*Aerosol and Air Quality Research,* 12: 981–993, 2012

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2012.03.0069

# Metals Present in Ambient Air before and after a Firework Festival in Yanshui, Tainan, Taiwan

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## ABSTRACT

Fireworks displays are among the most important events during Taiwan's annual Lantern Festival, although thus practice leads to metal and non-metal pollution in the air. In this study, we investigated the levels of 16 elements—Na, Mg, Al, Si, K, Ca, V, Cr, Mn, Fe, Cu, Zn, As, Sr, Ba, and Pb—during the fireworks festival in Yanshui, Tainan, Taiwan, and the chemical compositions and mass concentration distributions of these elements collected from the sampling site are reported. The airborne particles were mainly in the sub-micrometer regime, with coarse size ranges. The concentrations of most of the elements of interest in this study were higher in the post-fireworks display period than prior to it. Studies of respiratory epithelial cell death revealed that the levels of the elements collected in the sub-micrometer size range were more than two times lower than those in the micrometer size range in the post-fireworks display period, but the viability was 65.7% for the former compared with 73.3% for the latter. Accordingly, the toxicity of the sub-micrometer particles was greater than that of the micrometer-sized particles. We conclude that the burning of fireworks during the festival was the main source of the trace metals, and contributed significantly to the increase in airborne particulate matter.

***Keywords:*** Airborne particulate matter; Fireworks smoke emissions; Electrical low pressure impactor; Laser ablation; Inductively coupled plasma mass spectrometry.

## INTRODUCTION

Firecrackers and fireworks are products of the pyrotechnic industry that are used to celebrate special events (e.g., New Years Eve, National Day) and traditional festivals in many countries. The scale of fireworks displays can vary from as small as a birthday party up to a national day celebration (Drewnick *et al.*, 2006) or one-off worldwide events, such as the millennium celebrations in 2000 (Webner *et al.*, 2000).

Fireworks displays are becoming more frequent and are increasing in both their number and quality. In the United States, Independence Day is celebrated with very intensive fireworks displays at night on the 4th of July. In France, on the occasion of the revolutionary overthrow of the monarchy, fireworks are displayed on July 14. In the United Kingdom, Guy Fawkes Night is celebrated with fireworks and bonfires on November 5. The New Year in celebrated in many countries with fireworks, bonfires, and sparkler displays during the days before and after New Year's Eve. The Divali Festival in India (Barman *et al.*, 2008), the Las Fallas in Spain (Moreno *et al.*, 2007), and the Lantern Festival in Beijing (Wang *et al.*, 2007) consume hundreds of thousands of tons of fireworks and firecrackers every year.

In Taiwan, fireworks usually are displayed during the New Year's celebrations (including the Chinese New Year), National Day on October 10, and the Lantern Festival on January 15 of the Lunar Year. For the Lantern Festival, fireworks are organized in Yanshui, Tainan, where some of the town's 27,800 people dread the noise, smoke, and traffic congestion. It is perhaps the world's only audience-participation fireworks event, where tens of millions of firecrackers and bottle rockets are fired at, into, and around those watching. A huge amount of smoke is generated from the burning of the fireworks, covering the town and surrounding area and causing serious air pollution at very high levels over the next several days.

Apart from the benefits provided by the splendid scenes of multicolored lights in the sky and the excitement of continuous brittle and resounding firecracker detonations, the burning of fireworks is a source of airborne pollutants, including $O_3$ (Attri *et al.*, 2001; Kulshrestha *et al.*, 2004), $SO_2$, $NO_2$, CO, and suspended particulate matter (Wang *et al.*, 2007). Suspended airborne particles emitted by fireworks consist of various elements, including K, Al, Ba,

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Mn, Cd, Cu, and other heavy metals that are very harmful to human health (Ravindra *et al.*, 2003; Moreno *et al.*, 2007; Vecchi *et al.*, 2008). The fireworks displays also introduce black powders containing potassium nitrate and charcoal into the atmosphere (Liu *et al.*, 1997; Wang *et al.*, 2007) and perchlorates into aquatic ecosystems as well as the atmosphere (Witkin *et al.*, 2007; Shi *et al.*, 2011). The accumulation of various heavy metals in the form of airborne particles generated from the burning of fireworks is one of the greatest concerns to all living organisms and ecosystems on Earth (Kulshrestha *et al.*, 2004; Witkin *et al.*, 2007). The effects of airborne particulate matter on the environment and on human health are strongly dependent on their size and chemical composition. Although the analysis of airborne particles in the sub-micrometer (< 1 μm) regime is a challenging task, interest in the analysis of $PM_1$ or $PM_{0.1}$ is increasing (Lin *et al.*, 2005; Gligorovski *et al.*, 2008; Furuuchi *et al.*, 2010; Geiss *et al.*, 2010; Avino *et al.*, 2011; Kim *et al.*, 2011; Cheng *et al.*, 2012). Once these particles penetrate into living organisms through inhalation, they can cause many respiratory system diseases, including pneumonia, bronchitis, and lung cancer (Huang *et al.*, 2003; Veranth *et al.*, 2004). When these pollutants come into contact with the skin, they can burn it or induce cancers (Maynard and Kuempel, 2005). In addition, the number of young people who sustain fireworks-related injuries requiring medical care is increasing continuously (Green and Joholske). For these reasons, studies of airborne particles are necessary to aid scientists to determine suitable solutions to minimize or eliminate the negative impacts of fireworks on living organisms, in particular, and on the environment, in general.

In this study, we used an electrical low pressure impactor (ELPI) and a laser ablation (LA) technique combined with inductively coupled plasma mass spectrometry (ICP-MS) to investigate the levels of 16 elements and their size distributions in ambient air collected during the fireworks festival in February 2008 in Yanshui, Tainan, Taiwan. This technique has been used previously to determine the chemical composition and distribution of elements in airborne particulate matter collected on filters (Tanaka *et al.*, 1998; Chin *et al.*, 1999; Wang *et al.*, 1999; Okuda *et al.*, 2004; Gligorovski *et al.*, 2008; Hsieh *et al.*, 2011). For calibration, we employed a simple process consisting of spiking the filters with standard solutions, as applied by Tanaka *et al.* (1988) and recently by Hsieh *et al.* (2011). Similar calibration strategies have previously been applied to the determination of trace elements in liquid samples using LA-ICP-MS (Yang *et al.*, 2005; Do *et al.*, 2011) and Pb in blood (Hsieh *et al.*, 2009). Using this approach, we could perform quantitative elemental analysis using LA-ICP-MS within a short period of time. We could also distinguish the elemental concentrations in the various size fractions using the proposed ELPI/LA-ICP-MS method. In addition, we evaluated the comparative toxicity, toward respiratory epithelial cells, of the size-dependent airborne particulate matter collected at different times during the fireworks display.

## METHODS

### *Sampling site*

Yanshui is a small town, situated in northern Tainan City, Taiwan. It is located at 23°19'47" north and 120°15'36" east, on the Bajhang/Jishuei Creek delta river plain. The site of the major fireworks performance on the evening of February 21, 2008, the festival day, was the Yanshui junior high school playground. This place was selected for major fireworks displays because it is a very large open space, bordered by streets and the town wastewater discharge canal. The area is sufficiently large for thousands of people to participate and observe the fireworks performance. The weather in Tainan City during the sampling period was moderately cold, at the end of winter. The dominant wind direction in this season is northerly and northeasterly. On the fireworks festival day, a slight change in wind direction occurred from northern and northeastern to western and northwestern. The average temperature varied from 15°C in the morning to 22°C at noon, making it very pleasant to go outside. The location where samples were collected is displayed in Fig. 1.

### *Sampling Procedure*

An ELPI (ELPI$^{TM}$, Dekati Ltd., Tampere, Finland) equipped with polytetrafluoroethylene (PTFE) membrane filters (Pall Corporation, Ann Arbor, MI) was used to collect airborne samples that had been segregated into different particle sizes. This device required connection to an external vacuum pump, used to pull air through the filters in the impactor to maintain its pressure at 100 mbar during operation. The gas inlet of the ELPI was placed approximately 1.6 m above ground level. To investigate the elemental distribution in the air, aerosol samples were collected in 11 stages covering a size range from 0.03 to 10 μm, separated into 11 fractions of different size ranges: 0.03–0.06, 0.06–0.108, 0.108–0.17, 0.17–0.26, 0.26–0.40, 0.40–0.65, 0.65–1, 1–1.6, 1.6–2.5, 2.5–4.4, and 4.4–9.97 μm. Characteristic lower and upper cut-off diameters ($D_{50}$) for the 11 ELPI stages used in this study are presented in Table S1 (Supplementary materials). Sample collection began at 8 am on February 19 and finished at 7 pm on February 23, 2008. The sampling time for each set of samples was 11 h. During the sampling period, six sets of atmospheric samples were collected, including three (sets 1–3) collected before the fireworks display (from 8 am on February 19 to 7 pm on February 20) and three (sets 4–6) collected after the fireworks had finished (from 8 am on February 22 to 7 pm on the February 23). Between each set of samples, a short time was taken to change the filters and restart the sampling. A sampling break between the pre- and post-fireworks displays (from 7 pm on February 20 to 8 am on February 22) was also required for installation of the fireworks equipment and firecracker packages, for preparation and performance of the display, and for protection of the sampling equipment and human resources from fire. After removal from the ELPI, the collected filter samples were placed in Petri dishes and then transported to and preserved in a dehumidifier chamber in the laboratory for analysis. Details of the specifications of the ELPI, the sampling schedule, and the meteorological conditions during the

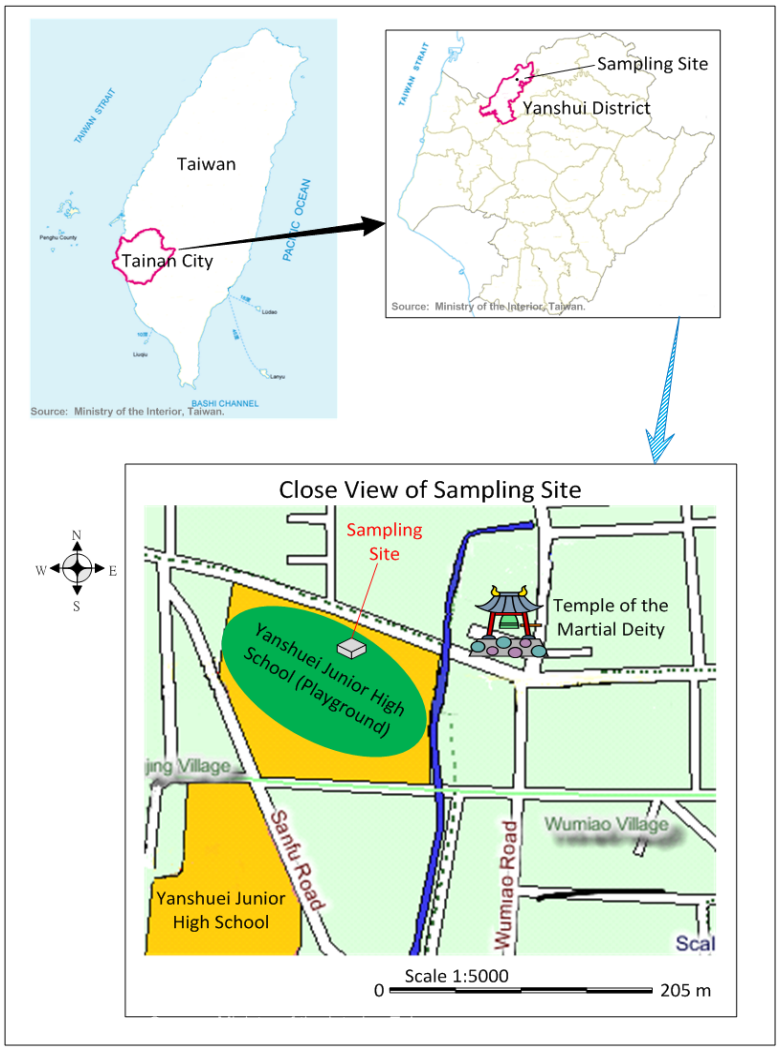


**Fig. 1.** Map of the sampling site.

fireworks festival are provided in Tables 1 and 2.

### *Chemical Analysis*

The elemental compositions of the collected samples were determined using the analytical procedure described by Hsieh *et al.* (2011). The calibration curves were linear over the studied concentration range (regression coefficients: > 0.97, from linear least squares fits) with very low detection limits, sufficient to allow determination of a wide range of elements in the samples. The accuracy of the method was validated using a standard addition method, making it applicable to determination of the elements in the airborne particulate matter. Briefly, standard filter samples and airborne particulate matter samples (after dehumidifying in the dehumidifier chamber) were analyzed using LA-ICP-MS. The LA device used to determine the elements in the airborne particle samples was a UP213 second-generation, high-performance Nd:YAG deep-UV (213 nm) system (New Wave Research, Fremont, CA, USA). LA was performed at a repetition rate of 10 Hz and a spot size of 110 μm, with a defocus of 2 mm, and using an ablation grid pattern mode for scanning spots at 100% laser output level. The selected grid pattern was a rectangular area of spots arranged in columns and rows. The spacing between the columns and rows was adjustable, such that the laser beam could reach and ablate any area of the spots on the standard filter samples (for calibration) as well as of the airborne particulate matter on the filter surface after defocusing. During ablation, the laser beam moved to each spot location, fired for 8 s, and then paused for 2 s to allow complete data collection. The ablated material was then transported into an ICP-MS 7500a system (Agilent Technology, USA) using Ar carrier gas (1 L/min) through a Tygon® R-3603 tube (internal diameter: 3.175 mm; length: 1 m). The optimized operating conditions of the LA and ICP-MS systems are provided in Table 3.

### *Particle Preparation and Cell Viability Assay*

In the framework of this preliminary study, particles in three size ranges, namely 0.06–0.108 (stage 2), 0.26–0.40 (stage 5), and 1.6–2.5 (stage 9) μm, in set 1 (the first set of the pre-fireworks display) and set 4 (collected 8 h after the fireworks display had ended) were selected to investigate the cytotoxicity of the airborne particulate matter collected from the fireworks display.

**Table 1.** ELPI specifications.

| Parameter | Value |
|---|---|
| Nominal air flow | 10 L/min |
| Particle size range | 0.03–10 μm with filter stage 0.007–10 μm |
| Number of channels | 12 |
| Time resolution | 2–3 s |
| *Operating conditions* | |
| + Ambient temperature | 5–40°C |
| + Ambient humidity | 0–90% |
| *Aerosol conditions* | |
| + Gas temperature | < 60°C with heated impactor < 200°C |
| Pressure under first stage | 100 mbar |

**Table 2.** Sampling schedule and meteorological parameters during fireworks display in Yanshui, Tainan.

| Sample set | Beginning date | Sampling time | Duration (h) | Temperature (°C) | Relative humidity (%) | Wind speed (m/s) | Wind direction |
|---|---|---|---|---|---|---|---|
| 1 | February 19 | 8:00 am–7:00 pm | 11 | 15.3–19.9 | 68–82 | 4.6–7.4 | N-NE |
| 2 | February 19 | 8:00 pm–7:00 am | 11 | 14.3–15.5 | 81–86 | 3.2–4.7 | N-NE |
| 3 | February 20 | 8:00 am–7:00 pm | 11 | 15.1–22.9 | 57–83 | 3.9–5.4 | N-NE |
| 4 | February 22 | 8:00 am–7:00 pm | 11 | 17.4–24.0 | 53–83 | 2.0–4.6 | N-NE |
| 5 | February 22 | 8:00 pm–7:00 am | 11 | 20.2–22.4 | 52–67 | 2.2–5.0 | N-E |
| 6 | February 23 | 8:00 am –7:00 pm | 11 | 18.8–21.0 | 61–89 | 2.0–4.1 | N-NE |

N-NE: North-Northeasterly; N-E: North-Easterly.

**Table 3.** Working conditions of the LA-ICP-MS system.

| Parameter | Value |
|---|---|
| *Laser ablation system* | |
| Wavelength | 213 nm |
| Repetition rate | 10 Hz |
| Dwell time | 8 s |
| Intersite pause | 2 s |
| Spot size | 110 μm |
| Spot number | 4; 6; 9 points |
| Output energy | 100% |
| Laser energy | 14.5 J/cm$^2$ |
| Raster and spacing | 300 μm |
| Grid spacing | 300 μm |
| Defocus distance | 2 mm |
| Carrier gas (Ar) | 1.0 L/min |
| *ICP-MS* | |
| RF power | 1.5 kW |
| Plasma argon gas flow | 15 L/min |
| Auxiliary argon gas flow | 1.0 L/min |
| Make up argon gas flow | 0.15 L/min |
| Carrier argon gas | 1.0 L/min |
| Sampler/skimmer cone | Ni |
| Acquisition mode | Time-resolved analysis |

The PTFE filters with parts of the samples from sets 1 and 4 reserved for this test were submerged in MeOH (J.T. Baker, Phillipsburg, NJ, USA; 10 mL) and sonicated using a probe sonicator (Vibra cell, Sonics and Materials, Newton, CT, USA) for 15 min to extract the particles. The particle suspension was then dried with $N_2$ and redissolved in serum-free LHC-9 medium (Gibco/Invitrogen, Carlsbad, CA, USA). The particles were then sonicated in the LHC-9 for 5 min prior to cell stimulation.

Human bronchial epithelial BEAS-2B cells ($8 \times 10^3$) were seeded in 96-well plates 24 h prior to treatment. Cell viability was determined using the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. Visible absorbance was recorded at 535 nm using an ELISA plate reader.

## RESULTS AND DISCUSSION

### *Chemical Composition of Airborne Particles Collected Using ELPI*

During the sampling time, six sets of 11-stage airborne particle samples were collected, including three sets collected prior to the fireworks display (considered as background samples) and three sets collected 8 h after the fireworks burning had stopped. Tables 4 and 5 list the mean concentrations of the elements grouped in three size ranges—the nanometer (0.03–0.108 μm), sub-micrometer (0.108–1 μm), and micrometer (1–9.97 μm) regimes—of the particles collected in the pre- and post-fireworks display periods, respectively. The fireworks festival began at 9:30 pm and finished close to midnight on February 21 (Thursday). Although we could not collect any samples during the burning of the fireworks, due to safety concerns, we found that most of the atmospheric elemental concentrations measured in the post-fireworks period were much higher than those measured in the pre-fireworks period, particularly in the sub-micrometer fraction. Among the elements of interest in this size regime, K and Ba were present at the highest concentrations (917 and 685 ng/m$^3$, respectively) after the fireworks display. The major elements concentrated in the micrometer fraction were Na, Mg, Al, Si, Ca, and

Fe, presumably originating mainly from re-suspension of soil or road dust. We suspect that the negligible elemental concentrations in the nanoparticles measured after the fireworks were due to the influence of atmospheric dispersion and coagulation. We collected the airborne particle samples nearly 8 h after the fireworks festival had ended because of the difficulty of sampling any earlier. Nano-sized particles have much shorter residence times (only a few hours) in the atmosphere and will convert to sub-micrometer particles through aggregation or coagulation.

We expected the detonation of firecrackers and fireworks to be a strong source of suspended particles. Large amounts of soot and metal oxide particles are emitted into the air during the detonation of fireworks. We found these high temperature–derived particles predominately in the sub-micrometer size range; the large amounts of metals in them could catalyze atmospheric reactions.

Figs. 2(a) and (b) display the average elemental concentrations associated with $PM_{2.5}$ and $PM_{10}$ collected during both the pre- and post-fireworks periods. The numbers superscripted above the vertical bars in the graph describe the increase factors, calculated as the concentration ratio between pre- and post-fireworks. Apart from Mg and Na, all elements in the present study exhibited elevated concentrations in the post-fireworks period. For the $PM_{10}$-associated elements, major increases were recorded for Cr, As, and Zn (ratio: > 10) and for Cu, Mn, Ba, V, Pb, and Sr (ratio: > 5), with clear increases also observed for K, Fe, Si, Ca, and Al. For the $PM_{2.5}$-associated elements, major increases were recorded for Cr, As, Mn, Zn, Ba, and Cu (ratio: >10) and for V, Sr, Fe, and Pb (ratio: >5), with clear increases also observed for Si, K, Al, and Ca. The element concentrations in $PM_{10}$ in the pre-fireworks display period followed the order Na > K > Si > Al > Mg > Ba > Ca > Fe > Zn > Pb > Mn > Sr > Cu > V > Cr > As. Notably, high levels of Na, K, Si, Al, Mg, Ba, Ca, and Fe were present in the atmosphere prior to the fireworks display. The concentrations of these elements in the post-fireworks display period

**Table 4.** Element concentrations (arithmetic mean ± SD; ng/m$^3$) in nanometer, sub-micrometer, and micrometer particles collected during the pre-fireworks period in Yanshui Township, Tainan County.

| Element | Pre-fireworks | | |
|---|---|---|---|
| | 0.03–0.108 μm (nanometer) | 0.108–1 μm (sub-micrometer) | 1–9.97 μm (micrometer) |
| Na | N.D. | 57.9 ± 12.6 (44.2–69.0) | 534 ± 90.6 (443–624) |
| Mg | N.D. | 4.81 ± 0.57 (4.23–5.38) | 182 ± 30.3 (160–216) |
| Al | N.D. | 22.5 ± 38.7 (0.29–67.1) | 203 ± 149 (31.6–293) |
| Si | N.D. | 15.7 ± 13.2 (1.74–28.0) | 364 ± 253 (72.3–525) |
| K | N.D. | 301 ± 261 (4.61–498) | 215 ± 114 (147–347) |
| Ca | N.D. | N.D. | 160 ± 85.10 (62.4–215) |
| V | N.D. | 3.14 ± 0.76 (2.63–4.01) | 0.88 ± 0.46 (0.35–1.22) |
| Cr | N.D. | 0.66 ± 0.55 (0.34–1.29) | 0.79 ± 0.22 (0.55–0.97) |
| Mn | N.D. | 4.94 ± 1.95 (3.51–7.16) | 8.19 ± 3.14 (4.57–10.2) |
| Fe | N.D. | N.D. | 153 ± 98.2 (40–210) |
| Cu | N.D. | 4.17 ± 4.69 (0.06–9.28) | 1.80 ± 1.40 (0.84–3.41) |
| Zn | N.D. | 18.2 ± 9.32 (9.14–27.8) | 27.4 ± 16.4 (16.3–46.2) |
| As | N.D. | 0.86 ± 0.37 (0.58–1.28) | 0.55 ± 0.11 (0.44–0.65) |
| Sr | N.D. | 4.55 ± 6.21 (0.27–11.7) | 7.10 ± 1.46 (5.55–8.45) |
| Ba | N.D. | 72.10 ± 90.30 (12.8–176) | 113 ± 32.4 (76.6–138) |
| Pb | N.D. | 16.5 ± 15.70 (1.97–33.10) | 4.42 ± 3.70 (1.63–8.62) |

Note: Data in parentheses are concentration ranges (n = 3); N.D., not detectable.

**Table 5.** Element concentrations (arithmetic mean ± SD; ng/m$^3$) of nanometer, sub-micrometer, and micrometer particles collected during the post-fireworks period in Yanshui Township, Tainan County.

| Element | Post-fireworks | | |
|---|---|---|---|
| | 0.03–0.108 μm (nanometer) | 0.108–1 μm (sub-micrometer) | 1–9.97 μm (micrometer) |
| Na | 7.06 ± 9.42 (0.0–17.8) | 90.8 ± 49.7 (35.0–131) | 120 ± 65.0 (70.9–194) |
| Mg | 1.32 ± 2.29 (0.0–2.29) | 17.6 ± 7.74 (10.9–26.1) | 66.1 ± 31.8 (38.3–101) |
| Al | N.D. | 25.5 ± 14.8 (8.36–34.4) | 261 ± 160 (108–427) |
| Si | N.D. | 172 ± 49.1 (135–228) | 559 ± 280 (298–855) |
| K | N.D. | 917 ± 455 (507–1407) | 330 ± 130 (181–407) |
| Ca | N.D. | 3.49 ± 2.10 (1.26–5.43) | 204 ± 122 (106–340) |
| V | N.D. | 22.7 ± 7.34 (17.1–31.0) | 3.04 ± 1.17 (1.83–4.17) |
| Cr | N.D. | 15.3 ± 10.80 (5.76–27.1) | 13.1 ± 6.48 (5.91–18.5) |
| Mn | N.D. | 83.0 ± 55.5 (49.9–147) | 31.3 ± 5.34 (27.8–37.4) |
| Fe | N.D. | 131 ± 65.3 (84.1–206) | 221 ± 98.0 (113–305) |
| Cu | N.D. | 36.6 ± 21.7 (18.7–60.8) | 19.7 ± 8.34 (12.3–28.8) |
| Zn | N.D. | 277 ± 177 (142–478) | 185 ± 83.7 (128–281) |
| As | N.D. | 15.8 ± 4.99 (10.1–19.3) | 7.43 ± 2.88 (4.59–10.4) |
| Sr | N.D. | 27.7 ± 20.2 (6.51–46.7) | 27.5 ± 17.1 (12.0–45.9) |
| Ba | 1.63 ± 2.56 (0.04–4.59) | 685 ± 372 (257–926) | 764 ± 370 (355–1075) |
| Pb | N.D. | 73.4 ± 24.1 (56.8–101) | 36.7 ± 6.37 (32.2–44.0) |

Note: Data in parentheses are concentration ranges (n = 3); N.D., not detectable.

followed a different order: Ba > K > Si > Zn > Fe > Al > Na > Ca > Mn > Pb > Mg > Cu > Sr > Cr > V > As. We infer that the detonation of firecrackers and fireworks on the occasion of the Yanshui Fireworks Festival was a strong source of metal elements in the ambient air.

The air pollution caused by the burning of fireworks could also be characterized by the airborne particulate matter in the form of $PM_{2.5}$ and $PM_{10}$ collected during the fireworks display. To distinguish the fireworks-induced changes in the elemental compositions of the fine particles from the coarse particles, we determined the $PM_{2.5}$-to-$PM_{10}$ ratios (concentration of element associated with $PM_{2.5}$/ concentration of element associated with $PM_{10}$) for each of the elements identified in this study. As indicated in Fig. 2(c), the $PM_{2.5}$-to-$PM_{10}$ ratios increased after the fireworks display, expect for Pb and Ca. This behavior can be explained by considering that the burning of fireworks increased the level of fine aerosol particles, which remained suspended for several hours to several days in the air before they coagulated into coarser particles that dropped on the ground. The high $PM_{2.5}$-to-$PM_{10}$ ratio found in this study agrees well with the conclusions provided by Moreno *et al.* (2007) and Wang *et al.* (2007).

Table 6 compares the elemental concentrations in $PM_{10}$ found in this study with those measured in $PM_{10}$ during other fireworks events from around the world. Our present data reveal that, although our samples were collected several hours after the burning of fireworks had stopped, the elemental concentrations remained very high and were not so different from those of other fireworks events—except in the case of Ba, the concentration of which was eight times higher than that from Las Fallas and 12 times higher than that from the FIFA World Cup 2006 celebrations in Italy. These fireworks displays create a strong source of air pollution, which contributes significantly high amounts of metals (especially K, Cu, Sr, and Ba) that typically employed in the creation of fireworks colors and result in gas pollutants and particulate matter in the ambient air.

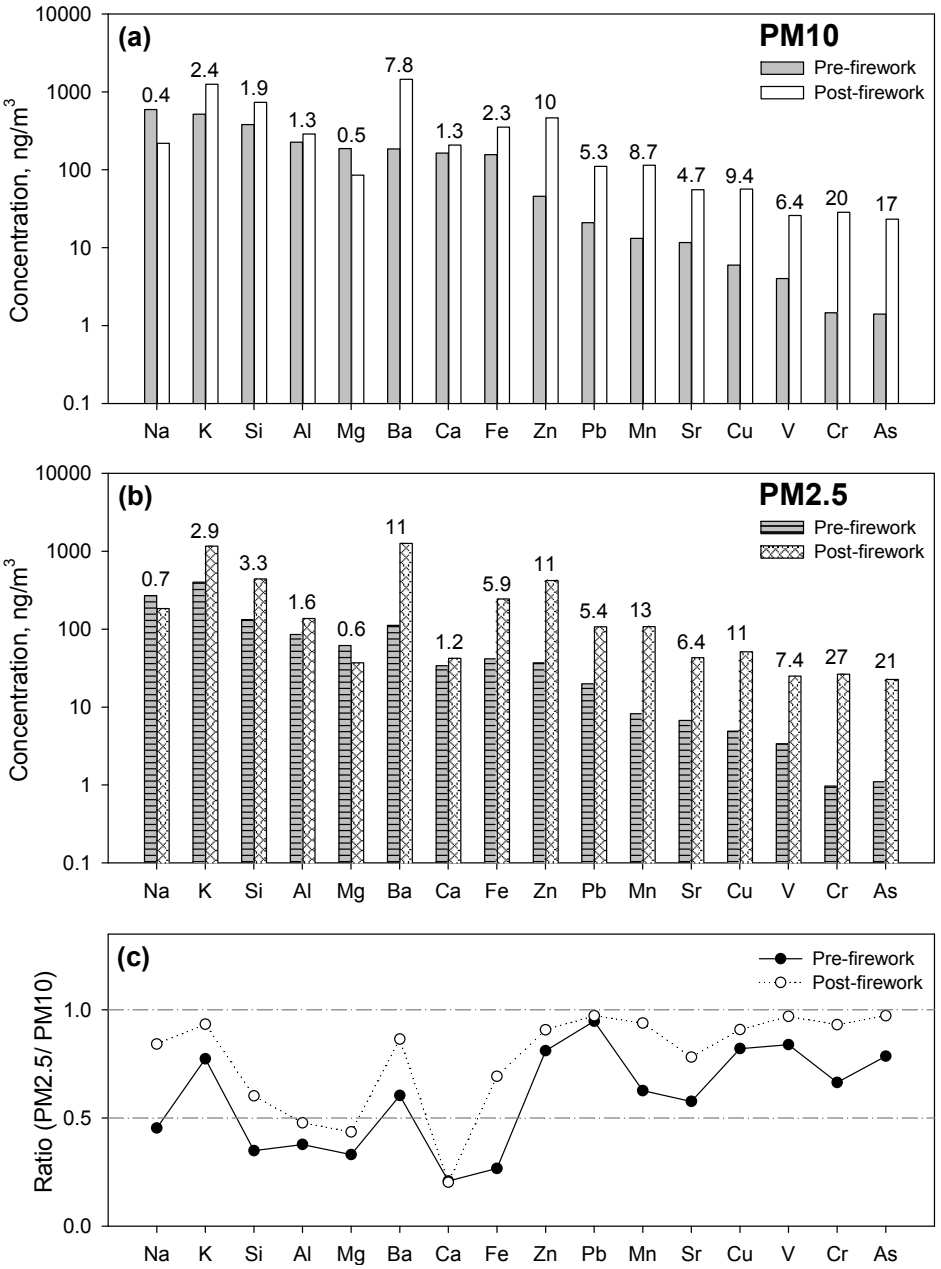


**Fig. 2.** (a, b) Average element concentrations in (a) $PM_{10}$ and (b) $PM_{2.5}$ (c) $PM_{2.5}$-to-$PM_{10}$ ratios during the pre- and post-fireworks display periods.

***Elemental Concentration Distribution with Respect to Particle Size***

Figs. 3 and 4 present the distributions of the concentrations of the individual elements collected in each ELPI particle size range from the six sets of samples obtained during the fireworks festival. The major elements of interest—Na, Mg, Al, Si, Ca, and Fe—are present in the Earth's crust and were contributed mainly from natural sources (Lin *et al.*, 2005), although some of them (Al, Si, Fe) also arose in significant concentrations from the pollution generated from the fireworks festival in Yanshui. In the nucleation mode, the concentrations of these elements were very low in the nanoparticles measured during the fireworks display period, presumably because of the influence of atmospheric dispersion and coagulation. Because of difficulties in sampling, we collected the airborne particle samples nearly 8 h after the end of the fireworks festival; nano-sized particles have much shorter residence times (a few hours) in the atmosphere and will convert to sub-micrometer particles through aggregation or coagulation. The airborne particles containing these elements did, however, have a tendency to increase their concentration through accumulation (i.e., from particle sizes of 0.108–1 to 4.4–9.97 μm). Fig. 3 presents the concentration distributions of these major elements. Although Si and Fe are not elements typically contributed from fireworks, they occupied very high proportions of the total elemental concentrations investigated. Iron is used to make gold sparks; its oxides are usually used

**Table 6.** Element concentrations in $PM_{10}$ ($\mu g/m^3$) observed during various fireworks festivals from around the world.

| | Present study[1] | Barman *et al.*[2] | Moreno *et al.*[3] | Vecchi *et al.*[4] |
|---|---|---|---|---|
| Event, yr | Yanshui, 2008 | Diwali, 2005 | Las Fallas, 2005 | FIFA World Cup Victory, 2006 |
| Location | Tainan, Taiwan | Lucknow, India | Valencia, Spain | Milan, Italy |
| Na | 0.33 | NR | 0.2 | NR |
| Mg | 0.12 | NR | 0.3 | 0.60 |
| Al | 0.46 | NR | 1.5 | 0.68 |
| Si | 0.99 | NR | NR | 1.37 |
| K | 1.25 | NR | 3.8 | 0.99 |
| Ca | 0.34 | 3.2 | 1.2 | 0.65 |
| V | 0.04 | NR | 0.01 | < 0.006 |
| Cr | 0.01 | 0.04 | 0.003 | 0.01 |
| Mn | 0.08 | 0.08 | NR | 0.03 |
| Fe | 0.41 | 0.75 | 0.4 | 1.7 |
| Cu | 0.05 | 0.45 | 0.06 | 0.11 |
| Zn | 0.34 | 0.54 | 0.08 | 0.19 |
| As | 0.03 | NR | NR | NR |
| Sr | 0.09 | NR | 0.03 | 0.14 |
| Ba | 1.95 | NR | 0.24 | 0.16 |
| Pb | 0.10 | 0.31 | 0.25 | 0.06 |

Note: NR, not reported.
[1] Data reported from 11-h sampling, 8 am–7 pm, February 22, 2008.
[2] Data reported as means from four sites, 12-h sampling, values reported for 24 h.
[3] 24-h sampling, Al reported as $Al_2O_3$.
[4] Data reported from 4-h resolution sample, 12 am–4 am, July 10, 2006.

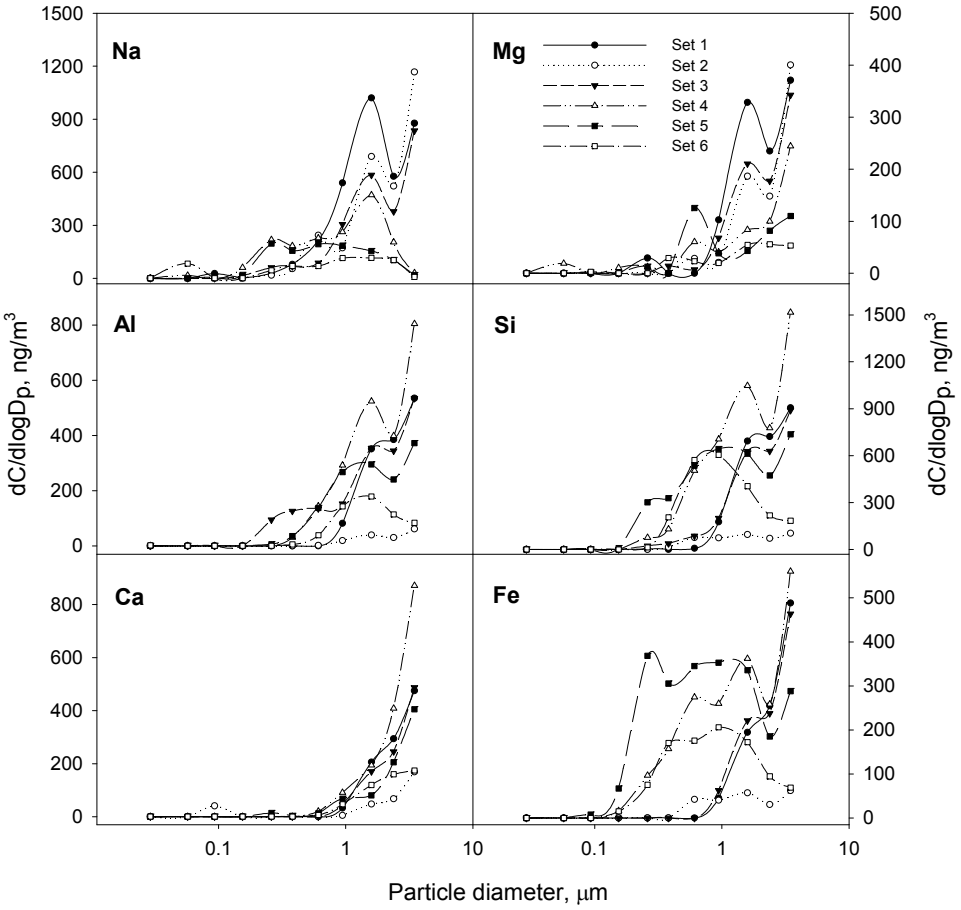


**Fig. 3.** Mass concentration distributions of Na, Mg, Al, Si, Ca, and Fe with respect to particle size in ambient air during the fireworks festival.

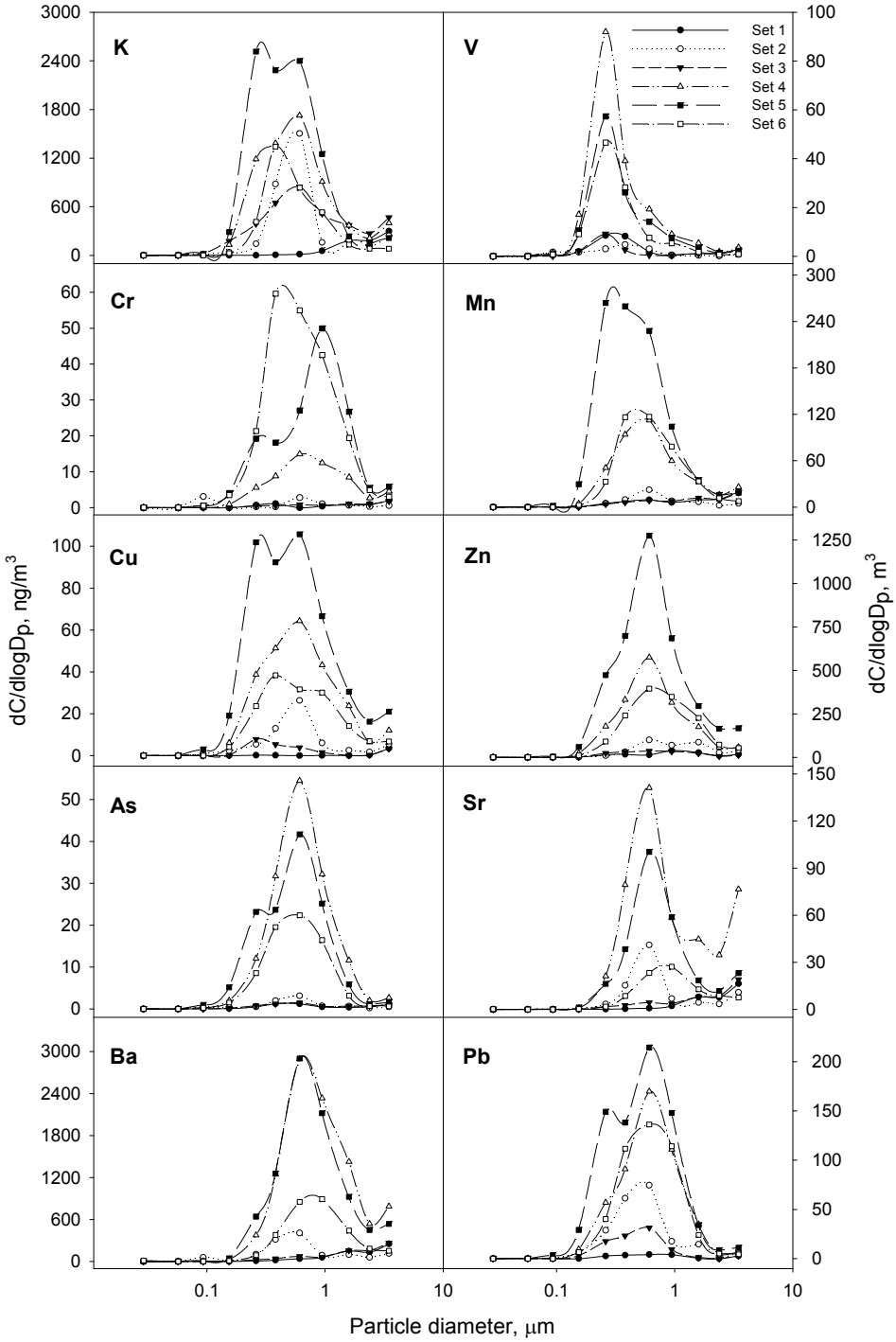


**Fig. 4.** Concentration distributions of K, V, Cr, Mn, Cu, Zn, As, Sr, Ba, and Pb elements with respect to particle size in ambient air during the fireworks festival.

as high-temperature oxidizers in fireworks. The fireworks display contributed much more to the levels of Si and Fe atoms than to the level of Al atoms.

While the concentrations of most of the elements of interest tended to increase after the fireworks display, the contribution of the fireworks to the Na and Mg concentrations decreased in comparison with those in the pre-fireworks display period. We suggest several explanations for this phenomenon. First, the elements Mg and Na are both contributed by sea spray (Hedberg *et al.*, 2005) and fuel combustion (Furimsky, 2000). During the fireworks festival, many factories and companies were closed, decreasing the number of trucks and other vehicles circulating on the roads, thereby decreasing the amount of exhaust released into the atmosphere and the concentrations of these metals in the air. Second, although Mg can be used as a metallic fuel in the form of flash powder for firecrackers and fireworks, it is more sensitive and violent than Al, increasing the

probability of spontaneous ignition in storage (Conkling, 1979). As a result, Mg is not recommended for use in firecrackers or fireworks for safety reasons; Al and Zn are typically used instead of Mg in pyrotechnic compositions to decrease the melting point and ignition temperature of the flash mixtures (Vermeij *et al.*, 2009). Finally, because fireworks displays are an uncommon phenomenon, occurring over a very short time, environmental studies on fireworks can focus only on single events, making abnormalities very difficult to verify.

Various anthropogenic sources, including vehicle emissions, industrial and power plants, tire wear, and diesel and gasoline combustion contribute to the atmospheric pollution caused by several of the tested elements, namely K, V, Cr, Mn, Cu, Zn, As, Sr, Ba, and Pb (Furimsky, 2000; Manoli *et al.*, 2002; Singh *et al.*, 2002; Wang *et al.*, 2003). In the post-fireworks display period, however, all of their concentrations were very high in comparison with those in the pre-fireworks period. K, Cu, Sr, and Ba are elements that are typically contributed by fireworks displays. Cu, Sr, and Ba are elements used to create fireworks coloring effects (blue, red, and green, respectively). Although Cu and Ba atoms also arise from vehicle emissions (Monaci *et al.*, 2000; Marcazzan *et al.*, 2001), their concentrations were significantly higher in the post-fireworks display period than in the pre-fireworks period. Burning different Cu compounds can generate blue colors, while Ba compounds can provide green ones (Vecchi *et al.*, 2008). Strontium, in the form of strontium nitrate and strontium sulfate, provides a red color to flares, fires, and stars. In addition, Sr atoms also serve as stabilizer for the mixtures. Potassium is a major element that is usually emitted from many sources, including traffic, soil dust, and biomass burning (Yamasoe *et al.*, 2000; Ikegami *et al.*, 2001). It is also one of the most important components in fireworks; black powder contains approximately 75% of $KNO_3$, which serves as a major oxidizer during burning (Liu *et al.*, 1997; Kulshrestha *et al.*, 2004; Drewnick *et al.*, 2006; Steinhauser *et al.*, 2008). In the nanoparticle size range or in the nucleation mode, the elements K, Cu, and Sr were nearly absent in both periods (pre and post), while Ba appeared only in very slight amounts in the post-fireworks display period. The concentrations increased in the sub-micrometer size range or accumulation mode, reaching their maximum values in the particle size ranges 0.40–0.65 μm for K and Cu and 0.65–1 μm for Sr and Ba in both the pre- and post-fireworks display periods. After that, the mass concentrations of these elements decreased quickly in the coarse size range before it rose slightly (see Fig. 4). Clearly, the sub-micrometer aerosol or accumulation-mode particles were suspended at very high concentrations in the air very close to the Earth's surface for very long periods, from days to weeks, potentially causing pollution to large areas. In the long run, the toxicity of these elements might affect the health of humans and other organisms if they were to be exposed to the polluted air.

Our analytical results also reveal that the levels of other metals (V, Cr, Mn, Zn, As, Pb) in the sub-micrometer fraction increased significantly in the post-fireworks display period, while no great differences appeared in the micrometer-sized fraction (Fig. 4). Lead can be used to produce crackling microstars and Zn is used to create smoke effects for fireworks and other pyrotechnic devices (Drewnick *et al.*, 2006; Moreno *et al.*, 2007; Wang *et al.*, 2007). The significantly high concentrations of the other metals may have been due to their use in firecrackers and fireworks to provide colorful effects. In addition, the low but detectable levels of Cu, Zn, Sr, Ba, and Pb in the sub-micrometer fraction on normal days might have arisen from vehicular traffic emissions (Lin *et al.*, 2005; Wang *et al.*, 2007; Vecchi *et al.*, 2008).

Although the daily contributions of these anthropogenic elements to the air at Yanshui in the pre-fireworks display time were very low, any unexpected increases in their mass concentrations in the atmosphere during the fireworks display period could cause serious air pollution to this area and its surroundings for a long time.

### *Comparative Toxicity of the Different Sizes of Airborne Particulate Matter*

Fig. 5 displays the cytotoxicity response data for the size-fractionated airborne particulate matter collected from the pre- and post-fireworks display periods in Yanshui. The viabilities of BEAS-2B cells after 24-h incubation with the particle extracts from the three size ranges of the samples collected in the pre-fireworks display period—nanometer (0.06–0.108 μm), sub-micrometer (0.26–0.40 μm), and micrometer (1.6–2.5 μm)—were greater than those of the samples collected in the post-fireworks display period. In other words, the samples collected in the pre-fireworks display period were less toxic than those in the post-fireworks display period. These results can be explained by considering that, in the pre-fireworks display period, the elements of interest were present at low levels because the ambient air was not affected by the fireworks display. The levels of these elements rose considerably as a result of the contribution of the airborne particulate matter generated from the burning of the fireworks. In particular, the toxic elements Ba, Pb, Cu, Cr, Mn, and Sr were present in very high concentrations in the post-fireworks display period; they were, presumably, important factors affecting the cell toxicity. Although the particles in the nanometer size range were present in negligible amounts in the post-fireworks display period, their toxicity toward BEAS-2B cells was considerable. Notably, the levels of the elements collected in the sub-micrometer size range were less than half of those in the micrometer size range in the post-fireworks display period, but the viability was 65.7% for the former compared with 73.3% for the latter. We conclude that the toxicity of the nanometer and sub-micrometer particles was higher than that of the micrometer particles and that the finer particles (nanometer and sub-micrometer particles) would be more detrimental to health than would be the coarser ones. Confirming the effects of particle sizes on respiratory epithelial cells will require further studies.

## CONCLUSIONS

We have investigated the chemical compositions and

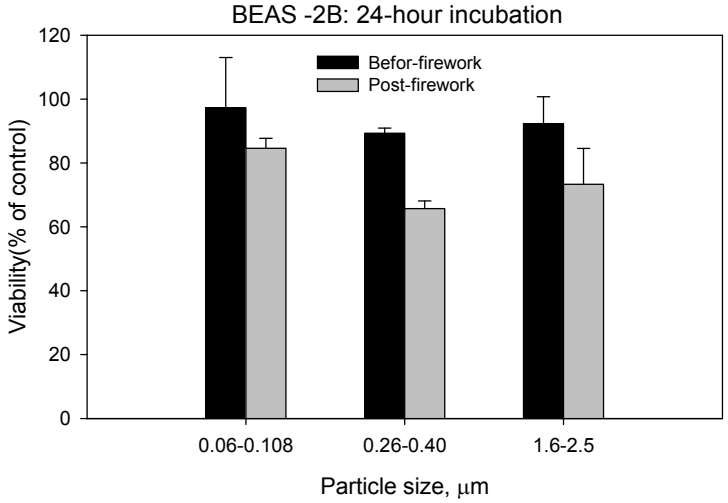


**Fig. 5.** Toxicity of different sized particles toward BEAS-2B cells after incubation for 24 h.

mass concentration distributions of 16 elements with respect to the sizes of particles present in ambient air during fireworks festivities in Yanshui, Tainan, Taiwan.

The concentrations of almost all of the elements of interest were higher in the post-fireworks display period than they were in the pre-fireworks period. Our analytical results revealed that the concentrations of many of the major elements were contributed mainly by the sub-micrometer and coarse fractions in both the pre- and post-fireworks display periods, while the concentrations of anthropogenic elements increased mainly in the sub-micrometer range.

Some other elements that play an indispensable role in forming the various colors seen during the burning of fireworks, namely K, Cu, Sr, and Ba, were typically contributed strongly by the fireworks display. They contributed to increases in pollution in the ambient air at the firing site and also in the surrounding areas. We confirmed that the particles generated by the burning of fireworks in Yanshui possessed higher $PM_{2.5}$-to-$PM_{10}$ ratios than those present in the pre-fireworks display period.

Among the different size-fractionated airborne particle, those in the sub-micrometer size range appear to have a more-negative effect on respiratory epithelial cells, relative to particles in the micrometer size range.

## ACKNOWLEDGMENTS

We thank the National Science Council, Republic of China, for financial support (project number 97-B0054-K6) and the Instrument Center at National Tsing Hua University, Taiwan, for the ICP-MS support. We gratefully acknowledge Dr. Pinpin Lin at the National Health Research Institute, Taiwan, for her valuable assistance and insight.

## SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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*Received for review, March 19, 2012*
*Accepted, May 30, 2012*

**Table S1.** Characteristic lower and upper cut-off diameters ($D_{50}$) for the 11 ELPI stages used in this study.

| ELPI stage | Lower cut-off $D_{50}$ (µm) | Upper cut-off $D_{50}$ (µm) | Size distribution (µm) |
|---|---|---|---|
| 1 | 0.03 | 0.06 | < 2.5 ($PM_{2.5}$) |
| 2 | 0.06 | 0.108 | |
| 3 | 0.108 | 0.17 | |
| 4 | 0.17 | 0.26 | |
| 5 | 0.26 | 0.40 | |
| 6 | 0.40 | 0.65 | |
| 7 | 0.65 | 1 | |
| 8 | 1 | 1.6 | |
| 9 | 1.6 | 2.5 | |
| 10 | 2.5 | 4.4 | 2.5–10 ($PM_{2.5–10}$) |
| 11 | 4.4 | 9.97 | |