The Impact of Hobby Rocket Motors on Atmospheric Fine Particle Zinc Concentrations

Andrew P. Rutter[1*], James J. Schauer[1,2], Charles C. Christensen[1], Martin M. Shafer[1,2], Michael F. Arndt[2]

[1] *Environmental Chemistry and Technology Program, 660 N. Park Street, University of Wisconsin- Madison, Madison, WI 53706*

[2] *Wisconsin State Laboratory of Hygiene, University of Wisconsin- Madison, 2601 Agriculture Drive, Madison, WI 53718*

Abstract

Zinc concentrations in hobby rocket exhaust aerosols were measured by ICP-MS to be approximately 300 mg/g, revealing that hobby rocket motors emit particulate matter highly enriched in zinc. Zinc is a commonly used indicator species in receptor models for atmospheric particulate matter and is assumed to be emitted only by well-established point sources and mobile sources. The potential impact of the ephemeral particle-bound zinc from hobby rockets on atmospheric particulate zinc concentrations was estimated using a Gaussian puff model. The results from the model were compared to 24-hour averaged particulate zinc concentration data collected in three US urban centers. Potential impacts several kilometers downwind of the rocket launch site were found to be significant. Clearly the impact of ephemeral and unregistered emissions such as those from hobby rockets needs to be considered when using zinc in source apportionment models.

Keywords: Aerosol; Indicator species; Positive matrix factorization; Source apportionment; Bias.

[*] Corresponding author. Tel.: 608- 262-4322, Fax: 608- 262-0454

E-*mail address*: aprutter@wisc.edu

INTRODUCTION

Trace metals are widely used as source indicators for atmospheric particulate matter in receptor modeling studies (Chueinta *et al.*, 2000, Ramadan *et al.*, 2000, Song *et al.*, 2001, Shah *et al.*, 2004, Zhou *et al.*, 2004, Bennet *et al.*, 2005, Lough *et al.*, 2005, Schauer *et al.*, 2006). In most cases, the sources which are considered in a model are limited to well-established stationary or mobile sources that are known to emit large volumes of particles of a previously determined trace metal composition. It is often assumed that sources that emit smaller masses of particles, and which may also be ephemeral in nature, are not sufficiently enriched in the indicator species of interest to significantly contribute to the chemistry of particles collected at a receptor.

Zinc is widely used as an indicator species for aerosol emissions from smelters, municipal waste incinerators, automobiles and motorcycles (Chueinta *et al.*, 2000, Ramadan *et al.*, 2000, Song *et al.*, 2001, Shah *et al.*, 2004, Zhou *et al.*, 2004, Bennet *et al.*, 2005, Lough *et al.*, 2005, Schauer *et al.*, 2006). Hobby rocket fuel is predominantly made of zinc and ammonium perchlorate (NH_4ClO_4). Therefore, it is reasonable to assume that the particulate matter emitted by hobby rockets is likely to be greatly enriched in zinc and chloride. Emissions of particles that are greatly enriched in zinc can significantly impact 24-hour averaged $PM_{2.5}$ (particles less than 2.5 μm in diameter) and PM_{10} (particles less than 10 μm in diameter) zinc concentrations without greatly impacting total particle mass. As is the case with many small point sources, hobby rockets are not expected to contribute significantly to the zinc content of atmospheric particles on a regional scale, but may significantly impact a sampler that is downwind of a location where rockets are being launched. Size distributions of hobby rocket particle emissions have not previously been characterized. This information is necessary for determining the exact influence of the emitted particles on $PM_{2.5}$ and PM_{10} concentrations.

The aim of this study was to reinforce the idea that sources emitting relatively small masses of particles highly enriched in an indicator species may bias receptor models. The size distribution and chemical fingerprint data of the particle emissions from hobby rockets were measured and these results were used to estimate the potential impact of hobby rockets on 24-hour averaged zinc concentrations in atmospheric particulate matter at three US urban centers.

METHODOLOGY

Four types of hobby rocket motors were discharged into a residence chamber and samples of the diluted exhaust particulate matter were collected on filters. The specific models of rocket used for the experiments are shown in Table 1 along with manufacturer and number of motors in

each composite. All are small enough not to be subject to FAA or other governmental restrictions, so are freely available to the general public on the open market.

The residence chamber used for sampling and collection has previously been described in detail (Hildemann *et al.*, 1989, Hildemann *et al.*, 1991a, b) and will only be briefly discussed here. A schematic of the apparatus is presented in Fig. 1. The residence chamber was an upright cylinder made of stainless steel, 1.5 m in height and 0.25 m in internal diameter. The rocket motors were discharged into the top of the residence chamber through an access port in the side wall. In some experiments, several motors were discharged into the residence chamber at once to provide a composite sample. The particulate matter in the residence chamber was then diluted with ambient air in order to permit filter collection of the particulate matter. Composite samples were made for several tests to increase the mass of diluted particulate matter collected by the sampling trains. The diluted exhaust aerosols were sampled using two $PM_{2.5}$ cyclones (Thermo-Andersen Instruments) and two Micro-Orifice Uniform Deposit Impactors (MOUDI; MSP Corporation, Minneapolis, MN). The $PM_{2.5}$ cyclones and MOUDIs were operated at 8.0 liters per minute (L/min) and 30 L/min, respectively, using downstream vacuum pumps controlled by critical orifices. The chamber was backfilled with room air.

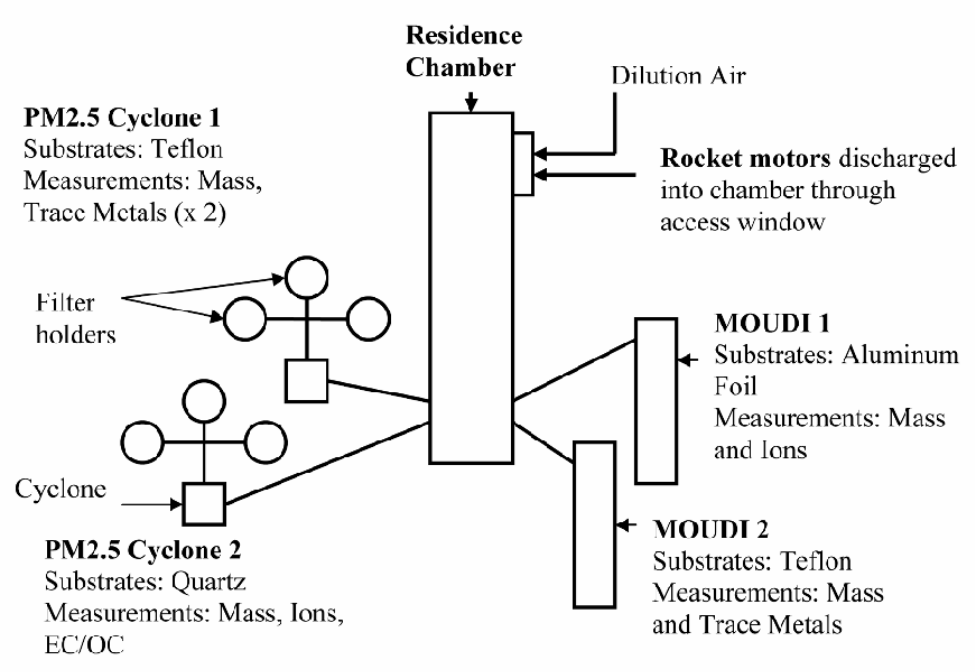

Fig. 1. Schematic of apparatus used to collect particles emitted by rockets.

Table 1. Rocket information, particle collection technique and composite information for each experiment.

Experiment	Rocket motor	Manufacturer	Collection Technique(s)						Motors per Composite
			$PM_{2.5}$			MOUDI			
			Mass	Metals	Ions	Mass	Metals	Ions	
1	White Lightning F20-7W	Aerotech	Y	Y	Y	N	N	N	1
2	Blue Thunder G-80-4T	Aerotech	Y	Y	Y	N	N	N	1
3	Black Jack F12-5	Aerotech	Y	Y	Y	N	N	N	1
4	Black Jack F12-5	Aerotech	Y	Y	Y	N	N	N	1
5	White Lightning F20-7W	Aerotech	Y	Y	Y	N	N	N	1
6	Blue Thunder G-80-4T	Aerotech	Y	Y	Y	Y	N	N	4
7	White Lightning F20-7W	Aerotech	Y	Y	Y	Y	N	N	2
8	Black Jack F12-5	Aerotech	Y	Y	Y	Y	Y	Y	2
9	Blue Thunder G-80-4T	Aerotech	Y	Y	Y	Y	N	N	1
10	White Lightning F20-7W	Aerotech	Y	Y	Y	Y	N	N	1
11	Black Jack F12-5	Aerotech	Y	Y	Y	Y	N	N	1
12	Estes	Estes	Y	Y	Y	N	N	N	4

Three filter packs (URG, Corporation, Chapel Hill, NC) were used on each cyclone to obtain mass and chemical speciation data. Teflon substrates (Teflo®, 2 μm, 47 mm Pall Life Sciences, East Hills, NY) were used in one $PM_{2.5}$ cyclone, whilst pre-baked quartz substrates (47mm Pall Life Sciences, East Hills, NY) were used in the other. Likewise, pre-baked aluminum-foil substrates were used in one MOUDI whilst Teflon substrates (47 mm Pall Life Sciences, East Hills, NY) were used in the other. Each MOUDI contains 12 stages that provide cutpoints ranging from 56 nm to 18 μm, along with an after filter to collect particles with aerodynamic diameters < 56 nm. In our analyses, we considered only the substrates that collected particles between < 56 nm and 5 μm in order to make a direct mass and chemical comparison with the samples collected by the $PM_{2.5}$ cyclones.

The filters were analyzed for: i) total mass; ii) ions such as chloride, sulfate, nitrate and ammonium; iii) trace metals, and; iv) elemental and organic carbon. Fig. 1 shows where in the sampling train each type of filter was used, and what analyses were performed on them. Teflon substrates were used in both $PM_{2.5}$ cyclone $^{\#}1$ and MOUDI $^{\#}1$ to measure the total and size-dependent mass and trace metal characteristics of the particles. Quartz-fiber filters were used in $PM_{2.5}$ Cyclone $^{\#}2$ to determine the mass, ion (Cl^-, SO_4^{2-}, NO_3^- and NH_4^+), elemental carbon and organic carbon content of the particles (Schauer *et al.*, 2003, Lough *et al.*, 2005). Aluminum foil substrates were used in MOUDI $^{\#}2$ to determine size-dependent ion contents of the particles. Loading blanks were performed for all of the $PM_{2.5}$ cyclone filter holders and all of the stages of both MOUDIs, which were subsequently used in blank correcting the data.

All substrates were cleaned before sampling. Teflon substrates were leached with trace metal grade 2N HCl and 2N HNO_3 by sequentially drawing the acids through a filter holder. The substrates were then washed with 18MΩ (Milli-Q) deionized water, then finally air-dried in a HEPA-filtered laminar flow hood. The cleaned Teflon substrates were transported and stored in acid leached polystyrene Petri dishes. Once loaded with the clean substrates the Petri dishes were tripled bagged and handled using trace metal clean handling techniques. All stages of the cleaning processes for the trace metal substrates and Petri dishes were conducted in a trace metals clean room. Quartz substrates were used for total mass, ion and EC/OC analyses. To prepare them for use, the substrates were baked for 12 hours at 550°C and stored in polystyrene Petri dishes lined with foil also baked to 550°C. Aluminum foils used for mass and ion analyses were baked for 12 hours at 550°C before use. All Teflon, quartz and aluminum substrates designated for mass analyses were preweighed after being cleaned.

The metal compositions of the particles were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, PQ Excell, ThermoElemental). Particulate matter deposited on the Teflon substrates from Cyclone $^{\#}1$ and MOUD1 $^{\#}1$ was dissolved by microwave-assisted acid digestion (HCl, HNO_3, HF) using techniques developed for the analysis of trace metals in ambient aerosol samples. These techniques permit sample solubilization with minimal

contamination (Schauer *et al.*, 2006, Lough *et al.*, 2005). The digestates were analyzed for a large suite of metals (refer to Supporting Information), although only Zn, Na, Ca, Mg, Al, K, Fe, Cr, Ni, Cu, Ti, Pb, Mn, Se, Pd, Cd, Zr, Ag and V were detected. Most elements were measured using standard plasma conditions (1350 watts forward power) and a desolvating microconcentric nebulizer (MCN6000, CETAC Technologies Inc.). Lighter elements (Na, K, Ca, Al, Mg and Fe) are impacted by polyatomic interferences in standard plasma mode and were therefore measured under cool plasma/shielded torch conditions. Propagated uncertainties from the ICP-MS analysis were calculated from the standard deviation of field blank measurements and standard deviation of replicate analyses of Standard Reference Materials (SRMs, NIST). To verify metal recoveries during analyses, 3 different SRMs were digested and analyzed in duplicate to give 6 recovery standards with every batch of 25 samples.

Mass analyses of samples on preweighed filters were performed using a microbalance (Metler MX-5) in a temperature and humidity controlled room following a 24-hour equilibration period. The average measurement precision was approximately 9%.

Sulfate, nitrate, chloride and ammonium were analyzed by ion chromatography (IC) after a water extraction of the quartz and foil substrates.

Elemental and organic carbon (EC/OC) were measured with a thermo-optical analyzer (Sunset Laboratory, Inc., Forest Grove, OR) using the NIOSH 5040 method (Schauer *et al.*, 2003).

Mass and chemical composition data for particles collected on the $PM_{2.5}$ cyclone filters are available for all of the experiments performed, while mass and chemical data from particles collected using the MOUDIs are restricted to experiments 6-11 and 8, respectively. All of the analyses were performed at the Wisconsin State Laboratory of Hygiene, Madison, WI.

To determine whether or not hobby rockets could cause a measurable interference in an atmospheric particle sampler we used a Gaussian puff model to simulate the emissions from a hobby rocket launch and calculated the mass of particulate zinc that would be deposited on an air sampling filter during a 24-hour collection cycle. The result from this calculation was compared with zinc contents of urban PM_{10} collected in Milwaukee, WI, Waukesha, WI, and Denver, CO (Lough, 2004). The Milwaukee sampling site (MKE) was located on top of the 16th Street Community Center, a three-story building close to downtown on the corner of 16th and Greenfield streets. The area is mixed residential and business district with constant road traffic. The Waukesha sampling site (WKA) was located 20 km west of the Milwaukee site on Cleveland Street close to the four-lane suburban highway 18/JJ. The sampler was located on a platform elevated 1 m above the ground. The area is mixed residential and industry with the sampling site located right next to a vehicle body repair workshop. The PM_{10} emissions of zinc listed for the Milwaukee, WI-Chicago, IL corridor in the EPA Toxics Release Inventory (TRI) were dominated by emissions from non-ferrous smelting and steel mills, but also included

smaller zinc emissions from electric power stations, metal plating and coating businesses, and lubricant manufacturers (USEPA, 2001).

The Denver sampling site (DEN) was located on a two-story building in a mixed residential and industrial area of central Adams County. The PM_{10} zinc emissions listed in the TRI for the Denver area were from electric power stations and metal plating facilities (USEPA, 2001). In addition, the Denver site was located near road traffic. Both cities are considered representative of urban centers with industrial areas and have high traffic densities Samples were collected using 24-hour sampling cycles combined with the EPA 6th day sampling schedule for one year, providing approximately 50 samples from each site. The average zinc concentrations in PM_{10} at the MKE, WKA and DEN sites were 0.018 ± 0.015 μg/m^3, 0.022 ± 0.022 μg/m^3 and 0.033 ± 0.03 μg/m^3, respectively (Lough, 2004).

A reflective Gaussian puff model was used to assess the zinc interference from rocket launches. A reflective, rather than an absorbing, model was chosen, as it was believed that the dry deposition of the majority of the particles detected in the exhaust aerosol would be minimal over the advection distances of interest. To test this hypothesis, the ratio of the mean particle diameter deposition velocity to the eddy correlation coefficient, described by Eqs. (1) and (2), was calculated (Seinfeld and Pandis, 1998).

$$\beta = \frac{\upsilon_d}{K_{zz}} \tag{1}$$

where

$$K_{zz} = \frac{1}{2}\sigma_z^2 \tag{2}$$

where ν_d is the particle settling velocity, K_{zz} is the eddy correlation coefficient of the atmosphere in the vertical direction and σ_z is the Pasquill-Gifford parameter in the vertical direction. For a perfectly reflecting puff, $\beta = 0$, meaning that turbulent eddy diffusion dominates over gravitational deposition in the motion of the particle in the vertical direction. Conversely, for a perfectly absorbing puff, $\beta = \infty$. Values of β were calculated for particles at the minimum and maximum size limits of the size distributions presented in Figs. 3 and 4 to assess whether or not a reflecting or an absorbing puff should be used to model the rocket emissions. Particle deposition velocities (ν_d) of 3×10^{-8} m/s and 8×10^{-2} m/s were calculated for particles 50 nm and 5 μm in diameter. A K_{zz} value of 500 m at 1km was calculated for a stability class D, where σ_z = 31.5 m. The β values for 50 nm and 5 μm particles were calculated to be 6×10^{-11} 1/ms and 2×10^{-6} 1/ms, respectively. The low β values of the 50 nm and 5 μm particles showed that the vertical movement of all of the particles in the puff was dominated by turbulent eddy diffusion. Therefore, the transport of all of the particles in the puff could be approximated well by a

reflecting puff model. The reflecting Gaussian puff model is presented in Eq. (3) (Seinfeld and Pandis, 1998):

$$C(x,y,z)=\frac{q}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left(-\frac{\left(x-x'-\bar{u}(t-t')^2\right)}{2\sigma_x^2}-\frac{(y-y')^2}{2\sigma_y^2}\right)\times\left[\exp\left(-\frac{(z-z')^2}{2\sigma_z^2}\right)+\exp\left(-\frac{(z+z')^2}{2\sigma_z^2}\right)\right] \quad (3)$$

where C is the concentration of zinc in kg/m^3, q is the emission rate of zinc from the rocket in kg/s, $\bar{u}$ is the wind speed in m/s, and σ_x, σ_y and σ_z are the Pasquill-Gifford dispersion parameters in the x, y and z axes. The coordinates x, y and z describe the center of the puff at emission when $t = 0$, whereas x', y' and z' are the puff coordinates of the puff center sometime after emission (i.e. when $t = t'$).

The modeling was performed using the Aerotech F20-7W White Lightning motor (Econojet, 2004) for which an emission rate had to be determined. This was achieved by combining information about the propellant formulation, assumptions regarding the conversion of zinc to particulate matter and assuming that the entire exhaust plume left by the rocket could be reasonably modeled as a point source emitted at the midpoint of the exhaust trail. The height of the exhaust plume was calculated to be 100 m using the thrust curve and rocket mass provided by Aerotech. The Aerotech F20-7W White Lightning motor had a propellant load of 0.03 kg, 7% (2.1 g) of which was believed to be zinc (Stuart Davies, Michigan Tripoli Rocketry Association, pers. comm., 2005). Fuel formulations are proprietary so it was not possible to obtain the exact zinc content in the motors used. Our data indicate that the vast majority of the emitted particle mass is composed of the zinc and chloride from the ammonium perchlorate. Assuming that all of the zinc is converted to particles, only 26% of the entire fuel load forms particles in the rocket exhaust.

A neutral atmospheric lapse (stability class D) was used for the base case. The sampler was assigned an inlet altitude of 5 m to simulate a 2-m tall sampler on a raised platform. The exhaust plume is modeled as a puff assuming that negligible amounts of the PM will deposit on the ground and obstacles between the launch site and sampler. Annual plots of daily average wind speeds for Milwaukee (thus Waukesha also) over the past 3 years were used to determine an annual average wind speed of approximately 5 m/s (GLERL, 2005). The annual average wind speeds in Denver, CO were determined to be approximately 4 m/s (NCDC, 2001). Therefore, a wind speed of 5 m/s was used to represent all three urban environments.

The particulate zinc concentrations at the puff center were determined and converted into masses of zinc that would be collected on the filter in the sampler at the different distances from

the launch site. To do this, the time of exposure of the sampler to the puff was calculated from the wind speed and puff dispersion along the direction of the puff travel, σ_x (units of m).

RESULTS AND DISCUSSION

A comparison of the zinc, chloride, ammonium and total $PM_{2.5}$ masses determined from the MOUDI1 and $PM_{2.5}$ cyclones revealed no statistical differences, indicating good agreement between the two techniques.

The bulk chemistries of the exhaust particles from the White Lightening, Blue Thunder, Black Jack and Estes rocket motors are shown in Fig. 2a. The compositions of the White Lightning, Blue Thunder and Black Jack rockets were dominated by zinc and chloride with mass concentrations of 250-300 mg of Zn per gram of particle mass and approximately 200-300 mg of chloride per gram of particle mass. The propellant compositions for these rockets were assumed to be a mixtures of zinc, ammonium perchlorate and a polymeric binder, analogous to the aluminum, ammonium perchlorate and polymeric binder fuel used in the commercial solid rocket motors, SRMs (Rutter, 2002). The chemistry of the exhaust particles generated by the Estes motor was dominated by potassium and sulfate, with mass concentrations of approximately 300 mg/g and 500 mg/g respectively. These combustion products imply that fuel for the Estes rocket was black powder (carbon, potassium nitrate, and sulfur). Fireworks typically use black powder fuel rather than a fuel based on zinc. Zinc emissions from black powder fuels are demonstrated by the Estes rocket (see Fig. 2a) to be negligible. Previous publications have measured particles emitted from fireworks and did not report Zn as a major component (Liu *et al.*, 1997, Kulshrestha *et al.*, 2004, Drewnick *et al.*, 2006).

The elements and ions shown in Fig. 2a are presented in probable parent compounds in Fig. 2b. Since aluminum oxide (Al_2O_3) and hydrochloric acid (HCl) are the exhaust products of the aluminum-based SRMs (Rutter, 2002), zinc and chloride are assumed to be present as predominantly as zinc oxide (ZnO) and HCl, although the ammonium present in Fig. 2a suggests that some unburnt ammonium perchlorate might have been present in the particles. The reconstructed mass in the White Lightning, Blue Thunder and Black Jack rockets accounted for about 60-85% of the total mass in the zinc-based rockets, leaving 15-40% of the mass as chemically unresolved. The unresolved mass could have been due to water generated from the ammonium perchlorate and the polymeric binder combustion which together probably constitute 80% of the fuel mass (Rutter, 2002; Stuart Davies, Michigan Tripoli Rocketry Association, pers. comm., 2005). Over 80% of the mass is accounted for in the Estes rocket as potassium sulfate (K_2SO_4), leaving less than 20% unresolved. Negligible concentrations of elemental and organic carbon (EC and OC) were detected in particles collected from all of the rockets. Emission profiles showing the chemical fingerprints of each rocket type are provided in Table 2.

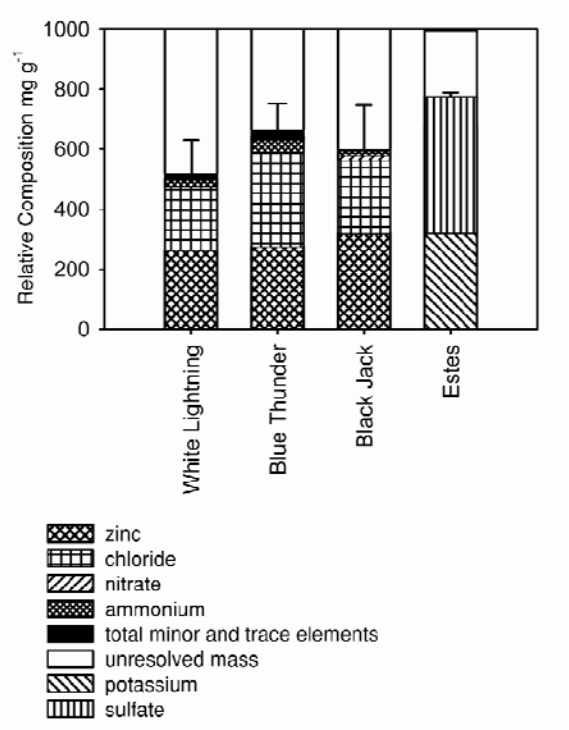

Fig. 2a. The bulk chemical compositions of the exhaust particles from the four different models of rocket motors used in this study.

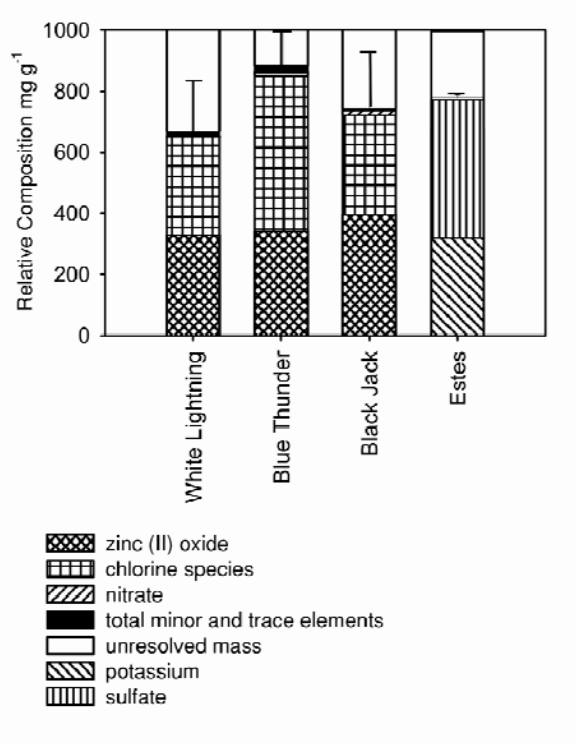

Fig. 2b. Reconstructed bulk chemistry for each of the rocket motor types studied. The chlorine species were assumed to be comprised of hydrochloric acid and unburnt ammonium perchlorate.

Table 2. Emission Profiles for Blue Thunder, White Lightening, Black Jack and Estes rockets. Data not in bold are not statistically different than zero.

Species	Blue Thunder mg/g	Uncertainty mg/g	White Lightening mg/g	Uncertainty mg/g	Black Jack mg/g	Uncertainty mg/g	Estes mg/g	Uncertainty mg/g
Zn	2.81E+02	1.09E+02	2.67E+02	1.29E+02	3.16E+02	1.45E+02	1.75E-03	3.92E-04
Cl	3.17E+02	2.36E+01	2.12E+02	1.83E+01	2.45E+02	2.10E+01	9.25E-01	3.96E-02
SO_4^{2-}	5.67E-01	3.11E-01	2.51E-01	1.93E-01	**0.00E+00**	**0.00E+00**	4.54E+02	9.55E+00
NH_4^+	9.14E+00	5.51E-01	1.33E+00	7.90E-02	1.67E+01	3.21E-01	3.52E-02	2.89E-04
NO_3^-	4.09E+01	5.86E-01	2.30E+01	4.50E-01	**1.49E+01**	**1.62E+01**	1.79E+00	5.43E-01
Na	2.23E-01	1.30E-01	**1.12E-01**	**1.42E-01**	**1.80E-01**	**5.08E+00**	1.35E-03	2.77E-04
Ca	1.69E-01	2.44E-01	1.45E+00	1.08E+00	**2.34E-01**	**1.06E+01**	4.89E-01	1.52E-01
Mg	3.18E-02	2.41E-02	1.12E+01	6.36E+00	**3.43E-02**	**1.16E+00**	7.79E-02	1.80E-02
K	1.18E+01	6.74E+00	7.54E+00	3.29E+00	6.93E-01	5.70E-01	3.17E+02	6.42E+01
Al	1.51E+00	8.28E-01	**4.74E-02**	**6.10E-02**	**2.20E-01**	**2.03E+00**	**4.02E-03**	**2.26E-02**
V	4.17E-04	3.90E-04	**3.11E-04**	**5.24E-04**	**1.95E-02**	**2.22E-02**	7.47E-04	2.51E-04
Ti	1.96E-02	6.53E-03	1.16E-01	5.75E-02	1.53E-01	1.27E-01	2.12E-02	3.72E-03
Cr	4.63E-02	1.72E-02	2.37E-01	1.16E-01	2.78E-01	1.67E-01	1.41E-02	2.26E-03
Mn	3.99E-03	2.32E-03	4.91E-03	3.37E-03	**7.31E-02**	**7.59E-02**	2.87E-02	7.61E-03
Fe	1.18E+00	1.03E-01	1.58E-01	2.40E-02	**4.14E-02**	**2.50E+00**	1.11E-01	3.16E-02
Ni	5.80E-03	2.59E-03	7.31E-03	2.61E-03	4.04E-01	2.29E-01	1.33E-02	3.42E-03
Cu	3.23E+00	5.16E-01	1.48E+00	2.31E-01	1.03E+00	1.65E-01	2.32E-02	4.05E-03
Se	1.79E-02	1.31E-02	**1.48E-02**	**1.48E-02**	**1.35E-01**	**1.69E-01**	2.67E-03	1.05E-03
Pb	5.34E-02	1.28E-02	4.94E-02	1.38E-02	1.89E-01	5.76E-02	5.61E-03	8.66E-04
Zr	3.65E-03	1.19E-03	9.70E-04	4.12E-04	9.31E-02	3.53E-02	4.10E-06	7.08E-07
Pd	9.15E-03	1.81E-03	1.01E-02	2.34E-03	1.25E-02	3.56E-03	2.31E-07	8.55E-08
Ag	2.84E-03	6.88E-04	7.25E-03	1.71E-03	1.40E-01	5.65E-02	6.75E-07	2.89E-07
Cd	1.38E-01	7.60E-02	7.10E-02	1.30E-02	6.28E-02	1.60E-02	1.36E-06	2.95E-07

The total mass size distributions obtained from MOUDIs 1 and 2 for experiments 6-11 are presented in Figs. 3 (a-f). The size distributions are normalized to the total mass for ease of comparison with the chemically speciated size distributions. The six figures present data from two experiments on each model of the zinc based rockets. The size distributions from MOUDIs 1 and 2 agree well with themselves and between each other over the course of the White Lightning and Black Jack experiments, showing a high level of precision. The size distributions collected in both of the Blue Thunder experiments are more tightly distributed than the other rocket measurements; around 1 μm. A disagreement between MOUDIs 1 and 2 is apparent in Fig. 3a at approximately 1 μm, which is not present in the duplicate experiment in Fig. 3b. It is not known why this disagreement occurred. Overall, the size distribution data for the Blue Thunder size distributions compare well with those presented for the other rocket measurements. In each figure, the ultrafine particles in the nucleation mode (mode 1) generated by gas-to-particle conversion were not clearly visible. Most of the particle mass was detected in the accumulation mode (mode 2) which was comprised of agglomerates of smaller mode 1 particles. The mean diameters and variances determined from each of the accumulation modes in the MOUDI

samples are shown in Table 3. Good agreement is seen between the mean diameter and variances of the total masses and the zinc and chloride data. All of the size distributions in Fig. 3 show that the particles in hobby rocket exhaust are less than 2.5 μm in diameter, and therefore, are capable of impacting $PM_{2.5}$ and PM_{10} samplers.

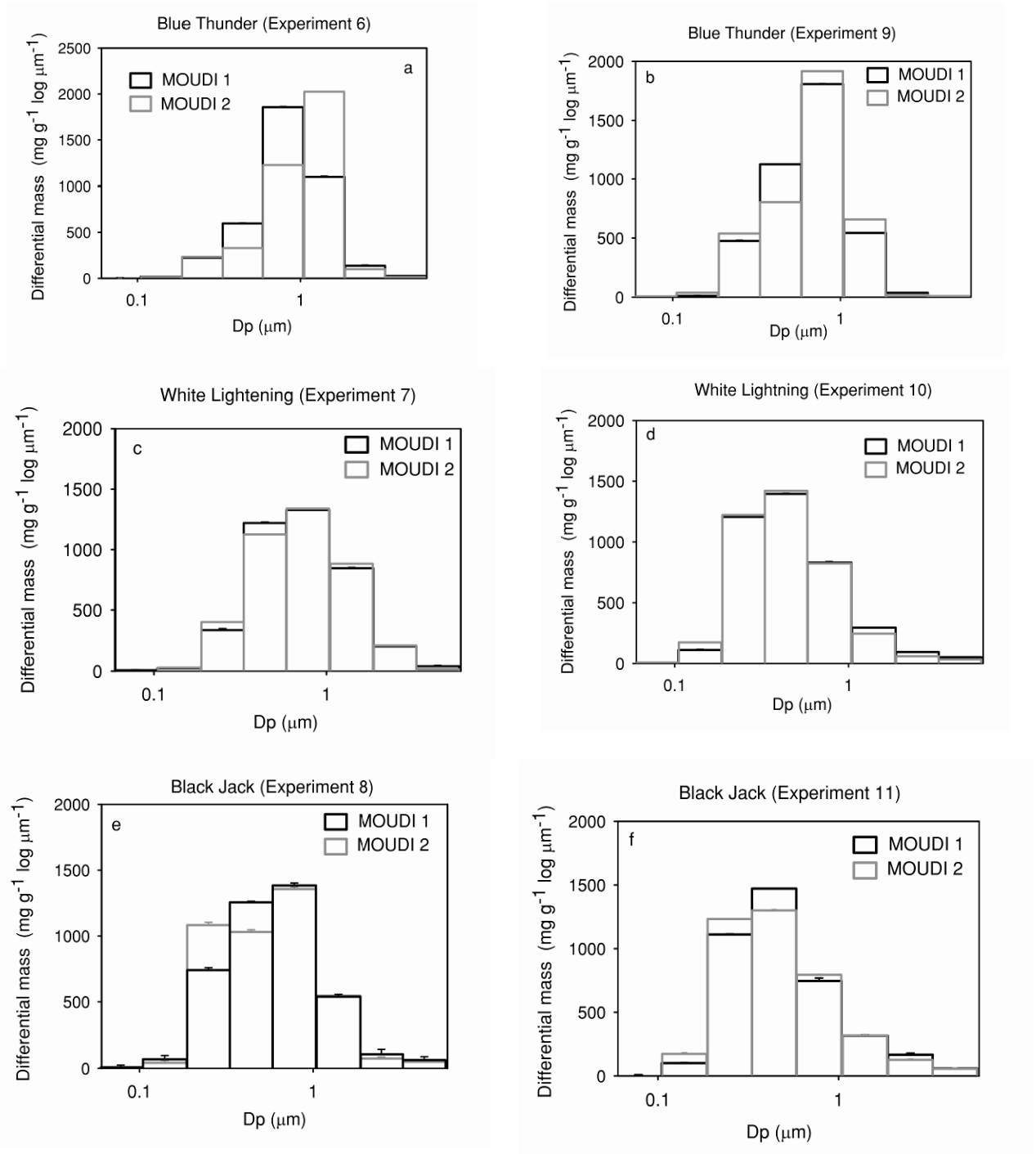

Fig. 3 (a-f). The comparison of the total mass size distributions collected by MOUDIs 1 and 2 for the Black Jack, White Lightning and Blue Thunder motors.

Table 3. Mean diameters, $\overline{D_p}$ and variances σ^2 for modes 1 and 2 in each of the size distributions presented in Figs. 3 and 4.

Species	Mode 1		Mode 2	
	$\overline{D_p}$ (μm)	σ^2 (μm^2)	$\overline{D_p}$ (μm)	σ^2 (μm^2)
Zinc	ND	ND	1.08	0.55
Chloride Ion	ND	ND	0.90	1.07
Avg. Mass MOUDI 1	ND	ND	1.31	1.26
Avg. Mass MOUDI 2	ND	ND	1.22	1.11

The size distributions of zinc and chloride ions from the MOUDI filters used to sample Black Jack exhaust aerosol are presented in Fig. 4 and are described with mean diameters, $\overline{D_p}$ and variances, σ^2 in Table 3. Small amounts of ammonium and trace species were detected on the MOUDI substrates, but were omitted from this graph for the purposes of clarity. Fig. 4 shows a single mode at approximately 1μm and agrees well with the total mass size distributions in Fig. 3 (a-f). Authors who have performed in-situ measurements of full-sized solid rocket motor (SRM) exhaust plumes in the stratosphere have typically seen bimodal and possibly trimodal size distributions (Ross *et al.*, 1999, Rutter, 2002, Whitefield, 1997), with modes having mean diameters of < 0.01 μm, 0.07-0.1 μm and 1-2 μm. The MOUDIs have limited resolution and the smaller modes typically seen at 0.01 μm and 0.1 μm may be present, but not clearly visible in Figs. 3 or 4. The minor and trace metal size distributions in Appendix 1 show the bimodal nature of the size distribution more clearly.

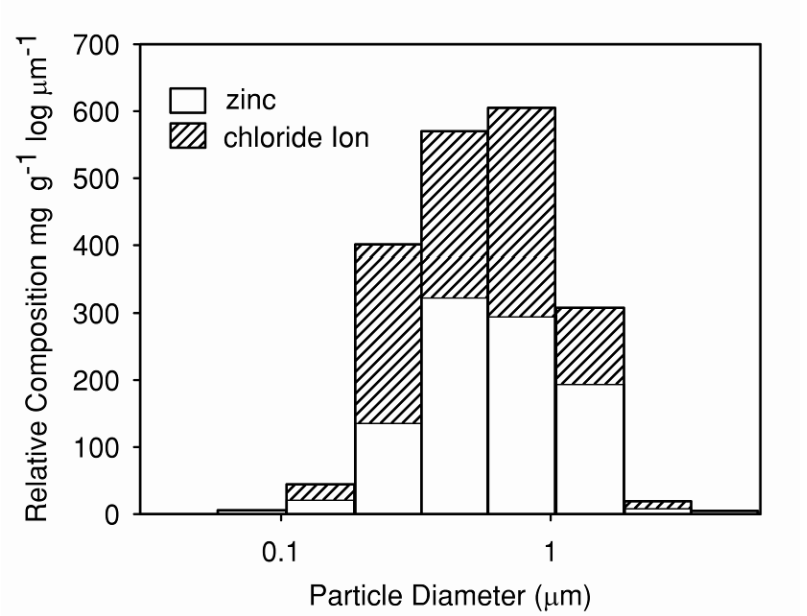

Fig. 4. The size-resolved bulk chemical composition of exhaust particles from the Black Jack motors.

To determine whether or not hobby rockets could cause a bias in an atmospheric particle sampler we used a Gaussian puff model to simulate the emissions from a hobby rocket launch and calculated the mass of particulate zinc that would be deposited on a filter during a 24-hour collection cycle. The masses of particulate zinc from one rocket exhaust puff that would be collected by a low volume $PM_{2.5}$ or PM_{10} sampler are presented in Fig. 5 as atmospheric concentrations, and are compared with the 24-hour averaged urban background concentrations of particulate zinc. A significant impact of particulate zinc from rocket exhaust was defined as when the rocket particulate zinc was 10% greater than the mass collected from the background air. This criterion was chosen under the assumption that an impact in the filter loadings of 10% or greater would represent a strong source contribution to a receptor; and therefore, produce an unacceptable error in the receptor model if the source were not accounted for. Sensitivity analyses were performed on the Gaussian puff model revealing that the stability class introduced the greatest uncertainty into the data. The largest daytime deviations from the base case results were for the atmospheric stability class C (unstable lapse rate) which returned particulate zinc concentrations that were between 80% and 15% those of the base case, depending on the distance of the sampler from the launch site. Nighttime deviations from the base case were explored with stability class E (stable lapse rate) which returned particulate zinc concentrations that were a factor of 1.5 to 2 higher than the base case.

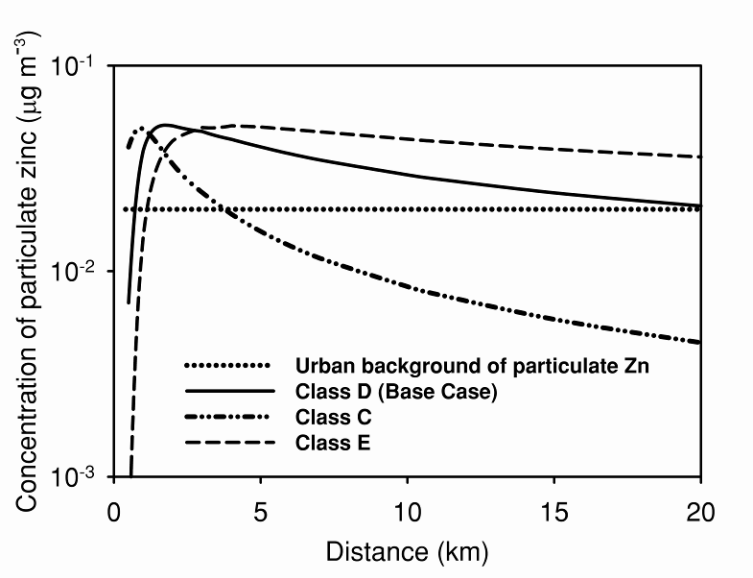

Fig. 5. The impact of zinc particulate matter from a hobby rocket launch on 24 hour averages of PM_{10} ambient zinc measurements as the exhaust puff is transported away from the launch site at a wind speed of 5 m/s under a range of atmospheric stabilities.

The data presented in Fig. 5 show the impact that one F20-7W motor, one of the smallest available, would cause on a 24-hour averaged filter sample collected in a low volume PM_{10} sampler located at distances less than 20 km from the launch site. The rocket exhaust puff contains enough zinc particulate to significantly impact the atmospheric particulate zinc concentrations up to 20 km distance from the launch site under all of the stability classes studied. Under stability classes D and E the impact is significant at distances greater than 20 km from the launch site.

Motors with propellant loadings larger than 30 g are available, but are subject to FAA regulations (MN TRA, pers comm., 2005). Therefore these motors are only used at rural launches organized by the Tripoli Rocket Associations (TRA) in each state. Such high-powered rocketry meetings occur as regularly as once a month and normally launch at least 20 to 30 rockets in a day. Some clubs have one or two meetings a year which are three or four days long during which time over 1000 launches may occur. The high-powered rockets typically use motors with propellant loads of 200-500 g, but on occasion may contain 1-5 kg of propellant (WI and MI TRA, pers. comm. 2005). Fuel formulations are proprietary (Aerotech, pers. comm., 2004) so without scientific tests it is unknown whether the fuels of these larger rockets are based upon zinc, aluminum (the typical fuel used in the full scale SRMs), or some other chemical. To assess the impact of aluminum-based motors on a sampler, aluminum contents of atmospheric particles measured in Milwaukee and Waukesha by Lough (2004) were used as a reference. Average background particulate aluminum concentrations were approximately two and a half times those of particulate zinc in both locations, and were probably due to soil material (Ramadan *et al.*, 2000, Song *et al.*, 2001, Zhou *et al.*, 2004). Therefore particles from a small rocket with an aluminum-based fuel might also cause sampling interference which could produce errors in receptor model results. Furthermore, both small monthly meetings and larger weekend events would cause large interferences with background PM_{10} zinc and PM_{10} aluminum data at distances far greater than 20 km downwind of the event site, meaning that nearby rural or urban locations could be significantly impacted by zinc and aluminum from hobby rockets. Such interferences with zinc and aluminum signals from background particulate matter could potentially cause large impacts on receptor model calculations.

CONCLUSIONS

This study illustrates how a small, unregistered and ephemeral source of particulate matter that is enriched in an atmospheric particulate indicator species, might significantly impact receptor model calculations performed using data from 24-hour averaged filter samples. The illustration presented in this study uses the zinc content of particulate matter collected from the exhaust plumes of hobby rocket motors to determine the downwind impact of the particulate zinc on a

sampler. A Gaussian puff model was used to estimate the dispersion of the exhaust plume as it is transported from the launch site to the sampler. The results presented imply that the use of zinc as an emission indicator species might be unreliable if hobby rockets are being launched upwind of the sampler. This raises the more general question of whether there are other unregistered sources that emit particulate matter which is highly enriched in other commonly used indicator species. Should such sources be identified they would need to be characterized to determine whether their emissions could interfere with receptor modeling performed using impacted 24 hour averaged $PM_{2.5}$ and PM_{10} filter samples.

ACKNOWLEDGEMENTS

We are very grateful to: the Strategic Environmental Research and Development Program (SERDP) for funding this work; the Kimberley Prather research group for the use of their laboratories in which the motor firing and particulate matter collection experiments were performed; and, Stuart Davies and the Wisconsin, Michigan and Minnesota Tripoli Rocket Associations for the technical insight they provided in this project.

APPENDIX 1: SUPPORTING INFORMATION

The size distributions of the predominant minor metals (sodium, magnesium, potassium, calcium and iron) and trace metals (chromium, nickel, lead, titanium, copper and cadmium) are presented in Figs. S1 and S2, respectively. The entire suite of metals analyzed by the ICP-MS consisted of: Li, Na, Mg, Al, K, Ca, Fe, Be, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, La, Ce, Ho, Yb, Hf, Ta, W, Os, Ir, Pt, Au, Hg, Tl, Pb, U.

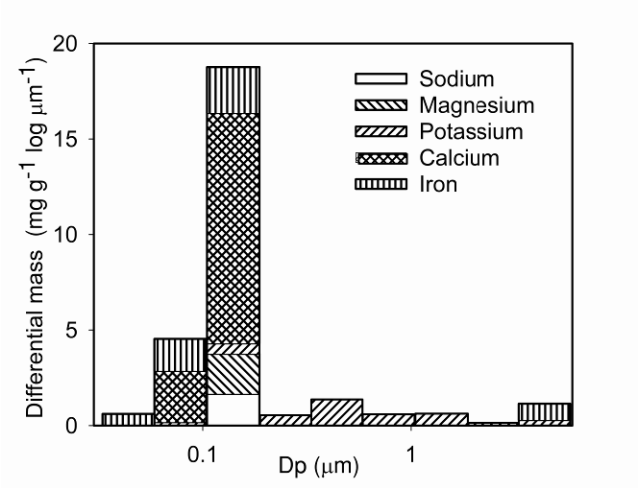

Fig. S1. The minor metal composition of the exhaust particles from the Black Jack motor.

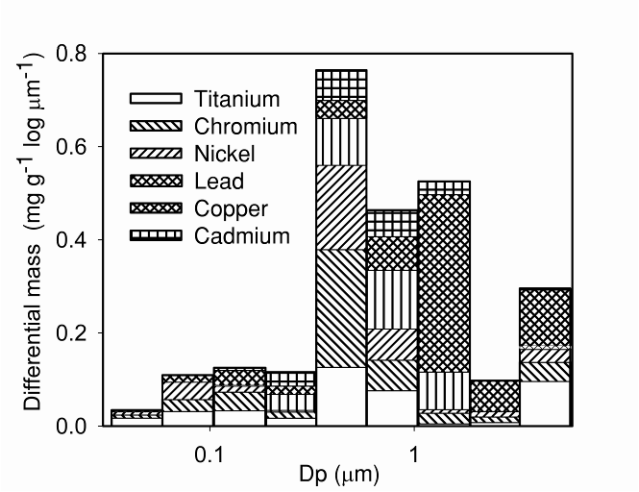

Fig. S2. The trace metal composition of the exhaust particles from the Black Jack motors.

The minor metals size distributions had a strong mode 1 at 0.1 μm in which all of the metals were present. Only potassium predominated in mode 2. The trace metals size distribution was more bimodal in character than any of the size distributions previously discussed. In contrast to the size distribution of the minor metals, the strongest of the trace metal modes was mode 2 at 1 μm, which also corresponded to the strongest mode in the zinc, chloride and total mass size distributions. Fig. S2 reflected size distributions of particles emitted by the full size SRMs with modes at 0.1 μm, and 0.9 μm (Whitefield, 1997, Ross *et al.*, 1999, Rutter, 2002). The detection of a nucleation mode and an accumulation mode, suggested that the particle formation occurred by nucleation from gaseous combustion products followed by agglomeration.

REFERENCES

Bennet, C., Jonsson, P. and Lindgren, E.S. (2005). Concentrations and Sources of Trace Elements in Particulate Air Pollution, Dar es Salaam, Tanzania, studied by EDXRF. *X-Ray Spectrom.* 34: 1-6.

Chueinta, W., Hopke, P.K. and Paatero, P. (2000). Investigation of Sources of Atmospheric Aerosol at Urban and Suburban Residential Areas in Thailand by positive matrix factorization. *Atmos. Environ.* 34: 3319-3329.

Drewnick, F., Hings, S.S., Curtius, J., Eerdekens, G. and Williams, J. (2006). Measurement of Fine Particulate and Gas-phase Species During the New Year's Fireworks 2005 in Mainz, Germany. *Atmos. Environ.* 40: 4316-4327.

GLERL (2005). Real-time Meteorological Observation Network Data for Milwaukee, WI. *N.O.A.A.* http://www.glerl.noaa.gov/metdata/mil/.

Hildemann, L.M., Cass, G.R. and Markowski, G.R. (1989). A Dilution Stack Sampler for Collection of Organic Aerosol Emissions - Design, Characterization and Field-Tests. *Aerosol Sci. Tech.* 10: 193-204.

Hildemann, L.M., Markowski, G.R. and Cass, G.R. (1991a). Chemical-Composition of Emissions from Urban Sources of Fine Organic Aerosol. *Environ. Sci. Technol.* 25: 744-759.

Hildemann, L.M., Markowski, G.R., Jones, M.C. and Cass, G.R. (1991b). Submicrometer Aerosol Mass Distributions of Emissions from Boilers, Fireplaces, Automobiles, Diesel Trucks, and Meat-Cooking Operations. *Aerosol Sci. Tech.* 14: 138-152.

Kulshrestha, U.C., Rao, T.N., Azhaguvel, S. and Kulshrestha, M. (2004). Emissions and Accumulation of Metals in the Atmosphere Due to Crackers and Sparkles During Diwali Festival in India. *Atmos. Environ.* 38: 4421-4425.

Liu, D.Y., Rutherford, D., Kinsey, M. and Prather, K.A. (1997). Real-time Monitoring of Pyrotechnically Derived Aerosol Particles in the Troposphere. *Anal. Chem.* 69: 1808-1814.

Lough, G.C. (2004). Sources of Metals and NMHCs from Motor Vehicle Roadways. PhD Dissertation published by the University of Wisconsin, Madison, WI.

Lough, G.C., Schauer, J.J., Park, J.S., Shafer, M.M., Deminter, J.T. and Weinstein, J.P. (2005). Emissions of Metals Associated with Motor Vehicle Roadways. *Environ. Sci. Technol.* 39: 826-836.

NCDC (2001). Comparative Climatic Data, *N.O.A.A.*. http://cdo.ncdc.noaa.gov/CDO/cdo.

Ramadan, Z., Song, X.H. and Hopke, P.K. (2000). Identification of Sources of Phoenix Aerosol by Positive Matrix Factorization. *J. Air Waste Manage. Assoc.* 50: 1308-1320.

Ross, M.N., Whitefield, P.D., Hagen, D.E. and Hopkins, A.R. (1999). In Situ Measurement of the Aerosol Size Distribution in Stratospheric Solid Rocket Motor Exhaust Plumes. *Geophys. Res. Lett.* 26: 819-822.

Rutter, A.P. (2002). The Aerosol and Chemical Characteristics of Rocket Exhaust in the Stratosphere. Master of Science published by the University of Missouri, Rolla, MO.

Schauer, J.J., Lough, G.C., Shafer, M.M., Christensen, W.F., Arndt, M.F., DeMinter, J.T. and Park, J.S. (2006), Characterization of Emission and Human Exposure to Metals Emitted from Motor Vehicles, Health Effects Institute Research.

Schauer, J.J., Mader, B.T., Deminter, J.T., Heidemann, G., Bae, M.S., Seinfeld, J.H., Flagan, R.C., Cary, R.A., Smith, D., Huebert, B.J., Bertram, T., Howell, S., Kline, J.T., Quinn, P., Bates, T., Turpin, B., Lim, H.J., Yu, J.Z., Yang, H. and Keywood, M.D. (2003). ACE-Asia Intercomparison of a Thermal-optical Method for the Determination of Particle-phase Organic and Elemental Carbon. *Environ. Sci. Technol.* 37: 993-1001.

Seinfeld, J.H. and Pandis, S.N. (1998). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change.* New York, NY, Wiley-Interscience.

Shah, M.H., Shaheen, N. and Jaffar, M. (2004). Screening of Urban Aerosol Particulate Composites for Selected Metal Distribution and their Dependence on Meteorological Parameters. *Anal. Chim.* 94: 805-815.

Song, X.H., Polissar, A.V. and Hopke, P.K. (2001). Sources of Fine Particle Composition in the Northeastern US. *Atmos. Environ.* 35: 5277-5286.

USEPA (2001). Toxics Release Inventory, United States Environmental Protection Agency.

Whitefield, P.D., Hagen, D.E., Hopkins, A.R. and Ross, M.N. (1997). Rocket Impact on Stratospheric Ozone: Submicron Aerosol Measurement, The 35th Aerospace Sciences Meeting and Exhibit: Reno, NV, Jan. 6-9, 1997, America Institute of Aeronautics and Astronautics, Inc

Zhou, L.M., Hopke, P.K. and Liu, W. (2004). Comparison of Two Trajectory Based Models for Locating Particle Sources for Two Rural New York sites. *Atmos. Environ.* 38: 1955-1963.

Received for review, October 11, 2006
Accepted, April 6, 2007