Exceptional Event Demonstration

Davenport, Iowa

July 4th, 2008

Stock Fireworks Photo Courtesy Linnell Esler

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Introduction

EPA has established health standards to limit ambient levels of seven common air pollutants. EPA regularly reviews these National Ambient Air Quality Standards (NAAQS) to incorporate the latest information from public health studies. Monitors that are accurate enough to implement the standards are designated as federal reference method (FRM) or federal equivalent method (FEM) monitors by EPA. Adverse health effects will be experienced by the public whenever pollutant levels exceed the thresholds established in the NAAQS.

Under normal circumstances, each NAAQS exceedance at a monitoring location results in a lower assessment of the air quality in the area near the monitor. Areas with sufficiently low air quality are declared to be in "non-attainment" with the NAAQS, and are subject to additional legal requirements under the Federal Clean Air Act to control air emissions. However, if the State can argue to EPA's satisfaction that a particular exceedance of a health standard is caused by an "exceptional event" that is not reasonably controllable or preventable; the exceedance can be excluded from EPA's calculation of the attainment status of an area.

On July 4, 2008, a fine particulate ($PM_{2.5}$) FRM monitor located at Jefferson Elementary School in Davenport Iowa recorded an exceedance of EPA's 24 hour NAAQS. Continuous monitors at the site indicated a large spike in the concentration of fine particles and combustion gases after sunset. Continuous $PM_{2.5}$ data were in good agreement with the results of FRM sampling, and indicated that the NAAQS exceedance would not have occurred were it not for the high levels of fine particulates that occurred in the hours after dusk. Meteorological data from the Davenport (KDVN) weather station showed that the winds were light after the sun went down, limiting dispersion of air contaminants. Chemical analysis of the $PM_{2.5}$ FRM filter showed high levels of metals (such as strontium) and other compounds associated with the smoke from fireworks displays. Local news sources document that several fireworks displays took place in the Davenport area on the Fourth of July, including one over the Mississippi river less than a mile from the monitoring location.

Prior this event, the department had not recorded a $PM_{2.5}$ NAAQS exceedance caused by a fireworks display in Iowa. On the Fourth of July 2008, the department did not anticipate an exceedance of the fine particulate standard; because it did not (and does not currently) have the capability to quantitatively predict fine particulate concentrations from a particular fireworks display. As such, no public warning was provided in advance of the event. Continuous $PM_{2.5}$ data from the Jefferson Elementary monitoring site was available during the event on EPA's website[1] and on the University of Iowa Hygienic Lab website.[2]

Legal Background of the Exceptional Events Exclusion

In the March 22, 2007 Federal Register, the Environmental Protection Agency (EPA) presented the final rule addressing the review and handling of air quality monitoring data influenced by exceptional events[3]. Exceptional events are events for which the normal planning and regulatory process established by the Clean Air Act (CAA) is not appropriate. In this rulemaking action EPA finalized the proposal to:

- Implement section 319(b)(3)(B) and section 107(d)(3) authority to exclude air quality monitoring data from regulatory determinations related to exceedances or violations of the NAAQS; and,
- Avoid designating an area as nonattainment, redesignating an area as nonattainment, or reclassifying an existing nonattainment area to a higher classification if a State adequately demonstrates that an exceptional event has caused an exceedance or violation of a NAAQS.

EPA requires states to take reasonable measures to mitigate the impacts of an exceptional event. In accordance with the language in section 319, EPA defines the term "exceptional event'' to mean 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 EPA through the process established in the regulations to be an exceptional event.

[1] http://www.airnow.gov
[2] http://www.uhl.uiowa.edu/services/ambient/realtime.xml
[3] http://www.epa.gov/EPA-AIR/2007/March/Day-22/a5156.htm

EPA treats emissions due to fireworks displays in a manner similar to exceptional events. Certain national or cultural traditions, such as the July 4th, Independence Day celebration and the Chinese New Year celebration have long included fireworks displays as important elements of their observances. While this issue is not specifically covered in CAA section 319, EPA has indicated that its position is that Congress did not intend to require EPA to consider air quality violations associated with such cultural traditions in regulatory determinations.

EPA has indicated that fireworks displays are potentially significant sources of air pollutant emissions. For this reason, it recommends that reasonable precautions should be taken to minimize exposures to emissions from fireworks displays. EPA suggests that these precautions may include alerting the public to the potential for short-term air quality impacts that may result from the discharge of fireworks at large displays.

Description of the Event

A $PM_{2.5}$ FRM monitor located in Davenport, Iowa near Jefferson Elementary School recorded an exceedance of the National Ambient Air Quality Standard on July 4th, 2008. The measured 24-hour $PM_{2.5}$ concentration was 62.3 µg/m3; the 24-hour NAAQS threshold is 35.5 µg/m3. Davenport is part of the Davenport-Moline-Rock Island, IA-IL Metropolitan Statistical Area (Quad Cities). There are 3,088 $PM_{2.5}$ FRM daily values in the AQS database from January, 1999 through August, 2008 at this site. The 62.3 µg/m3 value measured on July 4th, 2008 is the highest 24-hour average recorded since sampling began.

During the evening hours of July 4th, 2008 a continuous $PM_{2.5}$ monitor located in Davenport, Iowa near Jefferson Elementary School recorded elevated values. The department observed the short term spike in the hourly data the next day, and months later received the laboratory results establishing the FRM concentration. After review of web media the DNR established two large fireworks displays had occurred on the 4th in the Quad Cities area (see accounts in Appendix A). Figure 1 illustrates the location of fine particulate monitors and fireworks displays in the Quad Cities area on July 4, 2008. The Adams School and Arsenal Islands monitors are FRM monitors that are not on a daily sampling schedule, and the sampling schedule for these monitors did not allow for samples to be taken on the Fourth.

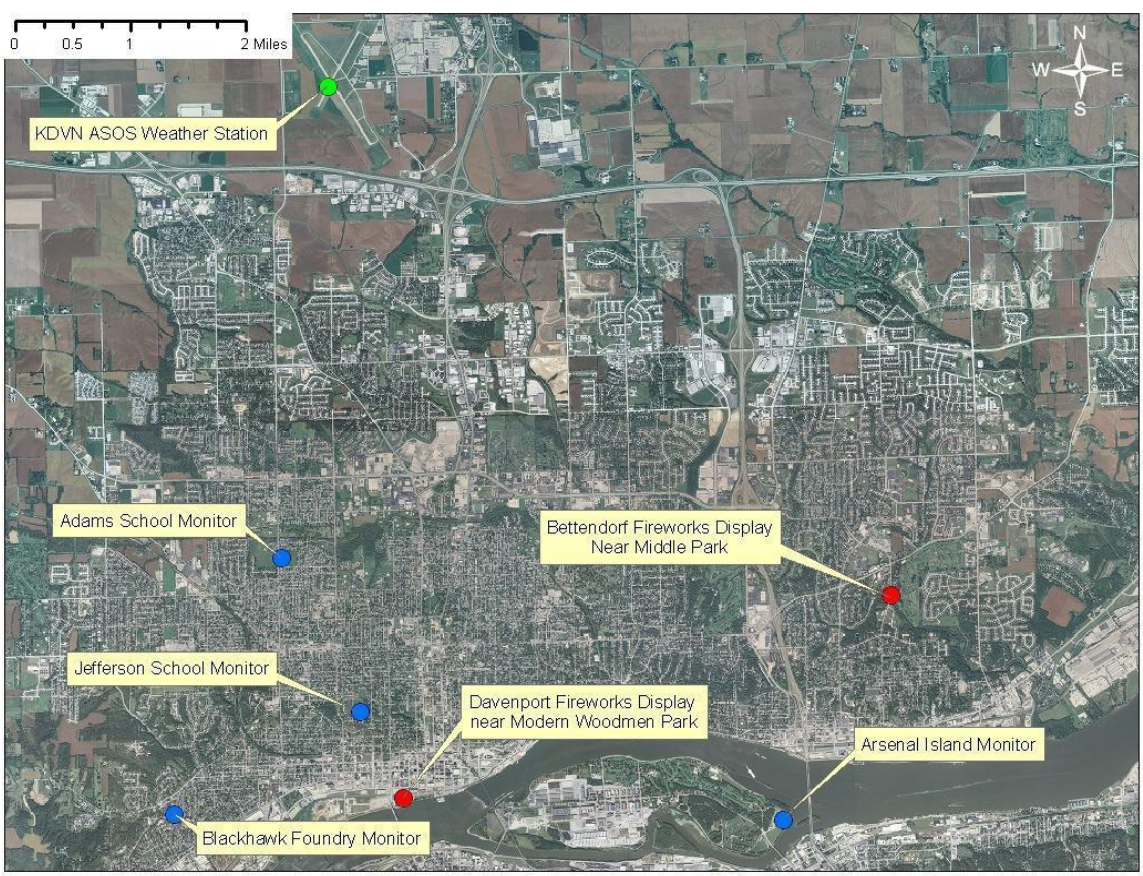

Figure 1. Fireworks and $PM_{2.5}$ Monitor Locations

Meteorological Data

A meteorological data set for the July 4th event is available from the Davenport Municipal Airport (KDVN) Automatic Surface Observation Station (ASOS). Winds were very light during the evening hours of July 4th. Wind speeds of less than 3 knots are considered calms. Calm winds (missing data points) were measured for three hours on the evening of July 4th. Chart 1 (below) illustrates that wind speeds of 3 knots or less were measured from 6:00 p.m. CST (7:00 p.m. local time) through midnight. These calm wind periods coincide with both the highest peaks in the hourly $PM_{2.5}$ data and the fireworks display. These light winds did not allow the pollution from the fireworks to disperse, resulting in high ground level concentrations.

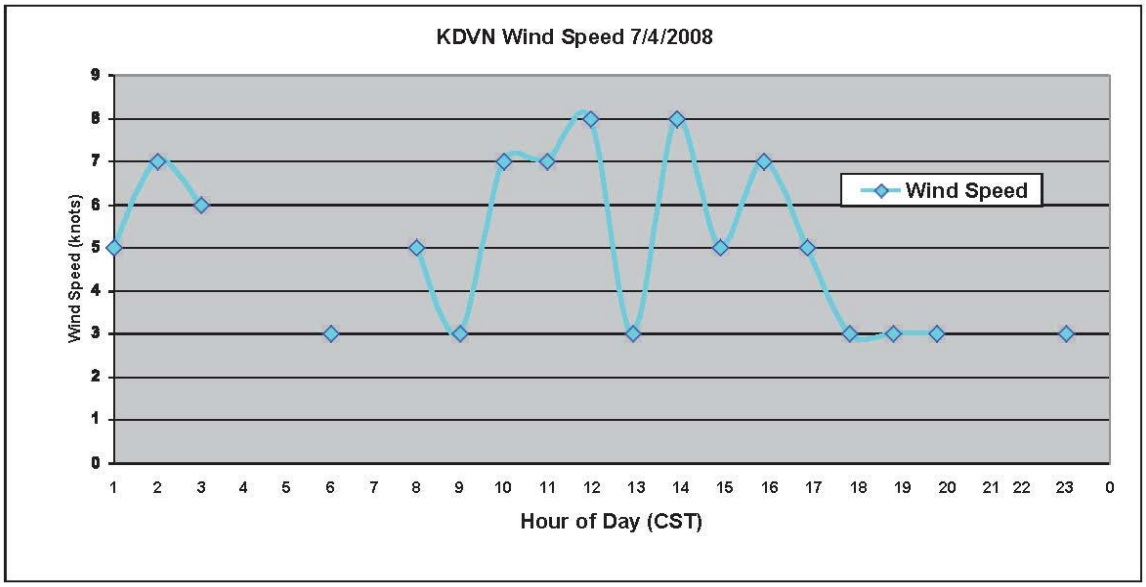

Chart 1. Hourly KDVN Wind Speed Data, July 4th, 2008

The wind directions reported from the KDVN met station were generally from the east or northeast throughout the day. There were two hours when the wind was reported as variable, and several hours when the wind direction could not be determined due to calm conditions. Chart 2 shows the hourly winds recorded at the KDVN station; hours without data points are due to either calms or variable wind directions.

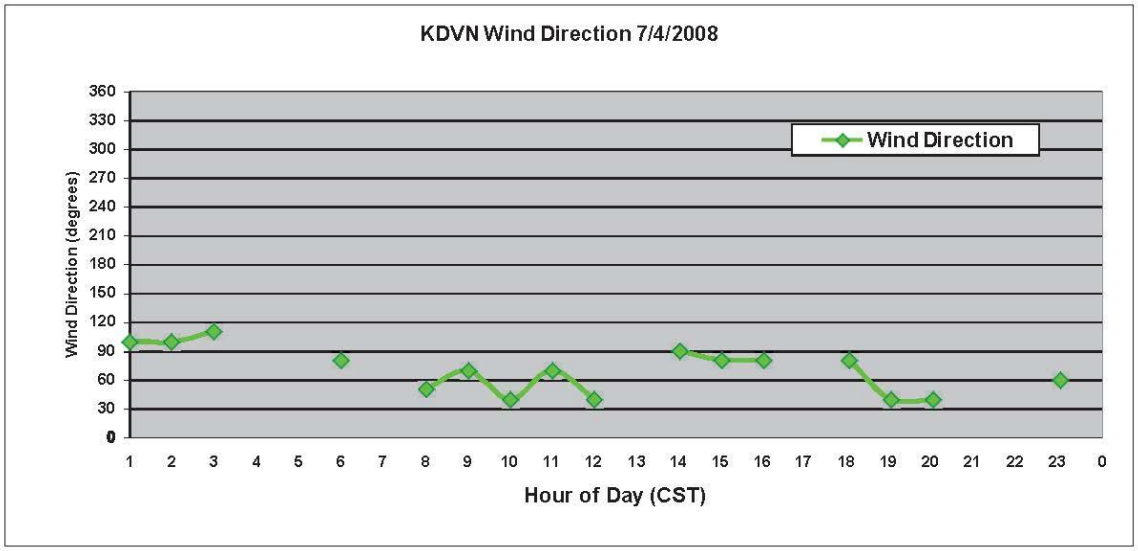

Chart 2. Hourly KDVN Wind Direction Data, July 4th, 2008

Air pollution can build up to high levels if vertical mixing is capped by a layer of warm air near the surface. Hourly surface data from KDVN indicate that winds were light and skies were clear after dusk on the evening of the fourth. These

conditions are known to favor formation of a radiation inversion, where the ground cools faster than the air above, creating a layer of warm air aloft. In river valleys, the denser cold air created by the radiation inversion on the valley slopes flows downhill to the valley floor, creating a deeper layer of cold air and a higher warm air layer than would be experienced on flat ground. The top of the inversion layer, where the temperature begins to fall with increasing height is known as the mixing height. Smoke from shells exploding above the mixing height would rise and be mixed upwards, and have little impact on pollutant concentrations in the valley below. However, if the burst zone of the fireworks display was below the mixing height, then owing to a lack of vertical mixing, an elevated layer of intense smoke would be created that would impact monitoring locations at the elevation of the burst zone. Ground level emissions from sparklers, firecrackers and black powder used to propel fireworks shells would also be trapped in stable air near the surface.

Unfortunately, the department has been unable to obtain any information about the burst height of shells used in fireworks displays in Davenport after dusk on the Fourth. There is also little data available to establish the mixing height after dusk; upper air soundings from KDVN are available at 7 pm on the Fourth and 7 am the next day. Rough attempts to estimate the mixing height based on interpolating the existing upper air soundings and by examining the surface data at ambient monitoring sites at different elevations in the valley are contained in Appendix B.

$PM_{2.5}$ FRM Measurements

Iowa operates $PM_{2.5}$ FRM monitors at many locations across the state. Monitor locations are indicated in Figure 2 below and addresses of monitoring sites and monitor identification numbers are provided in Appendix C. $PM_{2.5}$ FRM measurements from the Jefferson School monitor along with data from other monitors in Eastern Iowa are shown in Chart 3 below. Sites across Eastern Iowa recorded values that were significantly below the 35.5 µg/m3 standard in the days leading up to the measured exceedance. All sites except the Davenport, Jefferson School site measured levels below the NAAQS standard on July 4th, 2008. Table 1 provides the same data in tabular format and suggests that "but for" the fireworks elevated values, the $PM_{2.5}$ daily average value would have been between 7 and 22 µg/m^3.

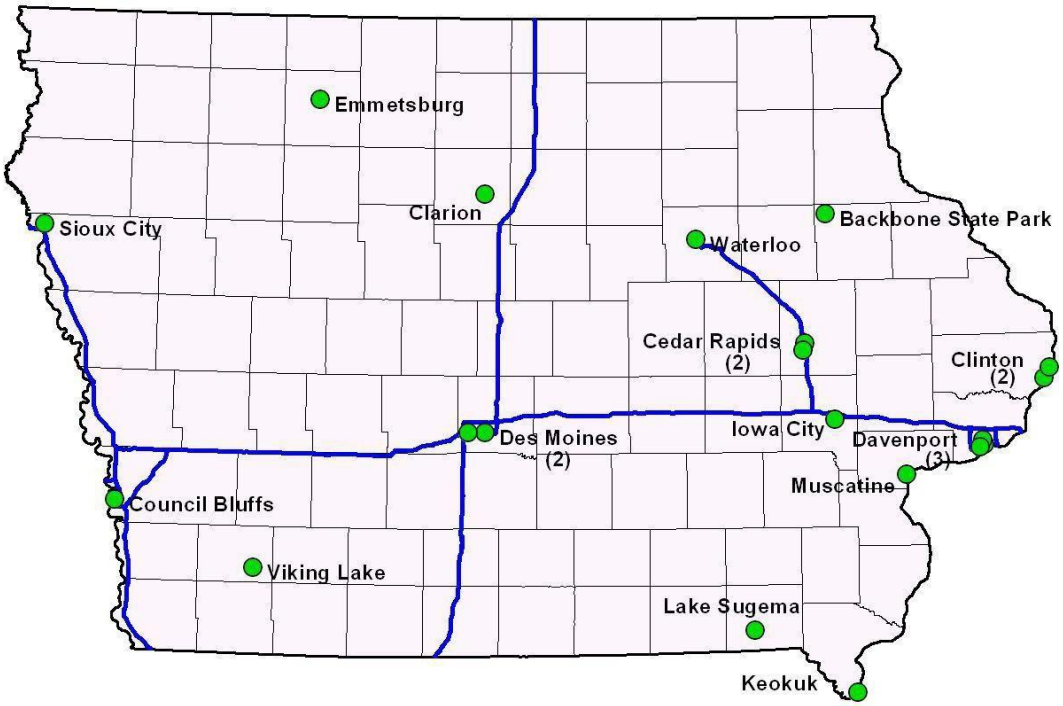

Figure 2. $PM_{2.5}$ FRM Locations in Iowa (2008)

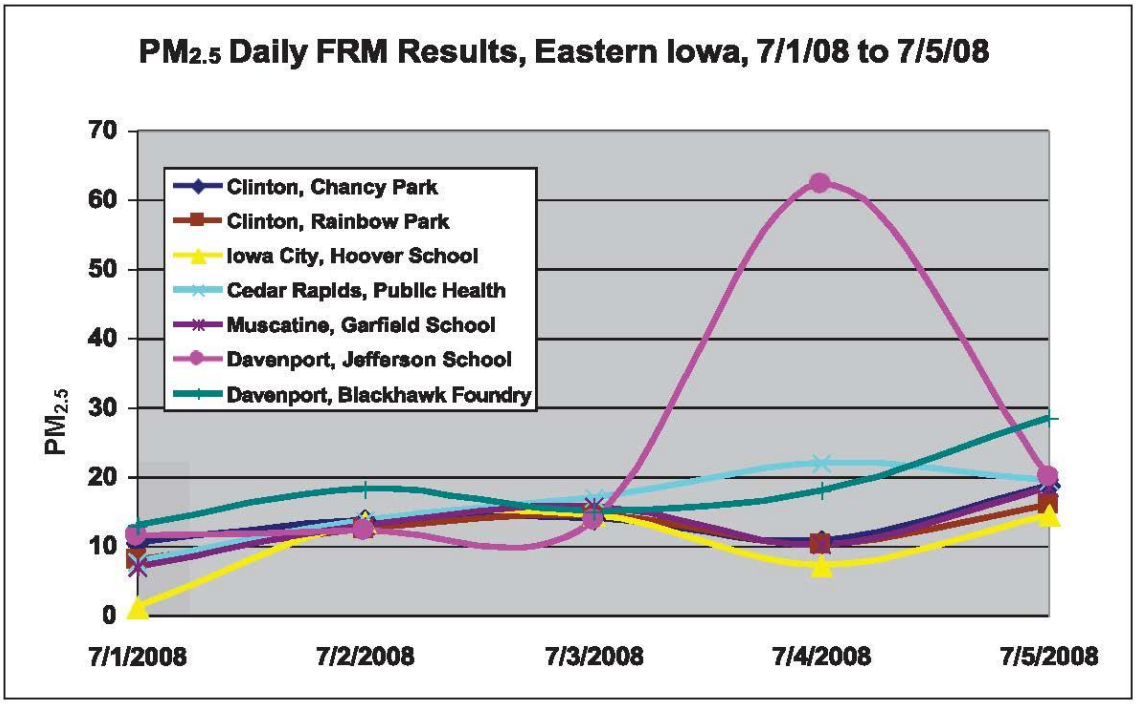

Chart 3. FRM Monitor Values Week of July 4, 2008

Table 1. PM2.5 FRM Filter Result Monitor Values in Eastern Iowa, Week of July 4, 2008 (μ/m^3)

Sample Date	Clinton, Chancy Park	Clinton, Rainbow Park	Iowa City, Hoover School	Cedar Rapids, Public Health	Muscatine, Garfield School	Davenport, Jefferson School	Davenport, Blackhawk Foundry
07/01/2008	10.5	8.1	1.3	7.8	7.1	11.6	12.9
07/02/2008	13.7	12.5	13.5	13.7	13.0	12.2	18.3
07/03/2008	14.0	14.5	14.6	17.0	15.7	13.7	14.9
07/04/2008	10.7	10.2	7.2	22.0	10.3	62.3	18.1
07/05/2008	18.7	16.0	14.4	19.5	18.4	20.1	28.4

Continuous Monitoring Data

Data from continuous ambient air monitors recorded how the pollutant concentrations varied with time on the exceedance day. Continuous ambient air monitoring data is recorded in Central Standard Time. Hourly average data taken between two hours is associated with the start hour. For example, if a spike in air pollution levels occurred at between 9 pm and 10 pm local time, this would correspond to 8 pm and 9 pm Central Standard Time, and the hourly average data would be stored in the 8 pm or 20:00 hour in the monitoring data set.

The DNR operates several continuous $PM_{2.5}$ (FDMS TEOM) samplers in Iowa. These monitors are not Federal Reference Method samplers, but are used for public reporting, and are being considered for FEM status by EPA. Hourly continuous $PM_{2.5}$ data from four sites in Eastern Iowa during the week of July 4 is shown in Chart 4 below. A significant spike in the PM2.5 concentration occurred during the evening hours of July 4. Chart 5 shows hourly data from the same monitors on July 4th. Chart 6 illustrates the data from noon on July 4th through 11 A.M. on July 5th. The spike in $PM_{2.5}$ data was short lived and died down quickly after the fireworks ended.

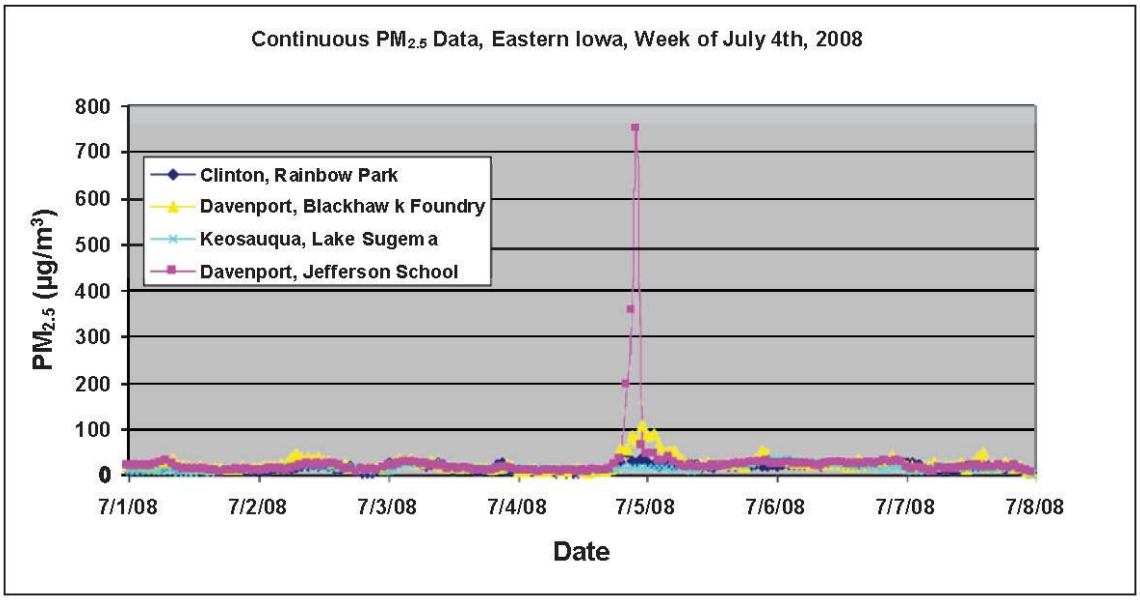

Chart 4. Continuous $PM_{2.5}$ Values, Week of July 4th, 2008

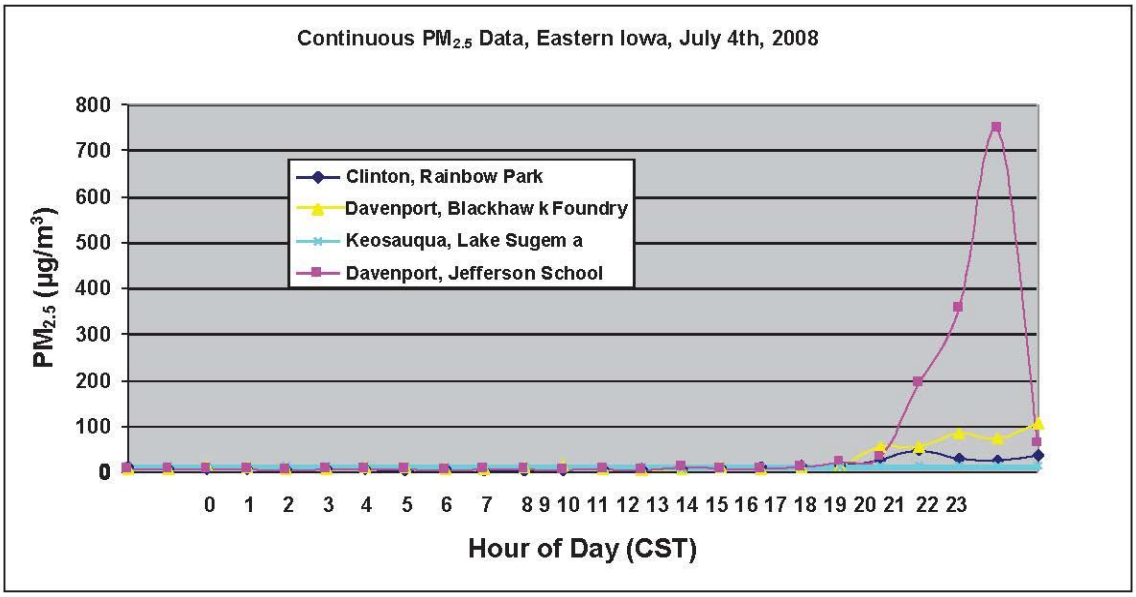

Chart 5. Continuous $PM_{2.5}$ Data, July 4th, 2008

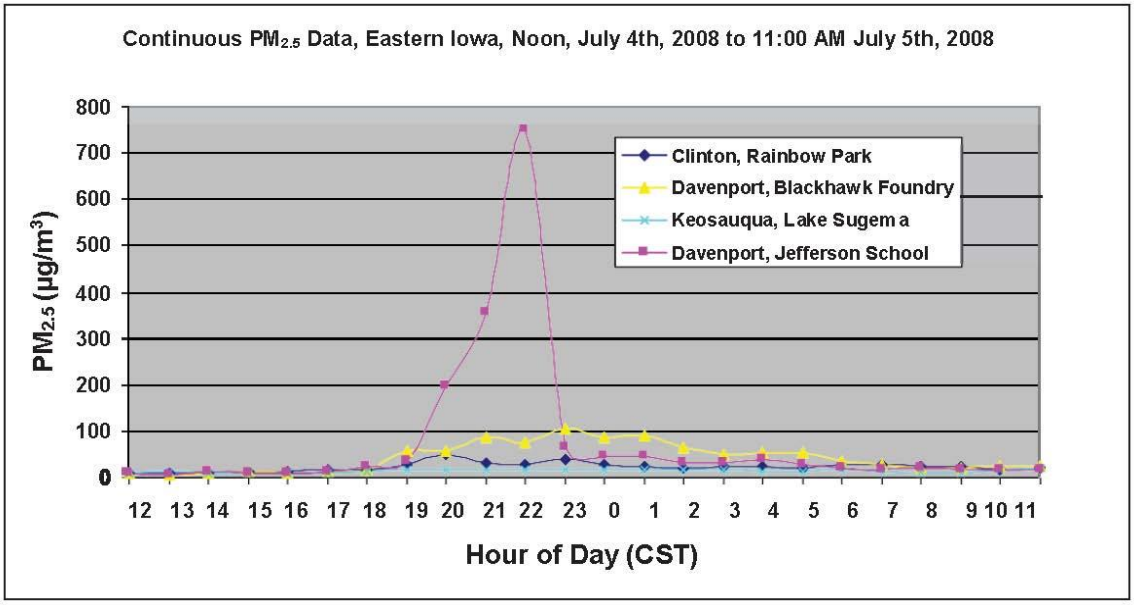

Chart 6. Continuous PM2D.5ata, July 4th and 5th, 2008

Several other continuous monitors are operated at the Jefferson School site. Chart 7 and Chart 8 below show that spikes in sulfate, carbon monoxide, nitrogen oxide, and nitrogen dioxide occurred nearly simultaneously with the spike in the $PM_{2.5}$ data.

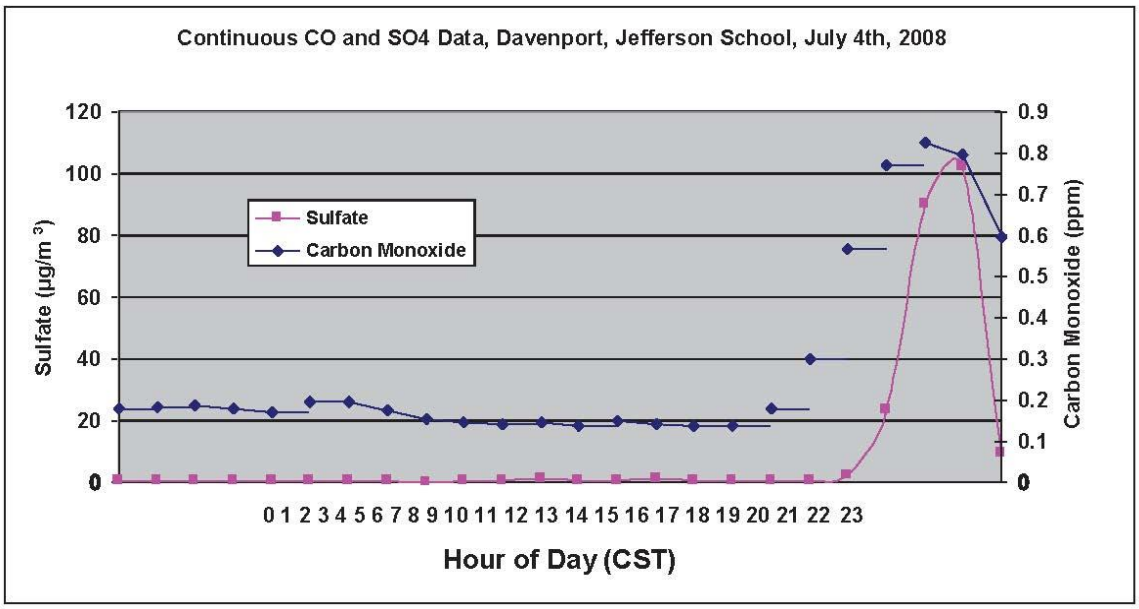

Chart 7. Continuous Sulfate and Carbon Monoxide Data, July 4th, 2008

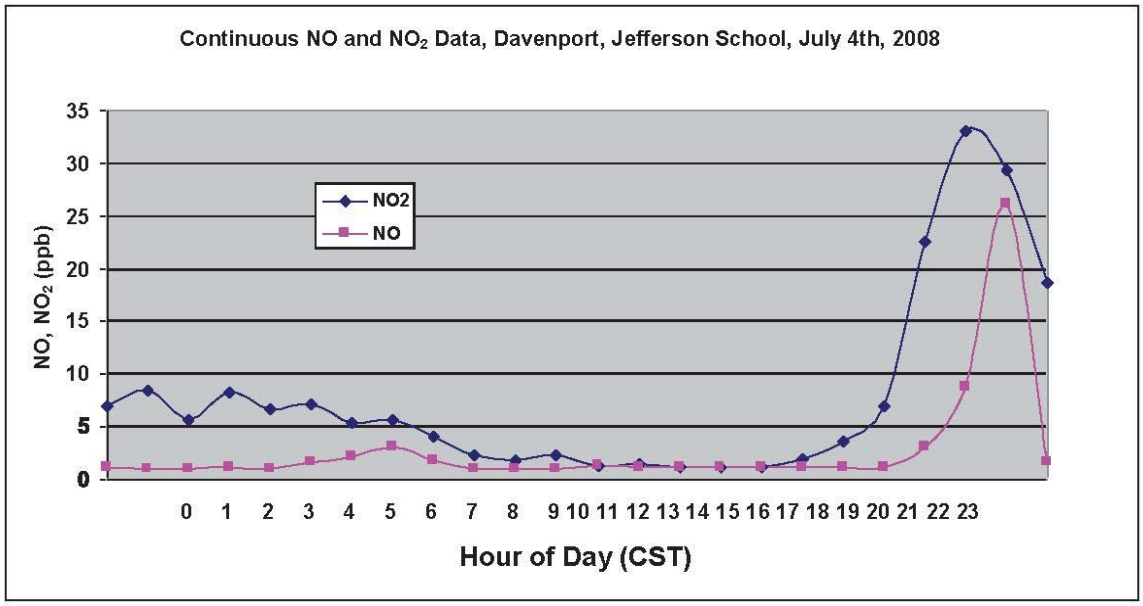

Chart 8. Continuous NO and NO2 Data, July 4th, 2008

No Exceedance "But For" the Exceptional Event

The FRM filter results (Table 2) from sites in Eastern Iowa show that $PM_{2.5}$ levels on July 4th, 2008 were much less than the 35 µg/m3 standard. The average of the results from the six monitors excluding Jefferson School is 13.1 µg/m3. This data suggests that there would not have been an exceedance at the Jefferson School site "but for" the fireworks event.

Table 2. $PM_{2.5}$ FRM Results in Eastern Iowa Excluding Exceedance, July 4th, 2008 (µg/m³)

Site Name	Concentration
Clinton, Chancy Park	10.7
Clinton, Rainbow Park	10.2
Iowa City, Hoover School	7.2
Cedar Rapids, Public Health	22.0
Muscatine, Garfield School	10.3
Davenport, Blackhawk Foundry	18.1
Six Site Average	**13.1**

Another method of assessing the "but for" argument is to compare the average concentrations for July 4th with and without the fireworks pulse. The 24-hour average measured with the continuous $PM_{2.5}$ monitor agreed quite well with the FRM filter result, the average of the continuous $PM_{2.5}$ monitor readings was 64.1 µg/m3 and the FRM filter measured 62.3 µg/m3. The hourly results from the continuous $PM_{2.5}$ monitor as well as averages with the pulse removed are shown in Table 3 below. The fireworks pulse was short lived and the pulse began in either the 18:00 or 19:00 hour on the 4th. When only the five top measurements during the fireworks pulse are excluded from the data set, the average of the remaining hourly data is 7.4 µg/m3. This suggests that there would not have been an exceedance of the (35.5 µg/m3) NAAQS "but for" the fireworks pulse.

Table 3. Davenport, Jefferson School Continuous $PM_{2.5}$ Hourly Data, July 4th, 2008

Date/Time	Continuous $PM_{2.5}$ ($\mu g/m^3$)	Continuous PM2.5 ($\mu g/m^3$)
7/4/2008 0:00	6.6	6.6
7/4/2008 1:00	7.8	7.8
7/4/2008 2:00	8.6	8.6
7/4/2008 3:00	7.1	7.1
7/4/2008 4:00	5.4	5.4
7/4/2008 5:00	6.1	6.1
7/4/2008 6:00	6.6	6.6
7/4/2008 7:00	7.1	7.1
7/4/2008 8:00	3.4	3.4
7/4/2008 9:00	7.3	7.3
7/4/2008 10:00	6.6	6.6
7/4/2008 11:00	2.5	2.5
7/4/2008 12:00	7.8	7.8
7/4/2008 13:00	3.9	3.9
7/4/2008 14:00	9.6	9.6
7/4/2008 15:00	6.4	6.4
7/4/2008 16:00	7.3	7.3
7/4/2008 17:00	10.3	10.3
7/4/2008 18:00	20.8	20.8
7/4/2008 19:00	34.5	-
7/4/2008 20:00	195.5	-
7/4/2008 21:00	355.0	-
7/4/2008 22:00	749.5	-
7/4/2008 23:00	63.0	-
Average	**64.1**	**7.4**

A Brief Review of the History and Chemistry of Fireworks

The first milestone in the history of pyrotechnics occurred when the Chinese discovered black powder (gun powder) over 1000 years ago.[4] The recipe involved grinding a mixture of 75 percent potassium nitrate, 15 percent charcoal and 10 percent sulfur. Another breakthrough was made in Italy in the 1830s, when potassium nitrate was replaced with potassium chlorate (perchlorate). This powerful oxidizer increased the temperature of combustion from 1700C to 2000C. They found that metals and metallic salts burned with brilliant colors at the elevated temperature.

A modern fireworks shell uses a black powder charge to propel a payload of pyrotechnic "stars". The exploding stars in the shell are made[5][6], by combining perchlorate and black powder with binding and coloring agents: zinc, magnesium or aluminum are used to make white sparks, sodium salts for yellow, strontium nitrate or carbonate for red, barium nitrate for green, copper salts for blue, and charcoal or other forms of carbon for orange. Stars are packaged in sealed cardboard compartments with centrally located black powder burst charges to ignite and disperse the stars. A typical multi-burst shell contains several of these compartments linked by a connecting fuse. The black powder lift charge is located at the base of the shell. To fire the shell, it is placed in a metal tube with a main fuse at the top. An electric signal

[4] The discussion on the history of fireworks and the design of a modern fireworks shell is adapted from the online materials from a PBS NOVA episode "Fireworks!" available at: http://www.pbs.org/wgbh/nova/fireworks.

[5] A discussion of chemical compounds commonly used in fireworks is available at: http://chemistry.about.com/od/fireworkspyrotechnics/a/fireworkelement.htm.

[6] Details of fireworks materials and construction are available at: http://www.skylighter.com.

is sent to the main fuse which simultaneously ignites a fast burning fuse at the bottom of the shell and a slow burning fuse that advances toward the first compartment. After the shell reaches its apex (as high as 1000 feet above the ground) the first burst occurs, and as the slow burning fuse advances, it eventually reaches each of the lower compartments of the shell triggering successive bursts.

Perhaps the most common pyrotechnic device in use during Independence Day celebrations in Iowa is the sparkler. A sparkler consists of a metal rod coated with a combustible mixture. The mixture contains a fuel (such as carbon and sulfur), an oxidizer (potassium nitrate or perchlorate), metal powder (zinc, iron, aluminum, magnesium or titanium) and a binder (dextrin or shellac). A sparkler burns slowly, releasing incandescent metallic sparks. The grind of the metal powder and the amount of binder may be use to control the speed of burning. Simple sparkler formulations may use the binder as fuel; more elaborate formulations add colorant for additional affect.[7]

Studies of the ambient air quality near fireworks displays have associated fireworks emissions with increases in ambient concentrations of colorant metals including Aluminum, Barium, Copper, Iron, Lead, Manganese, Potassium, Strontium, Vanadium, and Zinc.[8][9][10] Of these metals, Vecchi[11] indicated that Strontium may be the best fireworks tracer.

Results of Chemical Analysis of the Exceedance Filter

The department operates a fine particulate speciation sampler at the Jefferson School monitoring location. This monitor is part of a national network of samplers funded by EPA, known as the Chemical Speciation Network (CSN). Fine particulate monitors in the CSN are not FRM samplers, but collect multiple filter media on each sampling day that are suitable for different types of chemical analysis. CSN samplers utilize a standard set of field and analytical protocols developed by EPA to establish the chemical constituents of fine particles. The CSN sampler at Jefferson School is operated at a frequency of one sample every third day, and was not operational on July 4th 2008. The department enlisted EPA's Chemical Speciation Network (CSN) contract laboratory (Research Triangle Institute) to perform x-ray fluorescence (XRF) analysis on the filter using the CSN protocol. The results of this analysis are indicated in Appendix D.

XRF analysis of the July 4th filter from the FRM sampler at the Jefferson School site were compared with Chemical Speciation Network (CSN) XRF results obtained from the same site for 2005-2007. This comparison is indicated in Appendix E. Several species were measured at levels greater than the historical site maximum. Table 4 lists the FRM results and comparison to the historical results from the CSN sampler for these species.

Table 4. Comparison of Selected XRF Results from FRM Exceedance Filter at Jefferson School to 2005-2007 CSN Values

Parameter	CSN Historical Maximum (ng/m^3)	FRM Filter Results (ng/m^3)	Ratio
Copper	50.1	143.2	2.86
Chlorine	823.0	8681.7	10.55
Magnesium	137.0	654.9	4.78
Zinc	204.0	4658.0	22.83
Strontium	40.7	216.4	5.32
Potassium	1920.0	13488.4	7.03
Sodium	272.0	1949.3	7.17

Many of the species included in Table 4 are found in compounds that have been associated with fireworks emissions.

[7] The discussion on the composition of sparklers is adapted from the article by Anne Marie Helmenstine, PhD, available online at: http://chemistry.about.com/od/demonstrationsexperiments/ht/sparkler.htm.

[8] Attri, Arun K: Looking at Fireworks from Environmental Science Perspective, EnviroNews, Vol. 11 No. 4 - October 2005.

[9] Barman, SC, Ramesh Singh, MPS Negi, SK Bhargava: Ambient air quality of Lucknow City (India) during use of fireworks on Diwali Festival, *Environmental Monitoring and Assessment*, Vol. 137; No. 1-3, pages 495-504, 2008.

[10] Kulshrestha, UC, T Nageswara Rao, S Azhaguvel: Emissions and accumulation of metals in the atmosphere due to crackers and sparkles during Diwali festival in India, *Atmospheric Environment,* Vol. 38; Issue 27, 4421-4425, September 2004.

[11] Vecchi, R, V Bernardoni, D Cricchio, A D'Alessandro, P Fermo, F Lucarelli, S Nava, A Piazzalunga, G Valli: The impact of fireworks on airborne particles, Atmospheric Environment, Vol. 42, Issue 6, 1121-1132, February 2008.

Strontium measured on the Jefferson School July 4th FRM filter was more than five times greater than the highest value measured at the site between 2005 and 2007. Investigation into dates when historical maximum values were measured revealed that for strontium and potassium, historical maximums were also measured on days that were likely associated with fireworks. Three sampling dates (July 3rd, 2005, July 4th, 2006, and July 5th, 2007) were removed from the historical data set and the remaining CSN, XRF data was again compared to the Jefferson School exceedance filter data. Table 5 shows that the values measured for strontium and potassium were 38 and 49 times the maximum historical levels measured by the CSN sampler at the same site after excluding July 4th related filters.

Table 5. Comparison of Selected XRF Results from Filter Exceedance Filter at Jefferson School to 2005-2007 CSN Values Without Previous July 4th Events

Parameter	CSN Historical Maximum (ng/m^3)	FRM Filter Results (ng/m^3)	Ratio
Copper	50.1	143.2	2.86
Chlorine	823.0	8681.7	10.55
Magnesium	137.0	654.9	4.78
Zinc	204.0	4658.0	22.83
Strontium	5.7	216.4	38.03
Potassium	275.0	13488.4	49.05
Sodium	272.0	1949.3	7.17

Any piece of analytical equipment has finite resolution. The method detection limit[12] (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The minimum quantifiable value is the concentration at which the analytical uncertainty is 10%. White[13] has suggested that minimum quantifiable value for the XRF system in the national (IMPROVE) network used to quantify rural fine particle levels is about 10 times the MDL. The ratio of each measured concentration to the associated MDL for each analyte provides a measure of the "signal strength" of the concentration. These ratios are provided in Appendix F.

Conclusions

The department holds that fireworks displays were integral to the traditional Independence Day celebration that occurred on the exceedance day.

The fireworks event on the evening of July 4th, 2008 significantly affected air quality as measured by the $PM_{2.5}$ FRM monitor at the Davenport, Jefferson School monitoring site.

The measured concentration is in excess of normal historical fluctuations at the monitoring site. The concentration measured on July 4th, 2008 is the highest value measured since the FRM was installed at the site in January, 1999.

Data from FRM monitors located in Eastern Iowa on the day of the event indicate that the regional concentration of $PM_{2.5}$ was significantly lower than the 35.5 µg/m^3 level of the NAAQS. The hourly FDMS TEOM data indicate that the pollutant levels at the site were significantly lower than 35.5 µg/m3 in the hours prior to and immediately after this event. The available data suggests that there would not have been an exceedance measured at the site "but for" the fireworks event.

Metals commonly associated with fireworks displays were identified on the exceedance filter.

The department contends that the data shows a clear causal relationship between the $PM_{2.5}$ filter exceedance

[12] See: 40 CFR Part 136 Appendix B—Definition and Procedure for the Determination of the Method Detection Limit at: http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&tpl=/ecfrbrowse/Title40/40cfr136_main_02.tpl

[13] See: http://vista.cira.colostate.edu/improve/Activities/Meetings/2004Pres/WW_GlacierXRF.pdf, and http://vista.cira.colostate.edu/improve/Activities/Meetings/2008Pres/White_ISC_unc&mdl_NPH.pdf.

measurement at the monitoring site and the fireworks displays on July 4th, 2008 in the Quad Cities.

The department has flagged the affected $PM_{2.5}$ FRM data point in the in the official EPA database (AQS) as being impacted by an exceptional event and requests EPA's concurrence with this finding.

EPA's PM2.5 NAAQS applies to fine particles of any chemical composition. Asthmatics and those with respiratory difficulties, as well as the elderly and children were the groups most likely to have experienced adverse health effects associated with this event. Concern over the toxicity of chemicals[14] contained in fireworks smoke (including perchlorate and colorant metals) has lead to the development of a new variety of cleaner burning fireworks based on nitrogen-rich compounds. These fireworks do not require the use of perchlorate as an oxidizer, and because they produce less smoke, require smaller amounts of metal colorants.[15] The Disney Corporation[16] has pioneered the use of compressed air (instead of black powder) as a propellant at its fireworks displays.

The department intends to develop and publicize a webpage that alerts the public to the potential adverse health effects that may arise from exposure to the smoke from fireworks displays, and will recommend that communities with a history of elevated fine particulate levels during fireworks displays take measures to limit fireworks emissions and limit the exposure of sensitive individuals.

[14] Federal agencies that have provided online information about the toxicity of chemical compounds (including chemicals commonly found in fireworks) include the EPA http://cfpub.epa.gov/ncea/iris/ and the Agency for Toxics Substances and Disease Registry (ATSDR) http://www.atsdr.cdc.gov/toxfaq.html.

[15] For a discussion of "low smoke" fireworks see: http://www.jsonline.com/news/29412309.html or http://pubs.acs.org/cen/coverstory/86/8626cover.html.

[16] http://corporate.disney.go.com/environmentality/press_releases/2004/2004_0628.html

Appendix A. Accounts of Firework Events in the Quad Cities Area

From the "Our Sports Central" Web Site[17]

FRIDAY, JULY 4 - INDEPENDENCE DAY FIREWORKS EXTRAVAGANZA PRESENTED BY KWQC-TV6!

The show gets even better on Friday night, as the River Bandits celebrate Independence Day with a 6:00 pm game that will be followed the biggest, brightest, and most electrifying pyrotechnic extravaganza of the year!!! This fireworks show will be one to remember, so don't miss out on the opportunity to be there in person.

From the Quad-City Times[18] Web Site

Independence Day fireworks and parades

Here is a listing of area parades and fireworks displays. All dates are July 4, unless otherwise noted:

Iowa
Bettendorf — Veterans Memorial Park, dusk
Buffalo — City Park, 329 Dodge St., fireworks at dusk, parade 10 am July 5
Clinton — Riverview Park, July 5 after 8 pm concert
Davenport — Red, White, Boom! July 3, fireworks after River Bandits game; July 4, fireworks after River Bandits game
DeWitt — 10 am parade
Durant — High school at dusk
Eldridge — Sheridan Meadows at dusk, July 11
Morning Sun — High school athletic field at dusk; parade at 3 pm
Muscatine — Muscatine riverfront at dusk, parade at 5 pm
Tipton — City Park at dusk; parade at 2 pm

ILLINOIS
Aledo — Fenton Park (below the high school) at dusk
East Moline — Parade at 1 pm; The Quarter (7th Street and Riverfront) at dusk, July 3
Galva — Park District at dusk
Geneseo — Richmond Hill Park at dusk
Kewanee — Northeast Park at 9:30 pm
Matherville — Lake Matherville at dusk, July 3
Monmouth — Citizens Lake at dusk

From KWQC-TV6 News and Weather[19] for the Quad Cities

July 4th Fireworks Displays

July 4, Tuesday:
Aledo: Fenton Park
Bettendorf: Veterans Memorial Park
Buffalo: City Park
Clinton: Riverview Park at 10:15 pm
Galesburg: Lake Storey
Galva: Galva Park District
Grand Mound: Baseball Park
Kewanee: Northeast Park
Monmouth: Citizen's Lake

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[17] Our Sports Central. (2008 June 30). Bandits' Independence Day blowout. http://www.oursportscentral.com/services/releases/?id=3671213.
[18] Quad Cities Times. (2008 June 27). Independence Day fireworks and parades. http://www.qctimes.com/articles/2008/06/27/news/local/doc4865641aaac70795455364.txt.
[19] KWQC-TV6. (2008). July 4th Fireworks Displays. http://www.kwqc.com/global/story.asp?s=1332321&ClientType=Printable

Morning Sun: High School Athletic Field
Muscatine: Riverfront
Prophetstown: State Park
Tipton: City Park
Davenport: After Swing Game
Downtown Davenport: After Swing Game.
Galesburg: Lake Storey at dusk.
Galva: Galva Park District at dusk.
Grand Mound, Iowa: Ball Park at dusk.
Kewanee: Northeast Park at dusk.
Mount Carroll: Athletic field at dusk.
Monmouth: Citizens Lake at dusk.
Morning Sun: At dusk.
Muscatine: The riverfront at dusk.
Oxford Junction: Legionaire at dusk.
Park View: Meadowbrook Park by the water tower.
Sterling/Rock Falls: Centennial park.
Tipton: Ball Park at dusk.
Village of Oak Grove: At dusk.

Appendix B. Upper Air Analysis

The sun heats the ground during the daytime which in turn heats the air near the surface by conduction. The air near the surface is warmer than the air above it and it rises. The air will rise until it encounters a layer of air that is warmer than the one beneath it. Pollutant concentrations during the day are typically lower than those at night because the atmosphere is heated from below and the rising unstable air promotes good mixing of pollutants.

Inversions represent boundaries in the atmosphere that preclude mixing. There are various types of inversions associated with different meteorological conditions.[20] When the sun goes down, if skies are clear and the winds are light, the ground cools more rapidly than the air, and creates a layer of cold air near the surface. The surface layer is cooler than the air in the layer above and little vertical mixing of surface contaminants takes place. These circumstances, in which the temperature of the air increases with height, are known as a radiation inversion. The altitude at which the temperature begins to decrease with height defines the top of the inversion layer, and is also known as the mixing height.

In river valleys[21] during a radiation inversion, cool air generated on the slopes of the valley travels down slope and collects at the bottom of the valley, pushing the warm air aloft and causing the mixing height over the bottom of the valley to be higher than it would be over flat ground. The inversion height over the valley floor increases as the night goes on. Air pollutants are often emitted at temperatures that are higher than ambient temperatures and will rise until they are mixed to the temperature of the surrounding air. High pollutant concentrations are often noted at the top of the inversion layer, just below the mixing height.

Balloons (rawinsondes) that provide information on upper air conditions are released every twelve hours from the KDVN weather station. One was released at 7 pm local time on July 4th and another at 7 am local time on July 5th. The variation of the temperature with height for the lower portion of the sounding is indicated in Chart B-1.

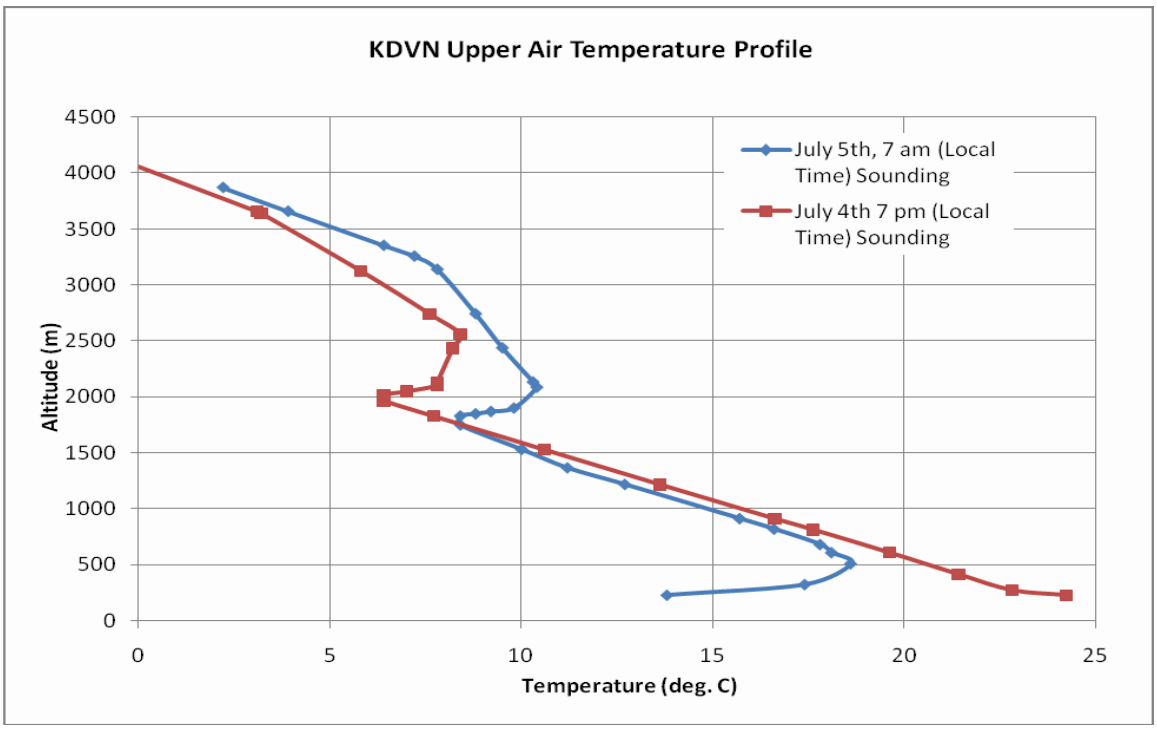

Chart B-1. Upper air temperature from KDVN rawinsondes from July 4th and 5th.

[20] For a discussion of inversions see: http://www.atmos.millersville.edu/~lead/SkewT_Inversions.html 21 Air Quality, Thad Godish, CRC Press, 2004. 77-78.

[21] See: http://weather.unisys.com/upper_air/skew/details.html

Complete results of the soundings in skew-T[22] format are indicated in Chart B-2 and Chart B-3. At 7 pm an inversion was noted at about 2000 meters over the surface, and at 7 am a low level radiation inversion was recorded at about 180 meters, along with another inversion at about 1800 meters.

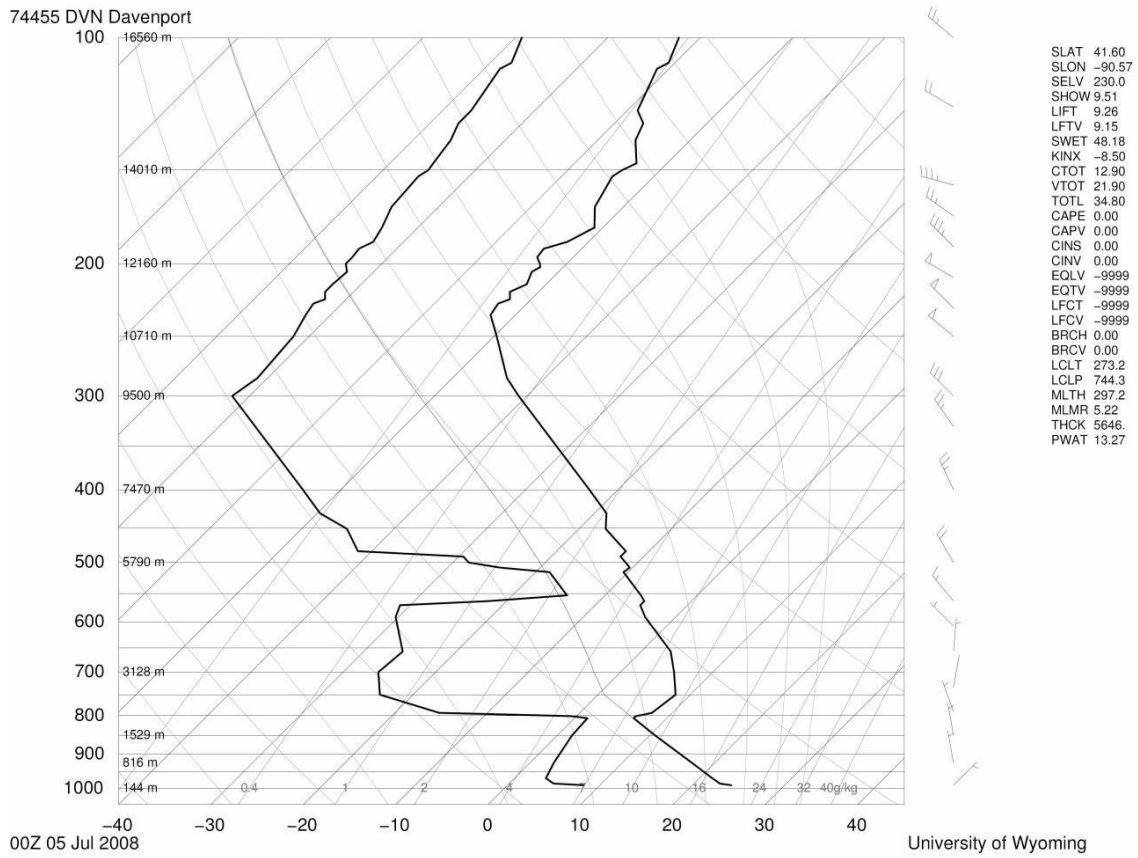

Chart B-2. Skew-T Diagram for the 7 pm (Local Time) sounding on July 4, 2008, Courtesy University of Wyoming

[22] See: http://weather.unisys.com/upper_air/skew/details.html

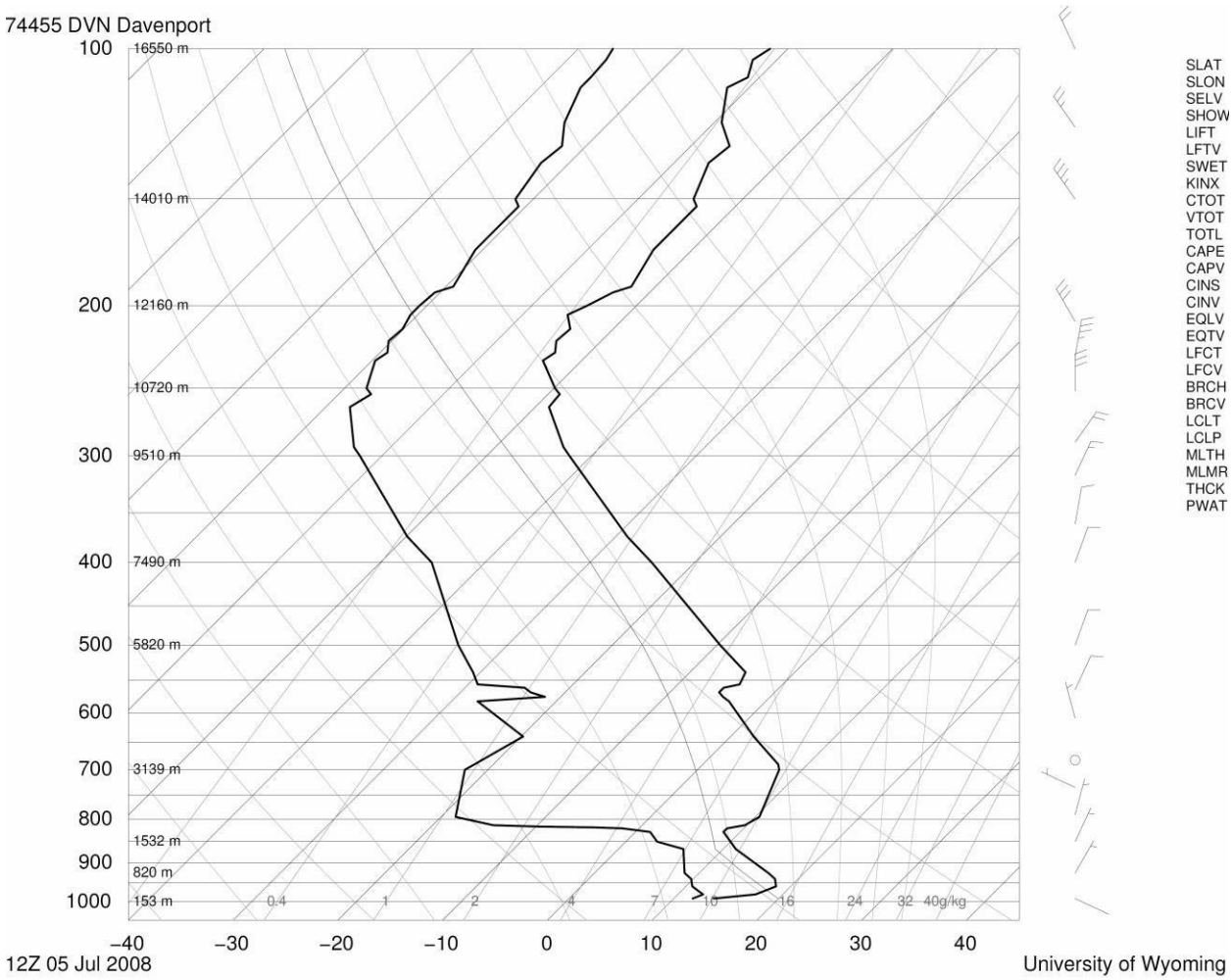

Chart B-3. Skew-T Diagram for the 7am (Local Time) Sounding on July 5, 2008, Courtesy University of Wyoming

EPA's AERMET calculator[23] can be used to estimate the mixing heights during the period after dusk on the 4th when fireworks displays were likely to have occurred (Table 1 below). AERMET was run using surface meteorology and upper air data from the KDVN ASOS station to determine hourly mixing heights. The calculator computes two mixing heights, convective and mechanical. During convective daytime hours the convective mixing height is used to compute dilutions (except in the early morning when mechanical mixing may still be dominant), then it switches to mechanical mixing heights to compute dilutions during non-convective hours. These estimates suggest that the mixing height was between 16 and 30 meters (50 and 100 ft) during the period of interest.

Table B-1. Estimated mixing heights after dusk on July 4th from EPA's AERMET calculations.

Date/Time	Convective (m)	Mechanical (m)
7/4/08 - 7pm	1654	97
7/4/08 - 8pm	Non-convective	30
7/4/08 - 9pm	Non-convective	16*
7/4/08 - 10pm	Non-convective	16*
7/4/08 - 11pm	Non-convective	29
Midnight	Non-convective	16*
7/5/08 - 1am	Non-convective	16*
7/5/08 - 2am	Non-convective	16*
7/5/08 - 3am	Non-convective	54

[23] http://www.epa.gov/scram001/metobsdata_procaccprogs.htm#aermet

Date/Time	Convective (m)	Mechanical (m)
7/5/08 - 4am	Non-convective	18*
7/5/08 - 5am	Non-convective	54
7/5/08 - 6am	Non-convective	31
7/5/08 - 7am	73	189

*Derived from filled wind data

Another method of estimating the mixing height is by examining the hourly surface temperature data from KDVN along with ambient monitoring locations in the Davenport area (Chart B-4 below). The surfacee temperature at KDVN is always colder than at Jefferson School during the period of interest. Moreover, the surface temperature at the Jefferson school monitor is always higher than at ambient monitors at lower elevations. This suggests that the mixing height was between the elevation of the Jefferson School and KDVN sites, between 700 ft and 750 ft (or between 160 and 220 ft above the river at the bottom of the valley). The reader should note that the temperature differences between sites used to establish the variability of the temperature with height are on the order of 1 deg C, and this is comparable to the accuracy of the temperature sensors at the ambient monitoring sites.

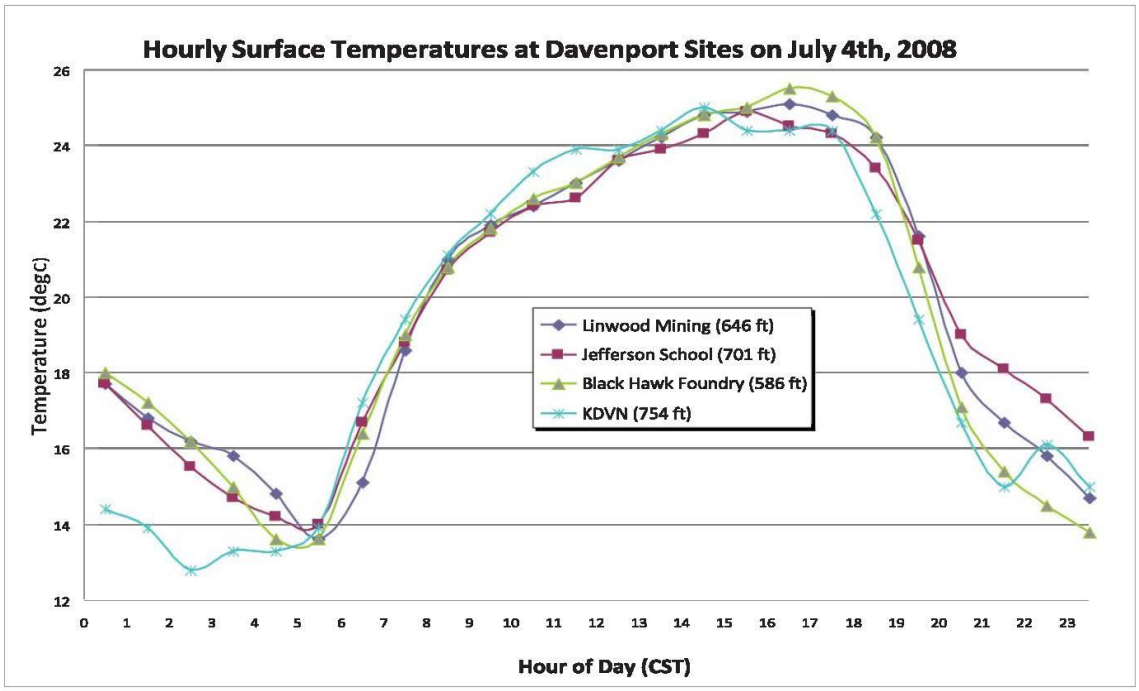

Chart B-4. Surface temperatures from the Davenport area on July 4th, 2008.

Appendix C. Iowa $PM_{2.5}$ FRM Monitors[24] 2008

AQS ID	Site	City	Address	County
190130008	Waterloo, Grout Museum	Waterloo	West Park St & South St	Black Hawk
190170011	Waverly, Airport	Waverly	Waverly Airport	Bremer
190450019	Clinton Chancy Park	Clinton	23rd & Camanche	Clinton
190450021	Clinton, Rainbow Park	Clinton	Roosevelt St	Clinton
190550001	Backbone State Park	Not in a city	Fish Hatchery	Delaware
191032001	Iowa City, Hoover School	Iowa City	2200 E Court	Johnson
191110008	Keokuk, Fire Station	Keokuk	111 S 13th St	Lee
191130037	Cedar Rapids, Army Reserve	Cedar Rapids	1599 Wenig Rd NE	Linn
191130040	Cedar Rapids, Public Health	Cedar Rapids	500 1th St NW	Linn
191370002	Viking Lake State Park	Not in a city	2780 Viking Lake Rd	Montgomery
191390015	Muscatine, Garfield School	Muscatine	1409 Wisconsin	Muscatine
191471002	Emmetsburg, Iowa Lakes College	Emmetsburg	Iowa Lakes Comm College, S Campus	Palo Alto
191530030	Des Moines, Public Health Bldg	Des Moines	1907 Carpenter	Polk
191530059	Des Moines, Bat By-Products	Des Moines	SE 18th & Scott St	Polk
191532510	Clive, Indian Hills School	Clive	9401 Indian Hills	Polk
191550009	Council Gluffs, Franklin School	Council Bluffs	3130 C Ave	Pottawattamie
191630015	Davenport, Jefferson School	Davenport	10th St & Vine St	Scott
191630018	Davenport, Adams School	Davenport	3029 N Division St	Scott
191630019	Davenport, BH Foundry	Davenport	300 Wellman St	Scott
191770006	Keosauqua, Lake Sugema	Not in a City	24430 Lacey Trl	Van Buren
191930017	Sioux City, Lowell School	Sioux City	27th at Morgan	Woodbury
191970004	Clarion, Jannsen Farm	Clarion	Jannsen Farm	Wright

[24] FRM Data summaries available at: http://www.epa.gov/air/data/

Appendix D. Results of XRF Analysis of the Exceedance Filter

Analyte	Concentration (ng/m^3)	MDL (ng/m^3)
K	13488.4	1.6
Cl	8681.7	2.0
Zn	4658.0	1.4
S	3539.3	3.0
Cu	143.2	0.5
Sr	216.4	0.9
Fe	98.3	0.6
Mg	654.9	4.6
Na	1949.3	16.1
Ca	81.6	1.9
Mn	15.7	0.7
Ti	22.9	1.8
Pb	21.5	2.0
Br	6.0	0.7
Co	3.6	0.5
Ba	16.1	4.1
V	4.0	1.2
Al	15.1	5.1
Ce	6.6	2.8
Tb	3.1	1.5
Hf	3.0	1.6
Zr	3.3	1.8
Se	1.4	0.8
Cr	1.5	0.9
Rb	1.1	0.7
La	4.4	3.2
Hg	4.2	3.8
Sc	15.0	14.9
Ni	0.3	0.5
Sb	5.7	16.8
Sn	1.9	12.8
Ag	0.0	5.9
As	0.0	0.7
Au	0.0	2.2
Cd	0.0	7.5
Cs	0.0	13.8
Eu	0.0	1.9
Ga	0.0	1.0
In	0.0	8.9
Ir	0.0	2.9
Mo	0.0	3.6
Nb	0.0	1.9
P	0.0	4.1
Si	0.0	4.5
Sm	0.0	1.9
Ta	0.0	4.0
W	0.0	3.0
Y	0.0	1.1

Appendix E. Comparison Historical XRF Data[25] with July 4, 2008 XRF Results

Summary of Historical CSN Values 2005-2007 (all values in ng/m^3)						July 4, 2008 FRM
Analyte	Minimum Conc.	25th %-tile Conc.	50th %-tile Conc.	75th %-tile Conc.	Maximum Conc.	Concentration (ng/m^3)
K	11	41	59	83	1920	13488
Cl	0	0	8	29	823	8682
Zn	0	8	12	19	204	4658
S	182	521	812	1325	7000	3539
Na	0	0	12	40	272	1949
Mg	0	0	2	16	137	655
Sr	0	0	0	1	41	216
Cu	0	1	2	4	50	143
Fe	5	33	51	79	540	98
Ca	1	33	56	105	642	82
Ti	0	0	2	4	39	23
Pb	0	3	5	8	103	21
Ba	0	0	0	1	1070	16
Mn	0	1	2	5	28	16
Al	0	0	13	27	91	15
Sc	0	0	0	0	137	15
Ce	0	0	0	1	319	7
Br	0	2	3	4	40	6
Sb	0	0	0	0	43	6
La	0	0	0	1	554	4
Hg	0	0	0	1	9	4
V	0	0	1	3	28	4
Co	0	0	0	0	2	4
Zr	0	0	0	0	8	3
Tb	0	0	0	1	22	3
Hf	0	0	0	0	14	3
Sn	0	0	0	1	20	2
Cr	0	0	0	1	12	1
Se	0	0	1	1	7	1
Rb	0	0	0	0	2	1
Ni	0	0	0	0	9	0
Ag	0	0	0	1	7	0
As	0	0	1	2	7	0
Au	0	0	0	0	3	0
Cd	0	0	0	0	13	0
Cs	0	0	0	0	684	0
Eu	0	0	0	0	20	0
Ga	0	0	0	0	3	0
In	0	0	0	0	9	0
Ir	0	0	0	0	4	0
Mo	0	0	0	0	4	0
Nb	0	0	0	0	4	0
P	0	0	0	0	7	0
Si	0	33	62	101	354	0
Sm	0	0	0	0	29	0
Ta	0	0	0	0	6	0
W	0	0	0	0	6	0
Y	0	0	0	0	2	0

[25] Historical Speciation data is available at: http://www.epa.gov/cgi-bin/htmSQL/mxplorer/query_spe.hsql

Appendix F. Signal Strength Analysis

Ratio of Concentration to Method Detection Limit			
Analyte	July 4, 2008 Exceedance Filter	Historical Maximum 2005-2007	Historical Maximum 2005-2007 Excluding 7/3/05, 7/4/06, and 7/5/07
K	8519	436	95
Cl	4341	183	183
Zn	3288	283	283
S	1196	2000	2000
Cu	264	63	63
Sr	236	59	6
Fe	168	783	783
Mg	143	19	19
Na	121	12	12
Ca	43	214	214
Mn	22	23	23
Ti	13	20	14
Pb	11	94	2
Br	9	74	74
Co	8	2	2
Ba	4	261	261
V	3	22	22
Al	3	10	10
Ce	2	97	97
Tb	2	12	12
Hf	2	1	1
Zr	2	6	6
Se	2	6	6
Cr	2	12	12
Rb	2	2	2
La	1	158	158
Hg	1	6	6
Sc	1	27	27
Ni	1	19	19
Sb	0	6	6
Sn	0	2	2
Ag	0	1	1
As	0	11	11
Au	0	2	2
Cd	0	2	2
Cs	0	171	171
Eu	0	10	10
Ga	0	1	1
In	0	1	1
Ir	0	3	3
Mo	0	1	1
Nb	0	2	2
P	0	2	94
Si	0	107	107
Sm	0	17	17
Ta	0	1	1
W	0	1	1
Y	0	2	2

Legend
1000 < Ratio ≤ 10000
100 < Ratio ≤ 1000
10 < Ratio ≤ 100
1 ≤ Ratio ≤ 10
Ratio = 0