. Adding the total unburnt ($2.3 \mu\text{g}/\text{m}^3$) and burnt ($3.3 \mu\text{g}/\text{m}^3$) produces a total of $5.6 \mu\text{g}/\text{m}^3$ excess.

There is also excess Mg of about $0.06 \mu\text{g}/\text{m}^3$, and excess organic material. The organic carbon data suggests about $1 \mu\text{g}/\text{m}^3$, and with moderate oxidation the organic material is approximately $1.4 \mu\text{g}/\text{m}^3$. Adding these two additional mass contributors to the excess K results in an estimated impact of $7.1 \mu\text{g}/\text{m}^3$.



The Exceptional Event Rule defines the "but for test" as follows: "There would have been no exceedance or violation but for the event." In this instance, under the Exceptional Events Rule the "but-for test" is satisfied if we estimate that the concentration on July 5, 2008, but for the fireworks impact, would have been below the NAAQS. Subtracting an estimated firework impact of $7.1 \mu\text{g}/\text{m}^3$ from the observed Granite City Fire Station value of $41.8 \mu\text{g}/\text{m}^3$ results in an estimated $\text{PM}_{2.5}$ mass of $34.7 \mu\text{g}/\text{m}^3$. This estimated value is below the $\text{PM}_{2.5}$ 24-hour NAAQS and thus using this mass reconstruction approach, the exceedance would not have occurred but for the event.

On this basis, EPA concurrence was given for the July 5th, 2008 observation collected at the Granite City Fire Station monitoring site (17-119-1007). In accordance with the Exceptional Events Rule and EPA's historic practice, when EPA concurs with a claim of an exceptional event it excludes the data for the entire day from its regulatory decisions. With the exclusion of the July 5th data impacted by the fireworks, there is no violation of the NAAQS.