

# Environmental Health

This article by Licudine et al. represents another important concept in epidemiology: exposure assessment. Environmental assessment is a relatively new concept; the first time it was formally addressed by the Environmental Protection Agency (EPA) was in the mid-1980s. In fact, exposure assessment represents the predominant part of EPA risk assessments. The revised EPA Guidelines for Exposure Assessment carefully address several key concepts, including measurement of exposure, intake, uptake, and dose. Each of these concepts is essential to the understanding of health effects related to environmental exposures.

The authors explore the seemingly innocuous activity of observing New Year fireworks displays. The authors measured exposure and documented the presence of several contaminants in ambient air during the New Year celebrations. These contaminants may pose long-term exposure risk and may be associated with adverse health effects. Hopefully, future investigators will take the next steps and evaluate potential longer-term environmental and health impacts by implementing the other concepts involved in exposure assessment: intake, uptake, and dose.

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## HAZARDOUS METALS IN AMBIENT AIR DUE TO NEW YEAR FIREWORKS DURING 2004–2011 CELEBRATIONS IN PEARL CITY, HAWAII

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Honolulu, Hawaii, has consistently recorded the cleanest air among large U.S. cities, except once a year during New Year celebrations, because of traditional fireworks displays statewide.<sup>1,2</sup> These fireworks result in increased levels of suspended particulates in residential air as high as 300% above the pre-fireworks level, and can cause adverse health effects.<sup>3,4</sup> In recent years, residential fireworks celebrations in Hawaii have become increasingly intense, resulting in more fires and increased human injuries despite laws enacted to curb their use.<sup>5–7</sup> Moreover, dangerous aerial fireworks from illegal importation and sales punctuate the problem, and may lead to even more health and safety hazards because they are unregulated and generate contaminants of largely unknown composition and toxicity.<sup>8,9</sup> Recent legislation has further banned fireworks on the island of Oahu after the 2011 New Year (2011NY) celebration because of health and safety concerns.<sup>10</sup>

Advanced technologies have transformed fireworks propellants, and new oxidizers and color producers enhance visual effects.<sup>11,12</sup> Chlorine-based oxidizers

such as chlorates or perchlorates can be used to achieve noise levels equivalent to trinitrotoluene and result in more violent explosions than traditional nitrates.<sup>13</sup> Demand for fireworks with designer colors has resulted in increased use of metals as color producers.<sup>14,15</sup> Lead (Pb) salts are widely used as igniters to initiate fireworks explosions.<sup>16</sup> Manganese (Mn) and Mn dioxide serve as fuel and oxidizer for brighter lights,<sup>17</sup> chromium (Cr) is used as a burn rate catalyst for propellants,<sup>18</sup> and nickel (Ni) acts as an electric firing device for fireworks.<sup>19</sup>

Concern regarding environmental and health risks has developed because metals are generally persistent in the environment, perchlorates have been associated with thyroid problems,<sup>20</sup> and toxic byproducts (e.g., dioxins) could be produced as a result of atmospheric reactions between metal oxides and organic fuels.<sup>21</sup> Before and after every New Year celebration, the Hawaii State Department of Health (HDOH) issues health advisories to the public and reports the amount of particulate matter (PM), specifically the PM<sub>10</sub> ( $\leq 10$  microns [ $\mu\text{m}$ ]) dispersed in the air during the festivities. The 2005NY celebration resulted in PM<sub>10</sub> levels that exceeded the state and federal 24-hour PM<sub>10</sub> standard of 150 micrograms per cubic meter [ $\mu\text{g}/\text{m}^3$ ].<sup>22</sup> Short-term exposure to very high levels of PM during fireworks episodes have caused asthma problems and other respiratory ailments in Hawaii<sup>3,4,23</sup> and elsewhere.<sup>24,25</sup> Furthermore, short- and long-term exposures to the smaller particulates PM<sub>2.5</sub> ( $\leq 2.5$   $\mu\text{m}$ ) have been associated with increased cardiovascular and lung cancer mortality.<sup>26,27</sup>

In 1975, the presence of potassium chloride and

sulfur dioxide in Oahu ambient air during the New Year fireworks celebration was documented by Smith and Dinh in connection with a health-related study.<sup>23</sup> In recent years, significant increases in ambient air barium (Ba), strontium (Sr), magnesium (Mg), Pb, Mn, and other metals have been reported during fireworks-related festivities in Spain,<sup>28</sup> China,<sup>29</sup> India,<sup>30</sup> and Italy.<sup>31</sup> To document the concentrations of metals in central Oahu ambient air during New Year fireworks celebrations, we sought additional air sampling from 2004NY–2011NY, following the U.S. Environmental Protection Agency (EPA) Air Toxics program methodology. In the Air Toxics program, the six core metals—Pb, Mn, Cr, Ni, cadmium (Cd), and beryllium (Be)—are monitored, arsenic (As) and mercury (Hg) are excluded from the inorganic hazardous air pollutant (HAP) list, and Pb is the only metal regulated.<sup>32,33</sup> The EPA began an assessment of cancer and non-cancer health risks associated with exposure to various toxic chemicals in 1999, and adverse health effects of HAP metals that were published in 2005<sup>34</sup> are summarized in Table 1. Additional toxicity associations<sup>35,36</sup> and cancer tissue metal accumulations<sup>37,38</sup> have been described in workers with well-characterized exposure to metal-rich

particles. Excessive exposure to some heavy metals may have led to mental dysfunction and neurological disorders.<sup>39,40</sup> Recent findings associated exposure to Pb, Mn, and other metals with the development of neurodegenerative disorders mimicking Parkinson's, Alzheimer's, and Huntington's diseases.<sup>41,42</sup>

Although some of these HAP metals have desirable characteristics in pyrotechnics, other materials should be used to avoid known toxicities. The American Fireworks Standards Laboratory (AFSL) has prohibited the use of Pb, As, and Hg salts in the manufacture of fireworks.<sup>43</sup> In this article, we document the presence of contaminants in ambient air collected over the HAP pilot site of Pearl City in central Oahu during 2004NY–2011NY celebrations.

## METHODS

### Air sampling

The metal sample collection was conducted in Pearl City on central Oahu because routine monitoring indicated historically high ambient particulates during New Year fireworks celebrations, as compared with other sites on the island of Oahu.<sup>22</sup> Air sampling for

**Table 1. Toxicological evaluation of EPA hazardous air pollutant metals, health risks, and benchmarks**

Metals	Health risk <sup>a,b</sup> (cancer/non-cancer)	EPA benchmark <sup>c</sup> (ng/m <sup>3</sup> )
1. Arsenic	Respiratory cancer/developmental	0.57
2. Beryllium	Lung cancer/respiratory	1.00
3. Cadmium	Lung cancer/kidney	1.40
4. Chromium <sup>d</sup>	Lung cancer/respiratory	0.20, <sup>e</sup> 0.01 <sup>f</sup>
5. Lead	None/developmental	1,500.00, <sup>g</sup> 150.00 <sup>h</sup>
6. Manganese	None/neurological	52.00 <sup>i</sup>
7. Mercury	None/neurological	310.00, <sup>j</sup> 31.00 <sup>k</sup>
8. Nickel	Lung cancer/immunological	10.00

<sup>a</sup>Environmental Protection Agency (US), National-Scale Air Toxics Assessment Program. Health effects information used in cancer and noncancer risk characterization for the 1999 national-scale assessment [cited 2010 Dec 10]. Available from: URL: <http://www.epa.gov>

<sup>b</sup>Agency for Toxic Substances and Disease Registry (US). ToxFAQS™ for HAP metals [cited 2011 Apr 11]. Available from: URL: <http://www.atsdr.cdc.gov/toxfaqs/index.asp#bookmark04>

<sup>c</sup>EPA benchmark for resident air based on minimum concentration for carcinogenic target risk or non-cancer hazard index (i.e., lead, manganese, and mercury) on lifetime exposure as of November 2011

<sup>d</sup>Total chromium (Cr) (1:6 ratio Cr VI:Cr III)

<sup>e</sup>Carcinogenic target risk based on total Cr before November 2010

<sup>f</sup>Carcinogenic target risk based on hexavalent Cr (Cr<sup>VI</sup>) starting with the November 2010 update

<sup>g</sup>National ambient air quality standard for lead before October 15, 2008

<sup>h</sup>New national ambient air quality standard for lead starting October 15, 2008

<sup>i</sup>Non-cancer hazard index for manganese

<sup>j</sup>Elemental mercury non-cancer hazard index

<sup>k</sup>Non-cancer hazard index for mercury salts as of November 2011

EPA = Environmental Protection Agency

ng/m<sup>3</sup> = nanograms per cubic meter

metals was performed using two Graseby Andersen high-volume samplers (Andersen Instruments Inc., Smyrna, Georgia) capable of maintaining a flow rate of  $\sim 1.0 \text{ m}^3/\text{minute}$  for 24 hours following EPA protocols.<sup>44</sup> The total suspended particulates (TSP) samples as defined by the EPA<sup>45</sup> were collected in 8-by-10-inch spectro-quality-grade glass fiber filters provided by the EPA. New Year's Eve sampling spanned 24 hours, starting at 12 a.m. on December 31 and ending at 11:59 p.m. on December 31 (Table 2). New Year's Day sampling also spanned 24 hours, starting at 12 a.m. on January 1 and finishing at 11:59 p.m.

The EPA has an official sampling schedule each year, and it included New Year's Day 2008 and 2009. EPA sampling dates that occurred closest before and after New Year's Day represented pre-fireworks and post-fireworks sampling, respectively. If New Year's Eve or New Year's Day sampling did not coincide with the EPA's official sampling date (years other than 2008 and 2009), special sampling for that day was conducted, except for 2006NY. For 2006NY, the official EPA sampling schedule interfered with the ability to sample 2006 New Year's Eve. Specifically, the EPA sampling ended on Friday, December 30, 2005, at midnight, and

no technicians were available to set up the sampler during the weekend for New Year's Day sampling, so those data were not collected. The  $\text{PM}_{10}$  data were generated from a BAM-1020  $\text{PM}_{10}$  continuous sampler (Met One Instruments, Inc., Grants Pass, Oregon) that measures particulates hourly. The meteorological data (wind speed and precipitation) based on Honolulu international airport weather station reports were downloaded from <http://www.wunderground.com> (Table 2).

#### Sample preparation and analysis

A  $1\frac{3}{4}$ -by- $2\frac{1}{4}$ -inch portion of the TSP filter was extracted with 40 milliliters of 0.25 normal (N) nitric acid ( $\text{HNO}_3$ ) solution using the Bransonic<sup>®</sup> 8510 Ultrasonic Cleaner (Branson Ultrasonics, Danbury, Connecticut) set at  $60^\circ \text{C}$  for about two hours. The acid extract was filtered through a  $0.45 \mu\text{m}$  nylon filter using a Pall Gelman magnetic filter funnel (Pall Life Sciences Inc., Ann Arbor, Michigan). Blank filters and quality control samples were also prepared and extracted following our standard laboratory procedure, which was audited and approved by the EPA in 2008.<sup>46</sup> The 2004NY and 2005NY fireworks samples were re-extracted and analyzed following the EPA approved methodology.

**Table 2. Meteorological conditions during fireworks: New Year celebrations in Pearl City, Hawaii, 2004NY–2005NY and 2007NY–2011NY**

Year <sup>a</sup>	Sampling date (24 hours)	Fireworks event (date/time) <sup>b</sup>	Average wind speed (miles per hour)	Precipitation (inches)
2004NY	12/31/2003 (12 a.m.–11:59 p.m.)	12/31/2003 (5:53 p.m.–11:53 p.m.)	5.5	0.03
2005NY	12/31/2004 (12 a.m.–11:59 p.m.)	12/31/2004 (5:53 p.m.–11:53 p.m.)	6.9	0.00
2007NY	12/31/2006 (12 a.m.–11:59 p.m.)	12/31/2006 (5:53 p.m.–11:53 p.m.)	9.1	NA
2008NY	1/1/2008 (12 a.m.–11:59 p.m.)	1/1/2008 (12:53 a.m.–5:53 a.m.)	8.3	NA
2009NY	1/1/2009 (12 a.m.–11:59 p.m.)	1/1/2009 (12:53 a.m.–5:53 a.m.)	8.6	0.44
2010NY	1/1/2010 (12 a.m.–11:59 p.m.)	1/1/2010 (12:53 a.m.–5:53 a.m.)	4.6	NA
2011NY	12/31/2010 (12 a.m.–11:59 p.m.)	12/31/2010 (5:53 p.m.–11:53 p.m.)	4.5	NA

<sup>a</sup>New Year fireworks event, except 2006NY (sampling not conducted)

<sup>b</sup>Actual meteorological data computed for the specified date and time

NY = New Year

NA = not available

**Table 3. Method comparative analysis for hazardous air pollutant metals during 2005 New Year celebrations in Pearl City, Hawaii**

HAP metals	Method quantitation limit			Quantitative analysis comparison <sup>a</sup>		
	Mass (amu)	GFAAS (ng/m <sup>3</sup> )	ICP-MS (ng/m <sup>3</sup> )	GFAAS (ng/m <sup>3</sup> )	ICP-MS (ng/m <sup>3</sup> )	RPD (percent)
1. Beryllium	9	0.20	0.20	<MQL	<MQL	NA
2. Cadmium	111	0.08	0.10	1.4	1.6	13.3
3. Chromium	52	0.79	0.29	144.7	157.6	8.5
4. Lead	208	0.98	0.29	307.0	253.0	19.0
5. Manganese	55	0.79	0.71	100.3	87.8	13.3
6. Nickel	60	1.18	0.10	5.3	6.0	12.4

<sup>a</sup>2005 New Year sample collected from the main site in Pearl City, Hawaii, with concentration in ng/m<sup>3</sup>

HAP = hazardous air pollutant

GFAAS = graphite furnace atomic absorption spectroscopy

ICP-MS = inductively coupled plasma mass spectrometry

RPD = relative percent deviation

amu = atomic mass unit (of the metal isotope)

ng/m<sup>3</sup> = nanograms per cubic meter

MQL = method quantitation limit (based on the lowest calibration standard)

NA = not applicable

We analyzed ambient air samples during 2004NY–2011NY celebrations by graphite furnace atomic absorption spectroscopy (GFAAS) using a PerkinElmer 4110ZL AA instrument with transversally heated graphite atomizer and AS-72 autosampler (PerkinElmer Corporation, Waltham, Massachusetts). Initial confirmation and comparison analysis of HAP metals was performed by inductively coupled plasma-mass spectrometry (ICP-MS) using a PerkinElmer ELAN DRC II ICP-MS (PerkinElmer) (Table 3). The ICP-MS methodology was also used to further analyze 2005NY and 2008NY samples, including pre-fireworks and post-fireworks ambient air samples, to determine peaks and dissipation of HAPs and other metals.<sup>47</sup>

#### Data analysis

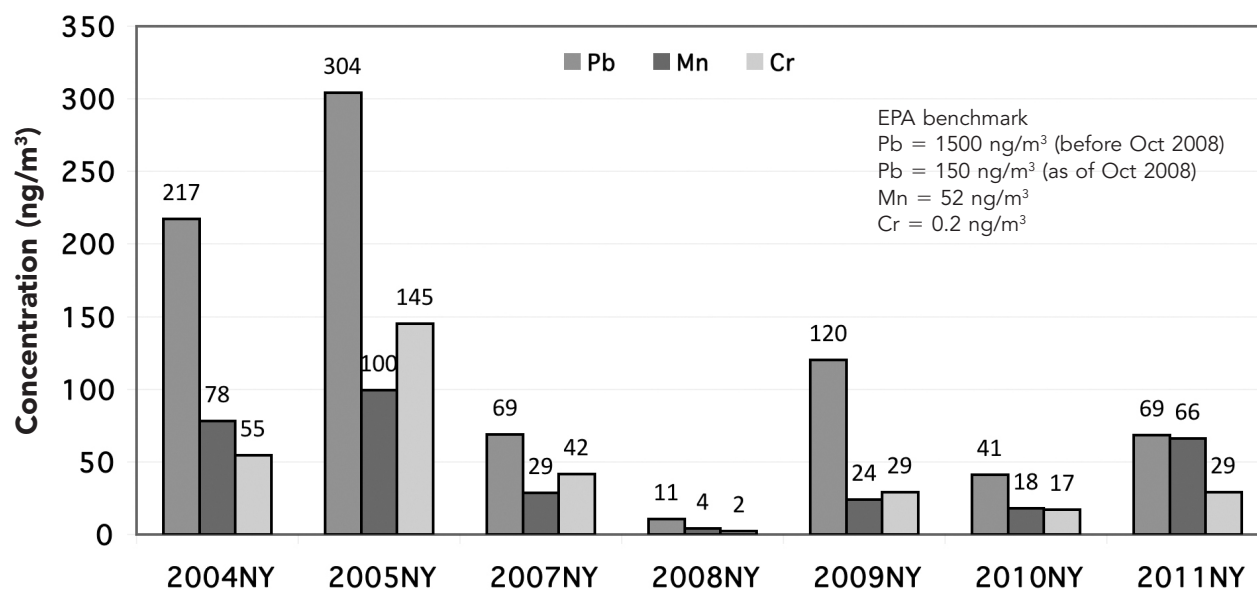
Mass data obtained from GFAAS and ICP-MS were corrected for filter blanks and then divided by the collected sampling volume to determine concentration of metal analytes in ambient air. We used the Pb-to-TSP ratio as an indicator of illegal fireworks activity and computed it as the quotient of ambient concentrations of Pb and TSP multiplied by 100. We compared the ambient air metal concentrations during fireworks displays with those before firework activity to determine peak and measured the dissipation as the time necessary for metal concentrations to return to pre-firework levels. We computed the residence time ( $\tau$ ) of PM<sub>10</sub> particulates by dividing the highest concentration of the particulates by the rate of removal in the atmosphere.<sup>48</sup> Quality management chemists from the

Environmental Health and Analytical Services Branch of HDOH reviewed and assured data quality.

## RESULTS

### Detection of HAP metals during 2004NY–2011NY celebrations

During 2004NY and 2005NY celebrations (Figure 1a), Pb peaks were highest at 217 ng/m<sup>3</sup> and 304 ng/m<sup>3</sup>, respectively, but these values were lower than the National Ambient Air Quality Standard of 1,500 ng/m<sup>3</sup> during that time. Levels of Cr at 55 ng/m<sup>3</sup> in 2004NY peaked even higher at 145 ng/m<sup>3</sup> in 2005NY. These values were 275 and 725 times the EPA benchmark of 0.2 ng/m<sup>3</sup> for Cr, respectively. Concentrations of Mn peaked at 78 ng/m<sup>3</sup> in 2004NY and 100 ng/m<sup>3</sup> in 2005NY, both of which exceeded the EPA benchmark of 52 ng/m<sup>3</sup>. From 2007 to 2011, Pb, Mn, and Cr concentrations decreased dramatically and, with the exception of Cr, were below EPA benchmarks. Cadmium concentrations exceeded the benchmark value of 1.4 ng/m<sup>3</sup> in 2007NY (1.9 ng/m<sup>3</sup>) and reached benchmark in 2005NY (1.4 ng/m<sup>3</sup>) (Figure 1b). Interestingly, Cd was detected below the benchmark level in 2004NY (1.1 ng/m<sup>3</sup>), 2009NY (0.8 ng/m<sup>3</sup>), 2010NY (0.6 ng/m<sup>3</sup>), and 2011NY (0.4 ng/m<sup>3</sup>), and below the method quantitation limit (MQL) in 2008NY. Peak Ni concentration was highest during 2005NY (8.2 ng/m<sup>3</sup>); however, none of the samples exceeded the EPA benchmark for Ni at 10 ng/m<sup>3</sup>. Beryllium was not found in any ambient air samples at the analytical limit of detection.

**Figure 1a. Ambient air concentrations of Pb, Mn, and Cr during 2004NY–2005NY and 2007–2011NY fireworks celebrations in Pearl City, Hawaii**

Pb = lead

Mn = manganese

Cr = chromium

NY = New Year

EPA = Environmental Protection Agency

ng/m<sup>3</sup> = nanograms per cubic meter**Detection of HAP metal peak concentrations during 2005NY and 2008NY celebrations**

The presence of the HAP metals was determined by ICP-MS based on their isotopic masses, as shown in Table 3. Comparison of the quantitative analysis of the HAP metals by GFAAS and ICP-MS from a 2005NY ambient air sample demonstrated a relative percent deviation of  $\leq 19\%$  for all metals. Although either method would have been acceptable in the analysis of the six HAP metals in this study, we chose ICP-MS because of its lower quantitation limits for most HAP metals (Table 3) and the convenience of analyzing multiple metals in a single analysis. Consequently, we used ICP-MS to determine peaks and dissipation of HAP metals including As, Hg, and other fireworks-related metals.

In 2005NY, HAP metal Pb increased 158-fold, and Cd, Mn, Cr, and Ni (Table 4) also increased substantially compared with pre-fireworks levels. Arsenic at 7.6 ng/m<sup>3</sup> was just higher than the MQL of 6.4 ng/m<sup>3</sup>, while Hg and Be were below the MQL and not listed in Table 4. In 2008NY, much lower concentrations of HAP metals Pb (11 ng/m<sup>3</sup>), Cr (2 ng/m<sup>3</sup>), and Mn (4 ng/

m<sup>3</sup>) were measured on New Year's Day. Pb levels were five times the pre-fireworks concentrations, while all other HAP metals had lower peaks (data not shown).

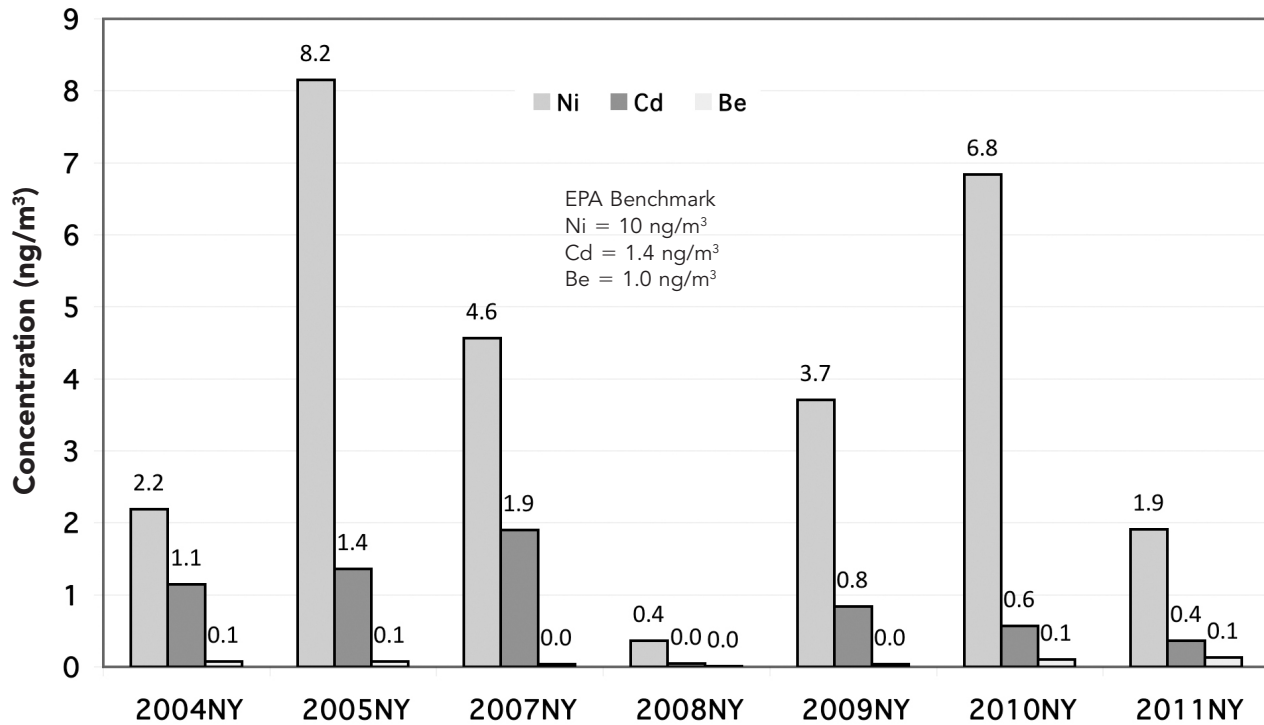
**Pb-to-TSP ratio compared with fireworks consumption during 2004NY–2011NY celebrations**

During regular monitoring, the Pb-to-TSP ratio ranged from 0.01% to 0.03%. After New Year's celebrations, the ratio increased above 0.04% and often rose much higher (Figure 2a; 2006NY data not available). Ratios occasionally increased after July 4 celebrations, but only reached the 0.04% level in 2003 and 2008. Very high Pb-to-TSP ratios were observed during the last three years (2009NY–2011NY), the highest ratio being in 2009NY (0.12%).

Fireworks importation has generally increased since 2004NY (Figure 2b),<sup>5</sup> although permits issued began declining in 2006NY. Starting with 2010NY, fireworks import measurements changed from cases to pounds and, thus, were no longer comparable with previous years' data. The 2011NY was the last year residential fireworks were to be allowed in Hawaii, and fireworks permit sales rose to 10,008 permits, which was a 24%



**Figure 1b. Ambient air concentrations of Ni, Cd, and Be during 2004NY–2005NY and 2007–2011NY fireworks celebrations in Pearl City, Hawaii**



Ni = nickel

Cd = cadmium

Be = beryllium

NY = New Year

EPA = Environmental Protection Agency

ng/m<sup>3</sup> = nanograms per cubic meter

increase from the previous year of 8,055 permits. Although the highest total volume of fireworks imports was recorded in 2007NY, a lower Pb-to-TSP ratio of 0.06% was observed for that year.

#### **Elevation of other metals in ambient air during the 2005NY and 2008NY celebrations**

During the 2005NY celebration, extremely high concentrations of Sr, potassium (K), copper (Cu), aluminum (Al), Mg, and sodium (Na), and moderately high concentrations of bismuth (Bi), antimony (Sb), zinc (Zn), Ba, titanium (Ti), and iron (Fe) were found (Table 4). Three days before the 2005NY celebration (on December 29, 2004), high concentrations of known fireworks-related metals (e.g., Mg, Al, K, and Ba) were already detected in ambient air, most likely due to sporadic fireworks use in the days leading up to New Year's Day. After midnight on New Year's Eve, ambient air

concentrations of Bi, Sr, K, Sb, Cu, Zn, Al, Mg, rubidium (Rb), and Ba increased dramatically compared with sampling three days earlier. Although measurement for Na was also high during New Year's Eve and could be attributed to fireworks, we could not rule out the effects of sea salt in the marine atmosphere.<sup>49,50</sup>

In 2008NY, metals that increased substantially compared with pre-fireworks concentrations included Ba (20-fold); selenium (sevenfold); Ag (sixfold); Sr and Ti (fourfold); Rb (threefold); and Bi, Cu, and K (twofold).

#### **Dissipation of PM<sub>10</sub> particulates, HAPs, and other metals during 2005NY and 2008NY**

The PM<sub>10</sub> particulate samples were collected hourly and used as an indicator of the dissipation rate of the fireworks-associated particulates in ambient air (Figure 3). In 2005NY, the particulates began increasing at about 8 p.m. on December 31, peaked around 1:30 a.m. on

January 1, and returned to pre-fireworks levels at about 5:30 a.m. on January 1. The atmospheric residence time ( $\tau$ )<sup>48</sup> of the PM<sub>10</sub> particulates was calculated to about four hours, which was fast considering the quantity of particulates. During 2008NY, particulate concentration fluctuated inconsistently, possibly due to stronger trade winds (Figure 3). The 2008NY particulates peaked at about 1:30 a.m. at 0.4 mg/m<sup>3</sup>, but dropped rapidly to the pre-fireworks level, resulting in an atmospheric residence time of about an hour.

The three-day post-fireworks concentrations of all metals, including HAP, had dissipated to pre-fireworks levels (Table 4) with the exception of Na and Cu, suggesting longer residence time for these metals.

However, high Na values measured for three days before and after the event suggested that the high background concentration of Na in Oahu's ambient air was most likely due to atmospheric sea salt from the Pacific Ocean, as reported in other studies.<sup>49,50</sup> Likewise, high background levels of ambient Cu, Al, Mg, and Fe may be explained by the transport of aerosols generated by the long sustained eruption of Hawaii's Kilauea volcano.<sup>51</sup>

## DISCUSSION

This study revealed that HAP metals Pb, Cr, Mn, Cd, Ni, and As, as well as other metals (e.g., Bi, Sr, K, Cu,

**Table 4. ICP-MS analysis of HAPs and screening of other metals detected in Pearl City, Hawaii, ambient air before, during, and after the 2005NY fireworks celebration**

Metals	Pre-FW (ng/m <sup>3</sup> )	During FW (ng/m <sup>3</sup> )	Post-FW (ng/m <sup>3</sup> )	Peak <sup>a</sup> fold increase
HAP metals <sup>b</sup>				
Lead	1.6	253.0	1.0	158
Cadmium <sup>c</sup>	0.1	1.6	<MQL	16
Manganese <sup>c</sup>	6.0	88.0	6.0	15
Chromium	11.0	158.0	9.0	14
Nickel <sup>c</sup>	1.2	6.0	1.0	5
Arsenic	<MQL	7.6	<MQL	1 <sup>d</sup>
Other metals <sup>e</sup>				
Bismuth	1	512	0 <sup>f</sup>	512
Strontium	8	1,719	6	215
Potassium	647	61,016	24	94
Antimony	1	86	0 <sup>f</sup>	86
Copper	137	6,697	200	49
Zinc <sup>c</sup>	32	581	22	18
Aluminum	797	7,295	212	9
Magnesium	2,040	18,409	1,299	9
Rubidium <sup>c</sup>	1	9	0 <sup>f</sup>	9
Barium	72	504	0 <sup>f</sup>	7
Silver <sup>c</sup>	1	6	0 <sup>f</sup>	6
Titanium	19	57	15	3
Zirconium	6	12	0 <sup>f</sup>	2
Iron	285	606	269	2
Sodium	16,767	21,743	19,450	1

<sup>a</sup>Peak was the fold increase of metals during fireworks vs. pre-fireworks concentration.

<sup>b</sup>Excluding beryllium and mercury

<sup>c</sup>Metals found in fireworks samples that are neither listed as permitted nor prohibited chemicals for consumer fireworks by American Fireworks Standards Laboratory

<sup>d</sup>Fold increase computed as 2005NY during FW/MQL (6.4 ng/m<sup>3</sup>)

<sup>e</sup>Other metals analyzed semi-quantitatively by ICP-MS

<sup>f</sup>0 value means that metal in blank filter is higher than exposed filter sample.

IC-PMS = inductively coupled plasma mass spectrometry

HAP = hazardous air pollutant

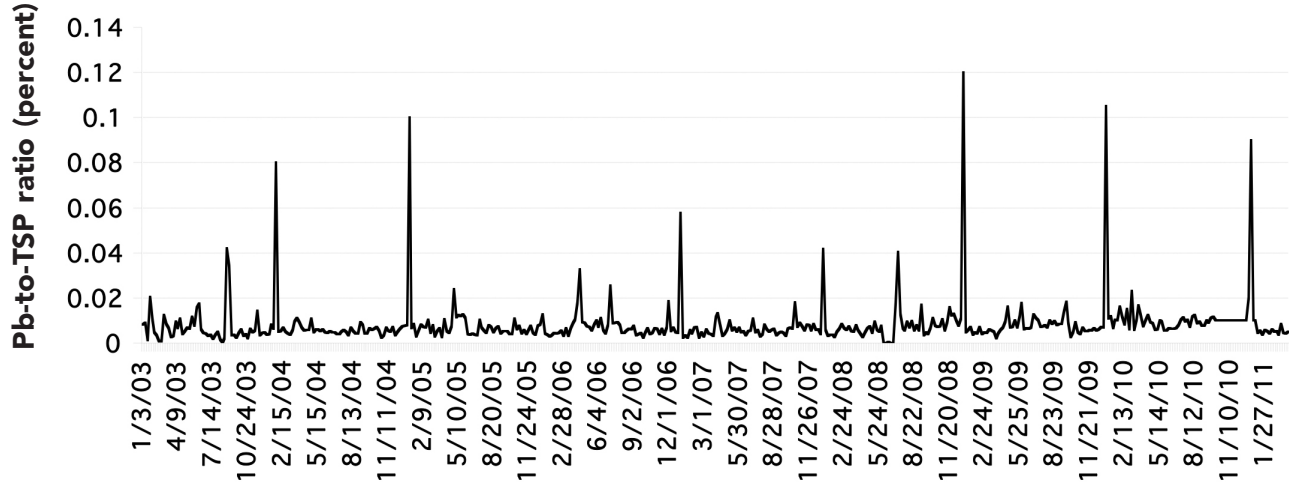
NY = New Year

FW = fireworks

ng/m<sup>3</sup> = nanograms per cubic meter

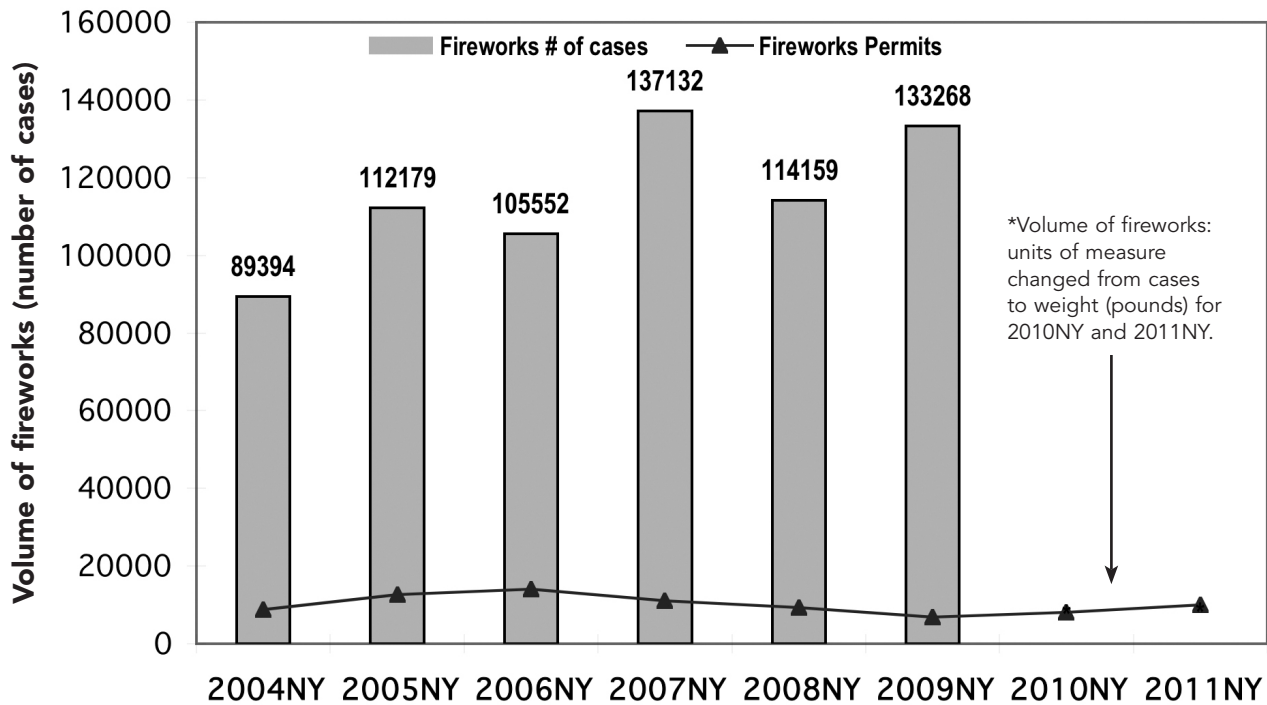
MQL = method quantitation limit

**Figure 2a. Trends of Pb-to-TSP ratio for fireworks particulates collected in Pearl City, Hawaii, during 2004NY–2011NY celebrations**



Pb = lead  
 TSP = total suspended particulates  
 NY = New Year

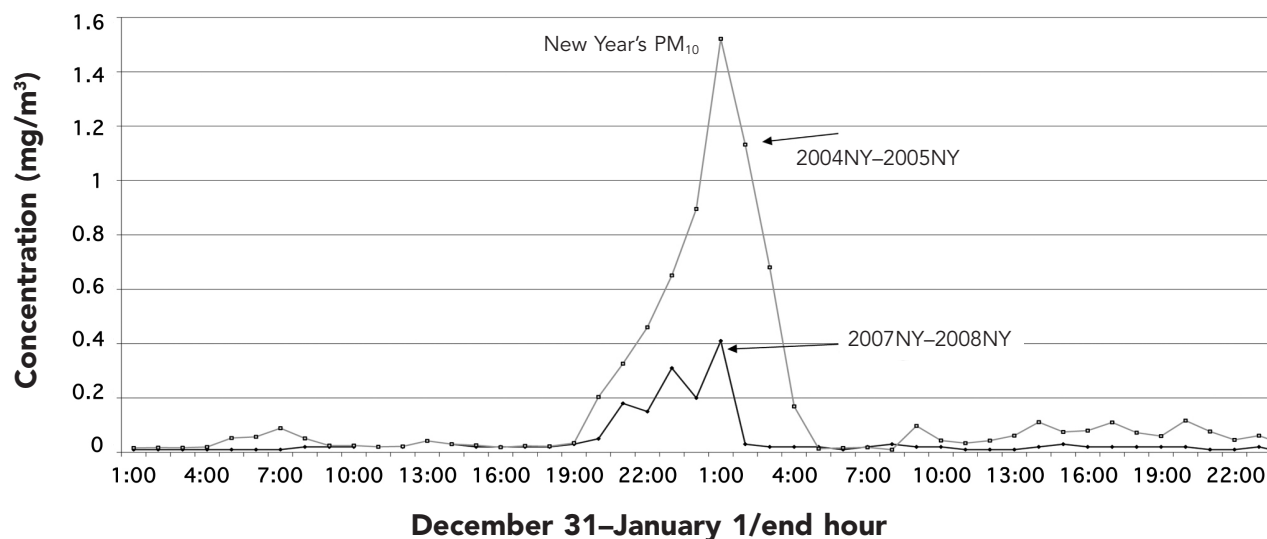
**Figure 2b. Fireworks imports and permits issued for 2004NY–2011NY celebrations in Honolulu, Hawaii**



Source: Honolulu Fire Department  
 NY = New Year



**Figure 3. Accumulation and dissipation of PM<sub>10</sub> particulates on 2005NY and 2008NY fireworks celebrations in Pearl City, Hawaii**



PM<sub>10</sub> = particulate matter 10

NY = New Year

mg/m<sup>3</sup> = milligrams per cubic meter

Zn, Mg, and Ba), reached high concentrations relative to pre-fireworks ambient air levels and then dissipated quickly. Among the HAP metals, only Pb is regulated by the EPA. In 2008, the three-month standard was revised downward from 1,500 ng/m<sup>3</sup> to 150 ng/m<sup>3</sup>. If the present 150 ng/m<sup>3</sup> standard had been in force during the 2004 and 2005 celebrations, Hawaii would have briefly (24-hour level vs. the three-month EPA standard) exceeded the Pb levels. Cd and As were also found, but the low concentrations indicate that these might just have been impurities in other metals such as Pb, Cu, or Zn.<sup>52,53</sup> Cr was analyzed as total Cr; however, based on the 2010 update of the Risk-Based Concentration (RBC) table,<sup>54</sup> the EPA benchmark was no longer listed for total Cr but only for the more toxic hexavalent Cr species (Cr<sup>+6</sup>), which was not analyzed in this study. Surprisingly, Cr as dichromate, a potential source of hexavalent Cr, is allowed by AFSL, although not exceeding 5% of the formulation. Also noteworthy was that neither Mn, Ni, or Cd metals (Table 4), nor their compounds, were listed as prohibited or permitted fireworks chemicals by AFSL.

Other metals that were found at high concentrations are well-known color producers in fireworks. Examples include Bi and Sr for producing blazing reds, Cu compounds for blues, and purples from K and Rb compounds. Hazard index information for all these metals in ambient air was not yet available in the EPA

RBC table<sup>54</sup> as of November 2011, although RBC is listed for Al (5,200 ng/m<sup>3</sup>) and Ba (520 ng/m<sup>3</sup>). During the 2005NY, the Al ambient air concentration of 7,295 ng/m<sup>3</sup> exceeded the hazard index, while Ba at 504 ng/m<sup>3</sup> was just below the hazard index value. Except for Rb, Ag, Ti, zirconium, and Zn, the other metals (Table 4) found in ambient air during the 2005NY were permitted by AFSL as standard fireworks chemicals.<sup>43</sup>

The American Pyrotechnics Association asserts that there are no Pb compounds used in U.S. manufacture; however, most fireworks products are imported from China. In 2001, AFSL began testing Chinese imports for pyrotechnic components, and those factories that did not meet standards were asked to reformulate their products to keep Pb-tainted fireworks out of U.S. markets. Recently, however, Pb and other prohibited metals were still detected in combusted fireworks in a study conducted under controlled conditions in Seattle, Washington.<sup>55</sup> Detection of Pb in ambient air in this study confirmed that some consumer fireworks being used, and perhaps sold in some U.S. states including Hawaii, were not AFSL tested and were probably illegal. In Hawaii, an increasing trend in fireworks imports with declining sale of consumer fireworks permits may have further indicated illegal fireworks trade. Moreover, high Pb-to-TSP ratios during the 2005NY and 2009NY–2011NY celebrations indicated that Pb-tainted fireworks were still being used or sold in Hawaii in recent years.



