Supplemental Information Concerning the October 30, 2003 Exceptional Event

Prepared by the Technical Services Program
Air Pollution Control Division
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PM_{10} Filter Chemical Speciation

The Colorado Department of Public Health and Environment (CDPHE) Air Pollution Control Division (APCD) annually identifies particulate matter filters for chemical speciation. Typically, the filter selection process begins in April and encompasses all filters back one year to the terminating bookend of the previous year's filter selection time period. The identified filters are shipped to a contract lab for speciation analysis in May with deliverables received by no later than June 30th. PM_{10} filters with concentrations in excess of 120 µg/m^3 STP (standard temperature and pressure), are automatically identified for chemical speciation and are archived in a refrigerated environment until shipment to a contract laboratory in May. Additionally, lower concentration particulate matter filters (<120 µg/m^3 STP), which are of interest to APCD, are also selected for chemical speciation. These filters are typically identified in April and stored at room temperature post gravimetric weighing. The distinction between filters archived in a refrigerated environment versus at room temperature may be of significance when observing volatile and semi-volatile particulate matter data.

A total of nine PM_{10} filters collected during the October 30, 2003 event were selected for chemical speciation. The following Table 1 lists basic sample information and the analytical methods applied to each filter. Analytical results from the contract laboratory for these samples are given in (appendix A)

Table 1

Filter Number	Site	Sample Date	Sample Type	Concentration STP (µg/m3)	Analysis OC/EC	Analysis XRF (Protocol #4)	Analysis Anion (IC)	Analysis Cations (IC)
Q3031268	Crested Butte	10/30/2003	PM-10	177	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4
Q3031452	Delta	10/30/2003	PM-10	215	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4
Q3031796	Durango - Cutler	10/30/2003	PM-10	109	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4
Q3031790	Durango - Courthouse	10/30/2003	PM-10	90	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4
Q3031789	Durango - Park School	10/30/2003	PM-10	104	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4
Q3031792	Durango - River City Hall	10/30/2003	PM-10	97	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4
Q3036514	Grand Junction - Powell	10/30/2003	PM-10	234	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4
Q3031680	Mt. Crested Butte	10/30/2003	PM-10	165	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4
Q3032715	Pagosa Springs	10/30/2003	PM-10	111	Yes	Yes	Cl, NO_3, SO_4	K, Mg, Na NH_4

The information acquired through chemical speciation analyzes brings insight into the types of sources that may have impacted the sample. Of particular interest to the October 30, 2003 samples is wildfire smoke. Back trajectory analysis supported by satellite imagery suggests that in addition to blowing dust, western Colorado may have been impacted by smoke from wildfires in California and Arizona. If so, chemical artifacts from smoke will be entrained in particulate matter filters sampled during the event.

The 10/30/03 samples were collected during routine compliance monitoring using Federal Reference Method (FRM) PM_{10} high-volume samplers. The PM_{10} high-volume Federal Reference Method is a poor sampling method for chemically elucidating volatile and semi-volatile compounds, such as artifacts from smoke. Chemical compounds with high vapor pressures are poorly retained in quartz filters due to a large pressure drop across the filter and high face velocities. Colorado uses FRM high-volume samplers for compliance monitoring throughout the state and are therefore limited in the quality of chemical speciation results for events observed during compliance sampling.

There are several unique chemical components in smoke that can be analyzed in particulate matter filters. These are K^+:K ratio (ionic potassium to total potassium ratio) and OC:TC ratio (organic carbon to total carbon) in conjunction with the OC:GMC ratio (organic carbon to total gravimetric mass ratio). Geologic material and plant matter are the two common sources of potassium in the natural environment. Both ionic and non-ionic potassium are inherent in plant matter. The burning of plant matter releases potassium into the air at a ratio of ionic potassium to total potassium of approximately 0.8-0.9 ($PM_{2.5}$ CMB source profile) , which is in contrast to a ratio of 0.01-0.03 ($PM_{2.5}$ CMB source profile) in re-suspended geologic material (Reference 1). Elevated ionic potassium concentrations are not prevalent in fossil fuels and are therefore an indication of biomass burning. OC:TC is the ratio of organic carbon to total carbon (total carbon = organic carbon + elemental carbon) and OC:GMC is the ratio of organic carbon to the total gravimetric mass. Organic carbon is abundant in wildfire smoke at an approximate ratio of organic carbon to total carbon OC:TC of 0.94 (Reference 1). Wind blown dust also has a high OC:TC ratio but a low OC/GMC ratio because its geologic component dominates the total mass of the sample. Samples not impacted by dust and heavily impacted by smoke will have a high OC:TC ratio in conjunction with an elevated OC:GMC ratio.

Listed below in the following tables and figures are two types of mass concentrations, Gravimetric Mass Concentration (GMC) and Reconstructed Mass Concentration (RCM). Gravimetric Mass Concentration is the value that is produced by the gravimetric laboratory and is the value that is reported to EPA's Air Quality System (AQS). Reconstructed Mass Concentration is an estimated value that is derived from a method that uses chemical speciation data to reconstruct the basic building blocks of particulate matter. The method that is used to create the reconstructed masses and their associated profiles is described in detail in APCD's annual technical note for particulate filter chemical speciation results (Reference 2). The RCM value is estimated and will therefore not always correlate well with the GMC value. Comparisons of the RCM and the GMC values are used as a measure of the reconstruction method's accuracy.

Table 2 lists the absolute concentrations for all the potassium and carbon species and K^+:K, OC:TC and OC:GMC ratios for all the 10/30/03 samples. These values are to be compared to data from known smoke and high wind dust events in Figure 1. Figure 1 lists the K^+:K, OC:TC and OC:GMC ratios and the reconstructed mass profiles for two June 2002, Hayman Fire smoke events at the Commerce City and Denver Visitor Center sites and two known high-wind dust events at Lamar and Alamosa. These events are unique because they offer clear examples of smoke and dust events without a lot of impact from other sources. The two Hayman Fire smoke event samples are heavily impacted by smoke, however, they also contain a sizeable dust component, as observed by the geologic fraction in the reconstructed mass profiles. It is expected that a sizable geologic fraction will exist in all ambient PM_{10} samples. Sizable increases in organic carbon, elemental carbon, sulfates and nitrates are an anomaly and indicate sources other than blown dust.

Table 2

Site / Date	Grav. Mass (GMC) $\mu g/m^3$ STP	K^+ (ionic) $\mu g/m^3$ STP	K (elemental) $\mu g/m^3$ STP	OC (Organic Carbon) $\mu g/m^3$ STP	TC (Total Carbon) $\mu g/m^3$ STP	K^+/K Ratio	OC / TC Ratio	OC / GMC Ratio
Crested Butte (10/30/03)	177	0.39	3.19	16.97	20.50	**0.12**	**0.83**	**0.10**
Delta (10/30/03)	215	0.82	3.77	25.24	26.89	**0.22**	**0.94**	**0.12**
Durango – Cutler (10/30/03)	109	0.66	1.98	22.21	24.08	**0.33**	**0.92**	**0.20**
Durango – Courthouse (10/30/03)	90	0.57	1.82	19.44	21.39	**0.31**	**0.91**	**0.22**
Durango - Park School (10/30/03)	104	0.58	1.97	20.14	21.96	**0.30**	**0.92**	**0.19**
Durango - River City Hall (10/30/03)	97	0.55	1.92	19.76	22.19	**0.29**	**0.89**	**0.20**
Grand Junction – Powell (10/30/03)	234	0.72	3.59	22.84	24.55	**0.20**	**0.93**	**0.10**
Mt. Crested Butte (10/30/03)	165	0.87	2.87	25.74	27.20	**0.30**	**0.95**	**0.16**
Pagosa Springs (10/30/03)	111	0.40	1.72	12.35	13.82	**0.23**	**0.89**	**0.11**

Figure 1

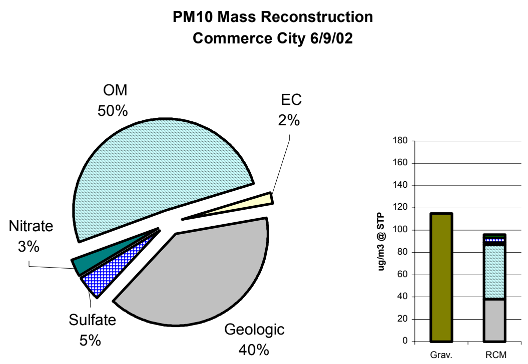
Example: Hayman Smoke Events

Commerce City 6/9/02

K^+/K ratio = 0.49

OC/TC ratio = 0.95

OC/GMC ratio = 0.30

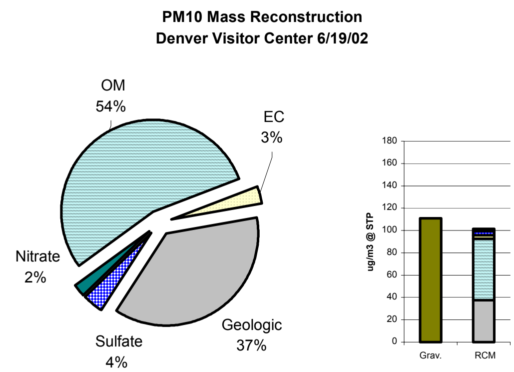


Denver Visitor Center 6/19/02

K^+/K ratio = 0.25

OC/TC ratio = 0.93

OC/GMC ratio = 0.35



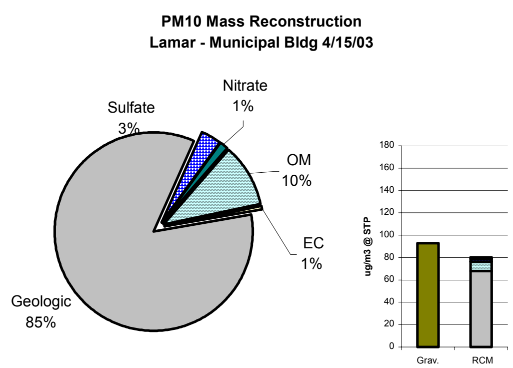
Example: High Wind Dust Events

Lamar – Municipal Bldg. 4/15/03

K^+/K ratio = 0.08

OC/TC ratio = 0.93

OC/GMC ratio = 0.06

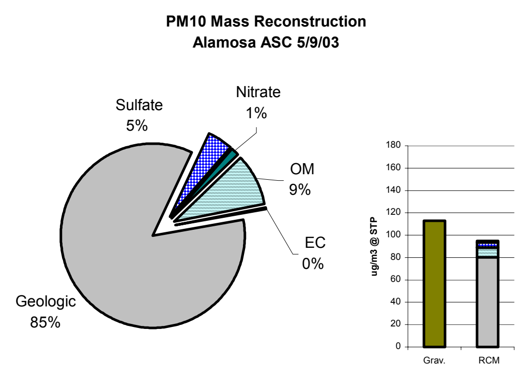


Alamosa - ASC 5/9/03

K^+/K ratio = 0.07

OC/TC ratio = 0.95

OC/GMC ratio = 0.06



OM = Estimation of Organic Matter (proportional to organic carbon)
EC = Estimation of Elemental Carbon
Nitrate = Estimation of all Nitrate species (proportional to nitrate ion concentration)
Sulfate = Estimation of all Sulfate species (proportional to sulfate ion concentration)
Geologic Material = Estimation of all Geologic Material (proportional to iron concentration)

The use of reconstruction mass profiles (also known as mass balance profiles) in Figures 1, 2, & 3 are a quick and practical way of summarizing chemical speciation data, and is commonly used in the development of receptor model studies. The pie chart in each figure represents reconstructed mass values that are normalized to total reconstructed mass (RCM). The bar chart to the right of the pie chart compares the actual gravimetric mass concentration (GMC) to the summation of all reconstructed mass fractions (RCM).

Reconstructed mass profiles for all the 10/30/03 PM_{10} samples are portrayed in Figures 2 and 3. These reconstructed mass profiles can be used in combination with information in Table 2 to assess the magnitude of the smoke and dust signatures in each sample. The 10/30/03 event is known to have a dust component and is suspected to have a smoke component. When held in context to the examples in Figure 1, the K^+:K ratio data in Table 2 indicate the presence of a smoke signature in all samples, with the Durango samples most apparent. Amongst the four examples, on average, the Hayman Fire examples had K^+:K ratios (~0.37) 4 times greater than the high-wind dust examples (~0.08). All the 10/30/03 samples that have K^+:K ratios greater than twice that of the high-wind dust examples (~0.16) and are characterized as having a distinct K^+:K smoke signature. All of the 10/30/03 samples except for Crested Butte had K^+:K ratios greater than or equal to 0.20. The Crested Butte sample has a K^+:K ratio of 0.12 which is one and a half times greater than the high-wind dust examples, and possesses only a slight K^+:K smoke signature. A low K^+:K ratio does not mean the sample has not been impacted by smoke from biomass burning, but rather a strong smoke signature does not exist. A sample that is impacted by both smoke and dust will have increased elemental potassium, which is contributed by the dust. Increased elemental potassium will increase the total potassium, thus lowering the K^+:K ratio and effectively diluting the smoke signature.

A high OC:TC ratio in conjunction with and elevated OC:GMC ratio is characteristic of smoke from biomass burning. Amongst the four examples, on average, the Hayman Fire examples had OC:TC ratios (~0.94) are proportional to those of the high-wind dust examples (~0.94). This is to be expected because smoke and dust have similar OC:TC ratios. All of the 10/30/03 samples except for Crested Butte had OC:TC ratios greater than or equal to 0.89, with and average of 0.91. The Crested Butte sample has a OC:TC ratio 0.83. A lower OC:TC ratio tends to indicate emissions from fossil fuel combustion, such as vehicles. Amongst the four examples, on average in Figure 1, the Hayman Fire examples had OC:GMC ratios (~0.33) 5 times greater than the high-wind dust examples (~0.06). Six of the nine 10/30/03 samples had OC:GMC ratios greater than or equal to twice that of the high-wind examples (~0.12) and are characterized as having a distinct OC:GMC smoke signature. The Crested Butte, Grand Junction and Pagosa Springs had OC:GMC ratios greater than one and a half that of the high-wind examples (~0.09) and are characterized as having a slight OC:GMC smoke signature. If smoke was indeed present, then OC:GMC ratio is a good indication of how significant the smoke was relative to the total mass of the sample.

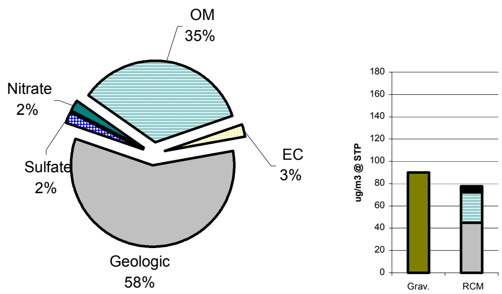
By evaluating the K^+:K, OC:TC and OC:GMC ratios together, a more accurate assessment of a smoke signature is attained. For most of the 10/30/03 samples, an assessment of just one of the ratios by themselves would seem inconclusive. However, when held in context to one another, a smoke signature becomes apparent. The Durango samples appear to have the most pronounced smoke signatures, which is most likely caused by the absence of a large dust component. The Grand Junction, Delta, Mt. Crested Butte and Pagosa Springs samples appear to have a less pronounced smoke signature, which is probably caused by a larger dust contribution, effectively diluting the smoke signature. The Crested Butte sample has the least pronounced smoke signature. This leads to the question: Why the difference between the Crested Butte and Mt. Crested Butte samples? This could be explained by an early morning inversion, which prohibited the mixing of upper air down into the valley. Meteorological reports (see Section 2, Technical Support Document for the October 30, 2003 Natural Event) suggest that across western Colorado, haze associated with smoke was most apparent in the early morning hours followed by high winds and blowing dust later in the afternoon. An inversion in the early morning could have prevented smoke in the upper air from mixing down low in the valley near town. The site at Mt. Crested Butte is significantly higher than the site in the town of Crested Butte and quite possibly above the valley inversion level on that day.

Increases of ionic potassium and organic carbon in PM_{10} samples, beyond what is typically expected for dust, is an indication of smoke from biomass burning. All the 10/30/03 samples appear to contain a smoke signature. Samples with the most pronounced smoke signature occurred in Durango and the least pronounced in the town of Crested Butte. The Grand Junction, Delta, Crested Butte, Mt. Crested Butte and Pagosa Springs samples have weaker smoke signatures that are probably a dilution effect caused by an increased blowing dust component. Because a smoke signature exists in these samples, the signature does not indicate from where the smoke originated. Possible sources include, but are not limited to, local slash burning, residential wood burning, and wildfire smoke transported from California and Arizona. Back trajectory analysis, satellite imagery, first hand observations and PM_{10} samples with the smoke signatures being regional in scope, provides merit to the hypotheses that smoke transported from wildfires in California and Arizona did impact western Colorado. The methods used in this document for the identification of a smoke signature with chemical speciation data are more qualitative than quantitative. Attempts to qualitatively apportion a smoke signature out of any ambient air sample will result in a certain amount of ambiguity. Because of this ambiguity, the result should not be taken out of context as absolute. If a more comprehensive analysis is required, it is recommended a receptor model be employed. Receptor models may provide a much higher quantitative analysis in which uncertainties are thoughouly evaluated.

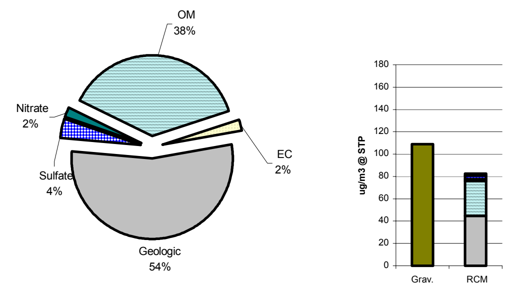
Figure 2

Reconstructed Mass Profiles For Durango and Pagosa Springs PM_{10} Filters October 30, 2003

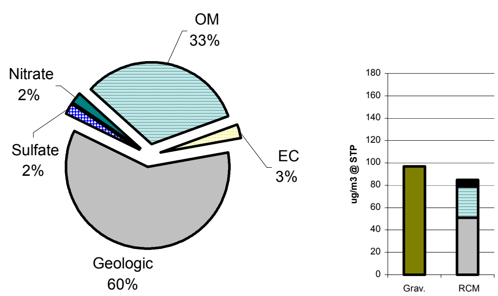
PM10 Mass Reconstruction
Durango - Courthouse 10/30/03



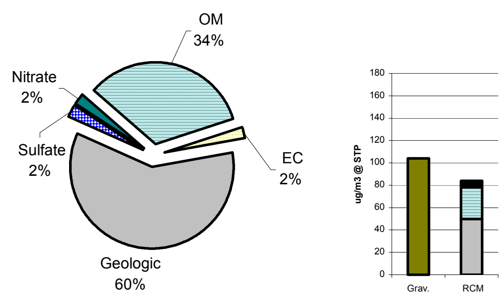
PM10 Mass Reconstruction
Durango - Cutler 10/30/03



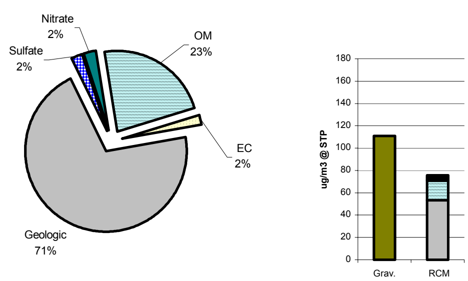
PM10 Mass Reconstruction
Durango - River City Hall 10/30/03



PM10 Mass Reconstruction
Durango - School 10/30/03



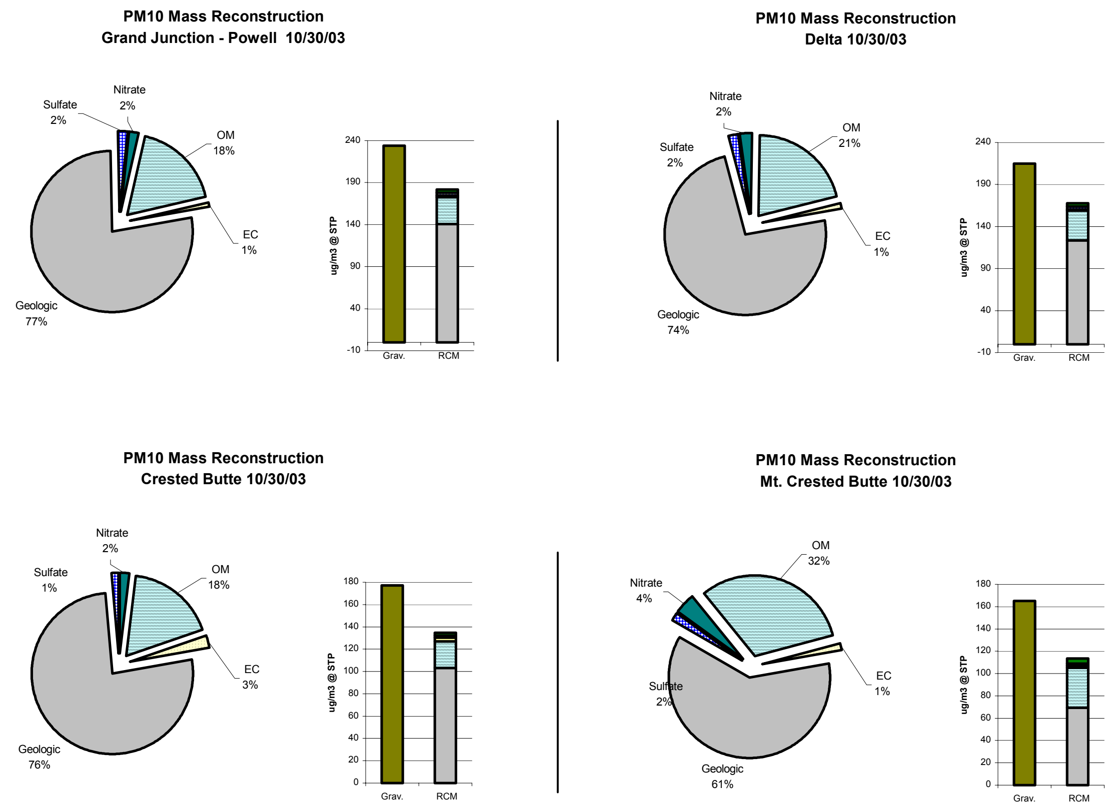
PM10 Mass Reconstruction
Pagosa Springs 10/30/03



OM = Estimation of Organic Matter (proportional to organic carbon)
EC = Estimation of Elemental Carbon
Nitrate = Estimation of all Nitrate species (proportional to nitrate ion concentration)
Sulfate = Estimation of all Sulfate species (proportional to sulfate ion concentration)
Geologic Material = Estimation of all Geologic Material (proportional to iron concentration)

Figure 3

Reconstructed Mass Profiles For
Grand Junction, Delta, Crested Butte and Mt. Crested Butte PM_{10} Filters
October 30, 2003



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References:

1. Watson J.G., Zhu T., Chow J.C., Engelbrech J., Fujita E.M., Wilson W.E. Receptor modeling application framework for particle source apportionment. Chemosphere 49:9 1093-1136.

2. Colorado Department of Public Health and Environment Technical Note. “Summary of Chemical Speciation Results from Select TSP, PM_{10} and $PM_{2.5}$ Particulate Samples, May 2002 to April 2003” April 2004.

Appendix A