DETERMINATION OF PERCHLORATE IN SOIL AND AIR SAMPLES DURING FIREWORKS DISPLAYS IN TAIWAN AND USA

by

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ABSTRACT

Perchlorate is considered an emerging persistent inorganic environmental contaminant. Perchlorate has been suspected of disrupting the thyroid uptake of iodide and subsequently causing the malfunction of metabolic processes. Firework displays are commonly referred to as a source of perchlorate in the environment. There are two types of fireworks displays: Near-ground fireworks or firecrackers and sky fireworks. During the explosion process, fireworks generate large amounts of smoke that is dispersed into the atmosphere, and the residuals of firecrackers or fireworks would further deposit on the ground or in the water.

In this study, sample analysis from the near-ground fireworks and firecracker events demonstrate that during the high time of the fireworks event, the concentration of perchlorate increased dramatically in the air. The outdoor air quality was more deteriorate than the indoor air quality during the fireworks events. However, when the events ended after 12 hours, both the anions and cations concentration in the air recovered to the original level. Unlike air samples, the cations and anions concentrations in the soil increased after the fireworks events.

Sample analysis from the sky fireworks display also showed the concentration of perchlorate in the air and soil. However, the concentration of perchlorate during the sky fireworks was smaller than during the near-ground fireworks. In addition, the concentration of cations, such as Ba(II), K(I), Na(I), Mg(II) and Sr(II) in the air and soil samples all increased as the concentration of perchlorate increased.

The risk of exposure to perchlorate during the near-ground fireworks/firecrackers events is higher than that during the sky fireworks event. It is found that all the age groups, adults, child age of 6-12 and child age of 2-6 were shown to have high hazard index when exposed to perchlorate during the near-ground fireworks events.

Chapter 1

STATEMENT OF PROBLEMS

Perchlorate is considered an emerging inorganic anion pollutant in drinking water sources. It has been reported [1] that perchlorate is present in groundwater and surface water at harmful concentrations in more than 26 states in USA (Figure 1-1). Perchlorate is used as an oxidant in solid fuel rocket propellants, explosives, pyrotechnics, and as a chemistry reagent.

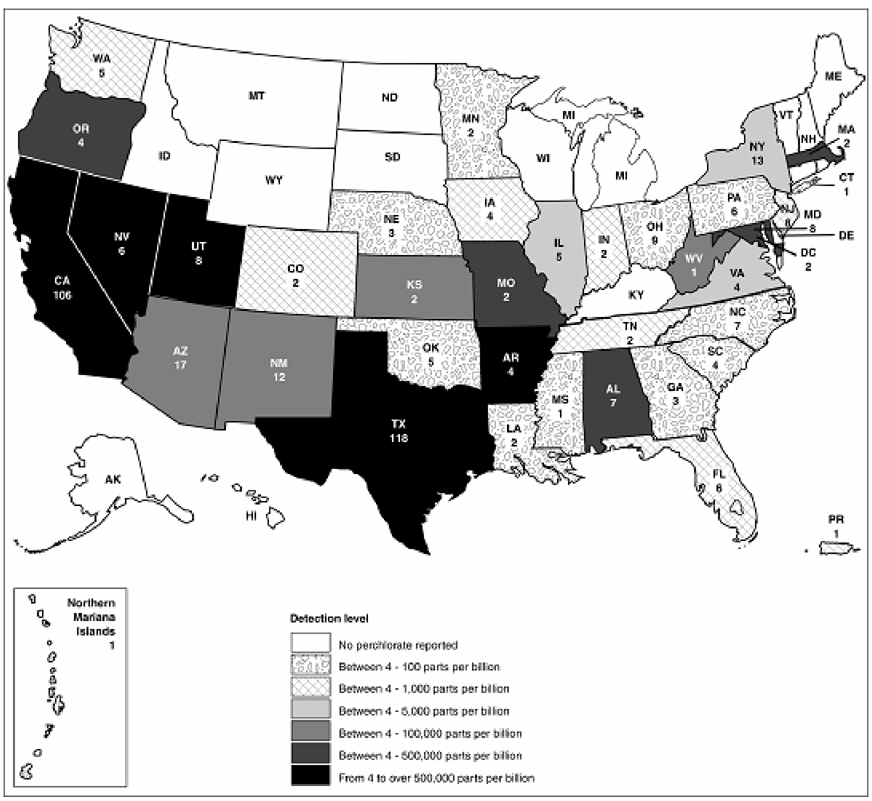


Figure 1-1. Maximum perchlorate concentrations reported in any media and number of sites, January 2005[1].

Firework displays are commonly referred to as a source of perchlorate in the environment, however only a few studies are available to evaluate its impact on groundwater or surface water resources. Furthermore, there are few reports on perchlorate pollution in the atmosphere. There are two types of fireworks display based on the explosion altitude: Near-ground fireworks or firecrackers and sky fireworks. Near-ground fireworks and firecrackers displays are common part of traditional cultural festivities in Asian communities. The sky fireworks display is common in many celebration ceremonies or holidays worldwide. During these events, more than hundreds or thousands of people gather together to celebrate and watch the fireworks displays. During the explosion process, the fallout from fireworks consists of fine particles of burnt black powder, paper debris and chemical residues. The adverse health effect from these aerosols or chemical residuals, especially for perchlorate species, during the fireworks display remains unclear.

The major objective of this research is to study the impact of (1) near-ground fireworks/firecracker event and (2) sky fireworks display on the environment, specifically air and soil, due to perchlorate emissions. Also, the risk assessment of the being exposure to perchlorate will also be calculated and discussed.

Chapter 2

LITERATURE REVIEWS

2.1 Properties of Perchlorate

Perchlorate ion (ClO_4^-) is an anion with one chlorine atom in the center and four oxygen atoms bonded to it at the corners. The whole ion is negative one charged and the charge is distributed evenly among four oxygen atoms due to the symmetric geometry. The chemical structure of perchlorate is sp3 hybrid tetrahedron with an angle of 109.5 degree between chlorine and oxygen bonding. The radius of perchlorate ion is about 5.5 Å. The length of Cl-O bond is about 1.44 Å to 1.55 Å. Perchlorate is known to be a very poor complexing agent and is used extensively as a counter anion in studies of metal cation chemistry[2]. Perchlorate is a strong oxidant due to having the highest oxidizing state (+VII) of the central chlorine atom. It is also the conjugate base of perchloric acid. Perchloric acid is one of the strongest acids with pKa value of about -10. Concentrated perchloric acid is in the concentration of 70% to 72%. Although perchlorate is a strong oxidant, dilute perchlorate solution is stable under room temperature and neutral pH conditions.

Perchlorate salts have highly solubility in the water, for example, the solubility of potassium, ammonium, or sodium perchlorate are 15, 200 and 2096 g/L at 298K, respectively. Therefore, due to the properties of the highly dissociation constant of perchloric acid and high solubility of perchlorate salts, perchlorate always exists in the ionic form in the water. In addition to the properties stated above, perchlorate ion is also poorly hydrated due to the even distribution of the negative charge. The hydration energy of perchlorate (about 205 kJ/mol) is among the lowest in common ions in natural waters. Therefore, these unique properties of perchlorate ion contribute to the fact that it is weakly adsorbed to an organic or mineral surface [2, 3].

2.2 Occurrence and Distribution of Perchlorate in the Environment

Both natural and anthropogenic origins are important contributing sources of perchlorate in the environment. Naturally occurring perchlorate in terrestrial soil has also been observed in a few locations of West Texas [4]. Low levels of perchlorate formed in the atmosphere by a heterogeneous reaction between ozone and volatile chlorine species or chloride salts can enter into the surface or groundwater via wet deposition [5]. Anthropogenic activities are mainly responsible for the wide spread perchlorate contamination of drinking water, surface water, groundwater, and soil. During the past few decades, rockets, missiles, fireworks, and explosives are major anthropogenic sources of perchlorate in the form of ammonium or potassium salts [6]. This compound is widely used as an oxidizer in solid propellants due to its high chemical stability and consistent performance. Moreover, perchlorate has been discovered in the range of 0.065 to 0.4 % (wt) as impurity in Peruvian and Chilean $NaNO_3$ fertilizers which have been used extensively in agricultural activities between 1830 and 1980 [4]. The high solubility of perchlorate salts and weak affinity of perchlorate ion toward to organic or mineral surfaces [2, 3] renders it widely transported into the aquatic environment.

As of 2004, perchlorate has been detected in public drinking water supplies serving more than 11 million people in the United States [7]. The minimum detection level of perchlorate for water samples collected under the Unregulated Contaminant Monitoring Rule is 4 ppb according to U.S. Environmental Protection Agency (US

EPA). Perchlorate has been detected at much higher concentrations in produce and dairy products due to bioaccumulation and food chain transfers. Dyke et al. have reported the average perchlorate concentration of 9.4 ± 2.7 and 5.9 ± 1.8 µg/L in cow's milk of Japan and United States, respectively [8, 9]. Anderson and Wu [10] reported that fish from contaminated sites have been found to contain perchlorate at several thousands of parts per billion (ppb) level in the head area and at hundreds of ppb level in the fillets. Sanchez et al. reported that the perchlorate content of selected foliage crops in southwestern United States irrigated with lower Colorado River water in the range of 43 to 2196 µg/kg on a dry weight basis [11]. In the human breast milk, the concentration of perchlorate has been found to be in the range of 0.5 to 39.5 µg/L.[12]

2.3 Health Effect of Perchlorate

Perchlorate ion (0.240 nm) is comparable in size to the iodide ion (0.216 nm) which is the key component of thyroid hormones. The thyroid gland is the largest endocrine organ that functions solely as an endocrine gland. The thyroid gland produces two major hormones, T_3 (L-triiodothyronine) and T_4 (L-thyroxine), which regulate the growth, cell differentiation, and the metabolisms of lipids, proteins and carbohydrates [13]. Ingestion of perchlorate contaminated waters or food products leads to perchlorate transport into the thyroid gland of mammals [14]. At sufficiently high levels and duration of exposure, perchlorate would block iodine uptake into the thyroid gland and impair thyroid hormone production. Consequently, thyroid hormone production decreases and potentially causes adverse effects on the metabolism and growth of newborns, hypothyroidism, thyroid cancer, and neurological dysfunction associated with other thyroid disorders [15, 16]. While most adults do not exceed perchlorate uptake in a regular diet, the full effect of perchlorate at any concentration is yet to be learned. Environmental exposure to perchlorate has been associated with elevated thyroid stimulating hormone and lowered thyroxine in adult women [17] and infants [18]. Furthermore, perchlorate seems to concentrate in breast milk, putting breastfed infants less than 6 months of age at risk for thyroid dysfunction [19].

Due to the toxicity and the health effect of perchlorate, there has been increased interest in setting the limit of perchlorate concentration in drinking water at a lower concentration (ppb) level. In January 2009, the EPA issued a heath advisory to assist state and local officials in addressing regional contamination of perchlorate in drinking water sources. The National Academy of Science has established the recommended reference dose (Rfd) for perchlorate to be 0.7 µg/kg-day [20]. New York State has implemented advisory levels of perchlorate at 5 µg/L for the drinking water planning in groundwater [21]. Perchlorate is already regulated in California and Massachusetts drinking water with the maximum contaminant level (MCL) of 6 and 2 µg/L, respectively [22, 23]. In February 2011, the U.S. EPA expressed the government's intent to establish a national primary drinking water regulation (NPDWR) for perchlorate [24]. The EPA expects to issue a proposal by the end of 2014 and a final ruling by September 2015 [25].

2.4 Perchlorate in Fireworks or Firecrackers

As mentioned above, perchlorate is widely used in the pyrotechnic industry for producing fireworks or firecrackers. Figure 2-1 shows U.S. fireworks consumption including consumer and display fireworks in year 2000 to 2013. [26] The annual fireworks consumption amount has increased from 150 million lbs. in year 2000 to

280 million lbs. in year 2005. The number dropped after year 2005 and remained stable around 200 million lbs between year 2008 and year 2013.

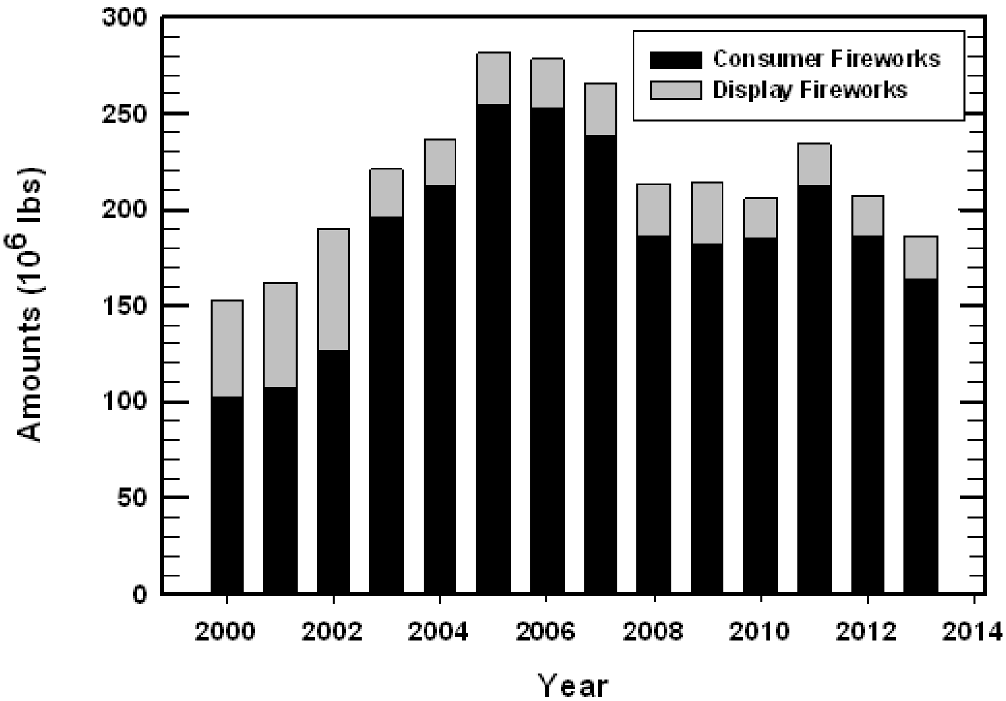


Figure 2-1. U.S. fireworks consumption in year 2000 to year 2013 [26].

Fireworks or firecrackers displays are an important source of pollution that generate substantial quantities of chemicals such as heavy metals, PAHs, and oxyanions on a regional or national scale within a short and specific period of time. Examples of such events are New Year's Eve and 4th of July celebrations in the US, and the Lantern Festival in Asian countries. During the burning or explosion process, fireworks generate large amounts of smoke, usually in plumes, that is dispersed into the atmosphere. Burning of crackers and sparkles during Diwali in India is a very strong source of air pollution which contributes significantly to the high amount of metals in air [27]. In USA, major fireworks displays are often held over lakes and other bodies of water to minimize the risk of fire, however, this can also lead to the deposit of significant amounts of perchlorate into the water. Backus et al. [28] reported that perchlorate was detected at several samples in selected surface waters in the Great Lakes Basin. Wilkin et al. [29] showed that a maximum perchlorate concentration of 44.2 μg/L was determined following a July 4th event in 2006. After the fireworks displays, perchlorate concentrations decreased to baseline levels within 20 to 80 days. Munster et al. [30] found that the mean perchlorate concentration in the deposition is 0.21 ± 0.04 and 18-fold increase above the mean concentration in July 2006 and July 2007 samples. In China, Shi et al. observed that the concentrations of perchlorate in the air samples were in the range of zero to 39.16 ng/m^3 during the Spring Festival in year 2007[31]. The pervasive presence of perchlorate makes it critical to study short-term deteriorated air, water or soil quality and to examine the potential human health impacts from the fireworks.

Chapter 3

EXPERIMENTAL MATERIALS AND METHODS

3.1 Chemicals and Materials

All chemicals were of analytical or reagent grade, or the highest purity available from suppliers. The certified standard anion solutions (1000 mg/L) of chloride (Cl^-), nitrate (NO_3^-), perchlorate (ClO_4^-), sulfate (SO_4^{2-}) and multi-elements standards were purchased from SPEX CertiPrep (Metuchen, NJ, USA). All aqueous solutions were prepared with de-ionized, distilled water (DIW) or 1% of HNO_3 solutions.

3.2 Sampling Procedures

In this study, the air and soil samples were collected before, during and after the time of fireworks display. For air samples, a sampling system was used to collect the aerosols and particles from the air as shown in Figure 3-1.

Where SV1: Sampling Vial 1(30 mL DIW)
SV2: Sampling Vial 2(30 mL DIW)
MA: Moisture Absorber (Silica gel desiccant)
CV: Check valve (Flow adjust)
FM: Flow-Meter (250 ml/min)
VP: Vacuum Pump

To get the background concentration of anions and cations in the air, several blank samples were performed before the fireworks/firecrackers launch. The above procedure was repeated with new sampling vials (1 and 2) to get air samples during and after the fireworks display.

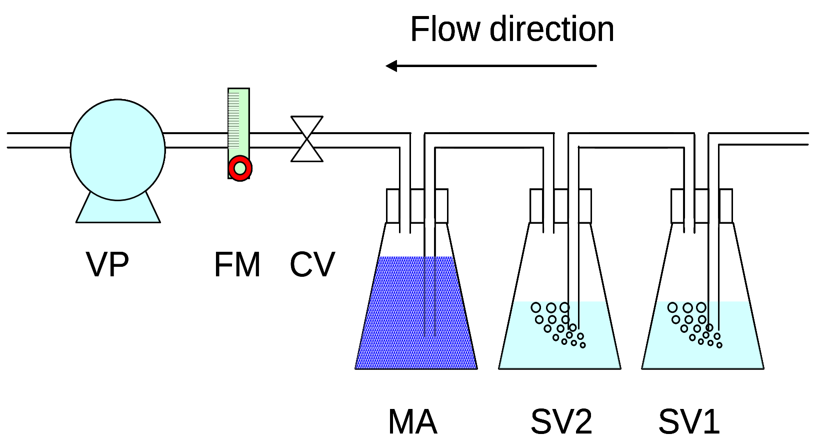


Figure 3-1. Air Sampling System.

To obtain a soil sample, the top layer of debris to the desired soil layer was first carefully removed with a pre-cleaned spade. Then 50 grams of the soil sample was placed into a labeled plastic container with a pre-cleaned plastic scoop, spoon or trowel, and then the caps were secured tightly and mixed thoroughly to obtain a homogenous sample representative of the entire sampling interval. Afterwards, all sample solutions were stored in 4°C refrigerator and the soil samples were stored in a dark site to avoid sun light radiation.

3.3 Analytical Methods

Both air samples and soil samples were pretreated before analysis. First, the water in the air sampling vial 1 and vial 2 were first filtered with syringe filters (0.2 micrometer Nylon). Then the samples were further diluted with DIW or 1% of HNO_3 solutions for analysis.

For soil samples pretreatment, soil samples ranging from 0.1g to 1g were placed into 30 ml, pH =9 NaOH solution for extraction 24 hours at 25℃. The solution was then filtered with a syringe filter (0.2 micrometer Nylon). Finally, the solution was further diluted with DIW or 1% of HNO_3 solutions for analysis.

The concentration of perchlorate and other anions, namely, chloride, sulfate, and nitrate, were analyzed by ion chromatography. A Dionex DX500 (CA, USA) ion chromatography system equipped with Dionex AS40 auto-sampler and the guard column (IonPac AG16, 50mm×4mm) and analytical column (IonPac AS16, 250mm×4mm). The concentrations of various cations were determined by Perkin Elmer 5000 DV ICP-OES.

3.4 Sampling Sites Description

In this study, air and soil samples were collected during fireworks events in Taiwan and USA. The details of each site are described in the following sections.

3.4.1 Yanshuei District, Tainan Taiwan

Our first study took place in Taiwan, between February 28 and March 1, 2010 during the annual Yenhsui Beehive Fireworks Festival in Yenhsui Township, Tainan, Taiwan. The GPS coordinate is 23.321906, 120.266842. The second sampling was in February 17 and February 18, 2011 during the same fireworks Festival at the same location.

Figure 3-2 illustrates the study site located in Yanshuei District, Tainan, Taiwan. The sampling sites were (1) police station, (2) Yanshuei High School, (3) Yanshuei Elementary school, (4) private residence A, and (5) private resident B. Location. The Yanshuei High School was the “Main-Theme Firework Site” of the annual Firework Festival, where all of the parades started. Before the parade, several "main fireworks" were performed at the sports field. Three sites surrounding the sports field were selected for collection of environmental samples including air and soil. The three sites (S1 to S3) were located around 3 to 5 meters from the runway and S1 is the site closest to the sports field. As shown in Figure 3-2, S1, S2 and S3 are located on the south side, north side, and north-western side of the runway, respectively. During the fireworks, it was observed that the site near the viewing stand was in the down-wind location (near S1). The police station, Residence A, and Residence B were on the parade routes. The elementary school was chosen as the background site in this study because no fireworks were set off at this location. Samples were collected before and after the parade.

Figure 3-2. Map showing the location of sampling sites near the fireworks/firecracker festival in Yanshuei District, Tainan City 737, Taiwan. (23.321906, 120.266842)

3.4.2 Newark, DE USA

The sampling site in USA is Newark, Delaware at GPS coordinate is 39.662132, -75.751169, where fireworks were launched on July 4th. The sampling dates were scheduled from July 1st to July 5th, 2010. Figure 3-3 illustrates the study site in Newark, Delaware. The soil samples were collected at the fireworks launch site and the air samples were collected at the observation sites. A total of 5 locations at the observation site were sampled during the fireworks display event. The total of 4 locations at the launch sites were sampled before and after the event.

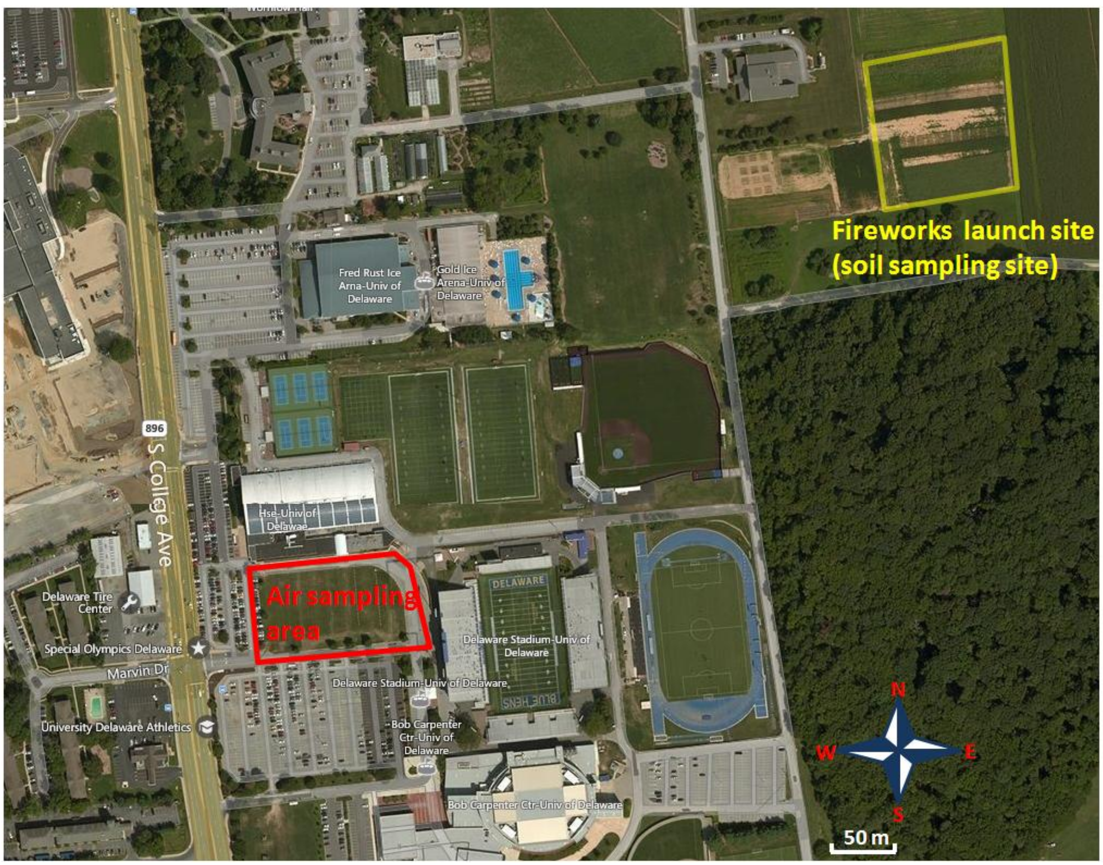


Figure 3-3.Map showing the location of sampling sites near the fireworks launch site in Newark, DE 19713, United States. (39.662132, -75.751169)

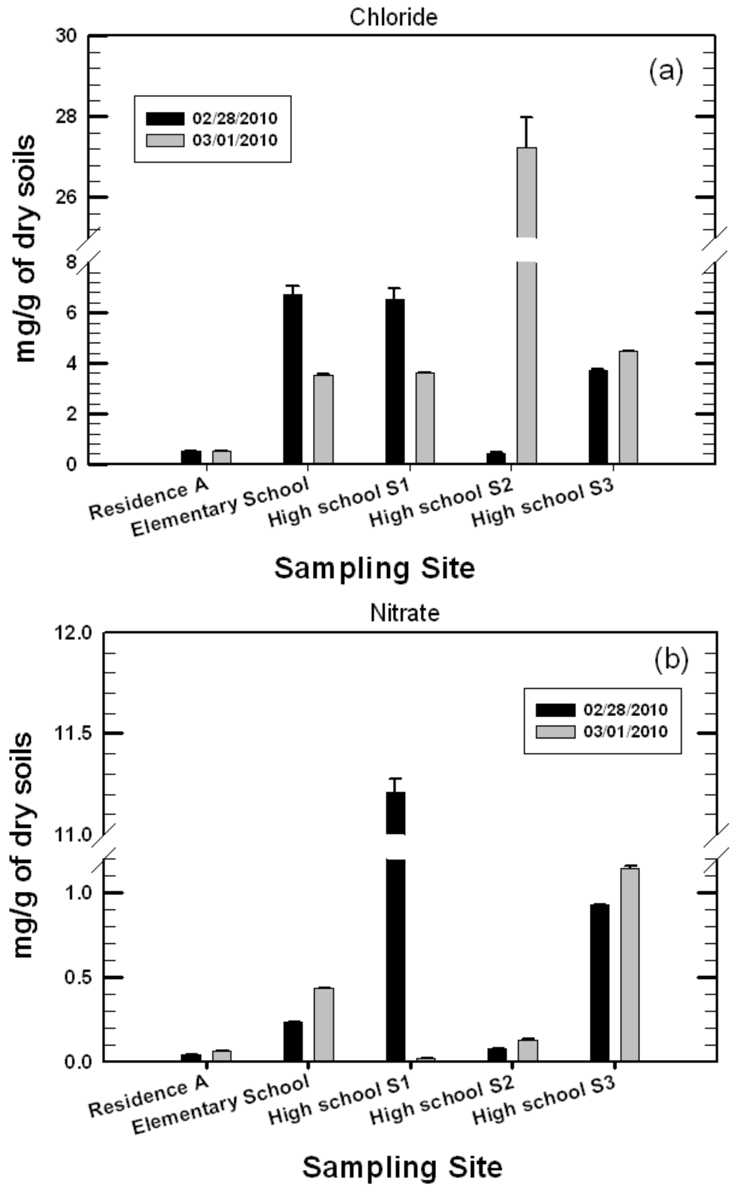
Chapter 4

RESULTS AND DISCUSSION

4.1 2010 Field Sample in Taiwan

4.1.1 Analysis of Soil Samples

Figure 4-1 shows the concentration of anions (a) chloride, (b) nitrate, (c) sulfate and (d) perchlorate in the soil samples before and a day after the firework and firecracker festival at 5 different sampling sites that is Resident A, Elementary school and three sites at High school sport field. The sampling site at the Elementary school is used as background concentration in this study since the site is not on the firework launch parade route. In Figure 4-1, the concentration of anions at the Elementary school remained stable before and after the fireworks event. The concentration of the chloride from the sampling site 2 at the high school increased from 0.45 mg/g of dry soil to 27.4 mg/g of dry soil (Figure 4-1a). This increase implies that the perchlorate compounds as strong oxidants in the fireworks were completely reduced to chloride during the combustion process. It has been reported that the thermal decomposition products of various metal perchlorate compounds would be the corresponding oxide or chloride [32]. Also, the combustion of ammonium perchlorate without metal would also yield HCl and $Cl_{2(g)}$ [33]. Therefore, the increased concentration of chloride in the soil samples would be from the final product of the combustion of the fireworks. The concentration of all anions, especially sulfate (Figure 4-1c) and perchlorate (Figure 4-1d) increased in the four sampling sites after the fireworks events. The concentration of perchlorate at the Resident A sampling site increased 5.3-fold from 3 µg/g to 16 µg/kg in the soil. The observation implies that residuals of firecrackers or fireworks deposited on the ground after the event, accumulating in the nearby soil.



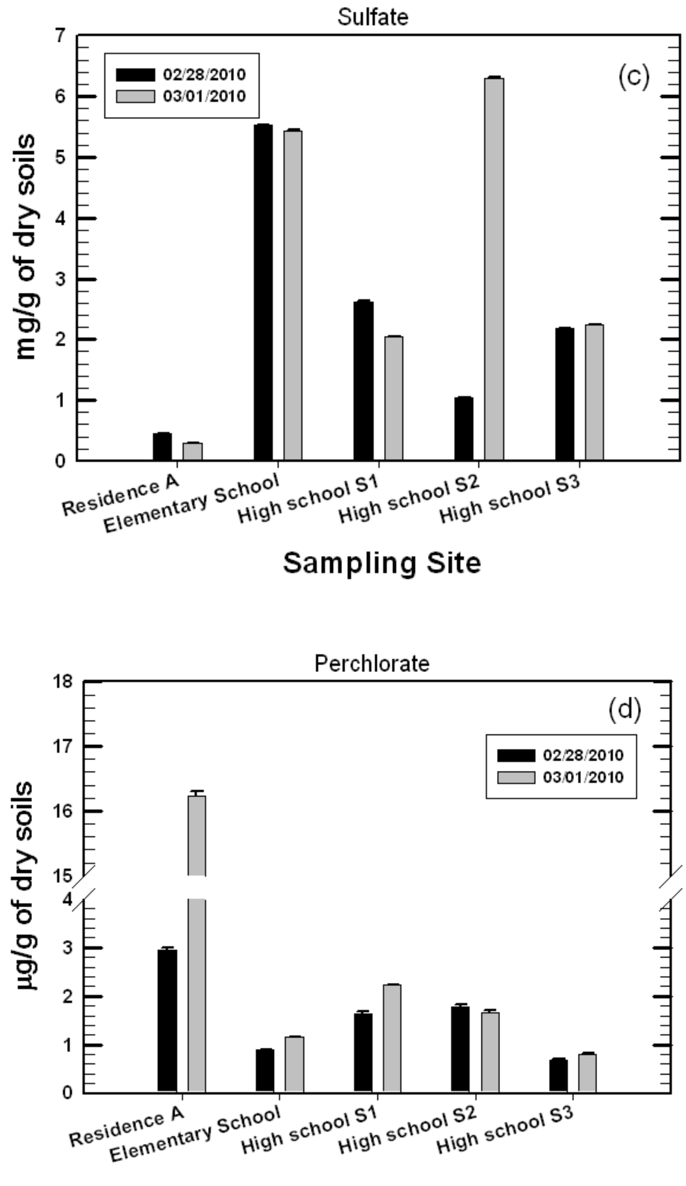


Figure 4-1. Concentration of anions (a) chloride, (b) nitrate, (c) sulfate and (d) perchlorate in the soil samples before and after the firework and firecracker festival at different sites. Experimental condition: soil sample= 10g.

4.1.2 Analysis of Air Samples

Figure 4-2 shows the concentration of anions in the air samples before and after fireworks events at the Elementary school. The left y-axis represents the concentration of chloride, nitrate and sulfate in the air and the right y-axis represents the concentration of the perchlorate in the air. The x-axis indicates the sampling time before and after event. The results indicated no significant changes in emission in the air sample before and after the event. As mentioned above, the Elementary school is considered as the control location where no firework activity were performed nearby in this study. However, 0.07 ppbv of perchlorate was still found after 12 hours of the event. It is believed that the wind direction would spread the distribution of the perchlorate containing particles or aerosol in the air.

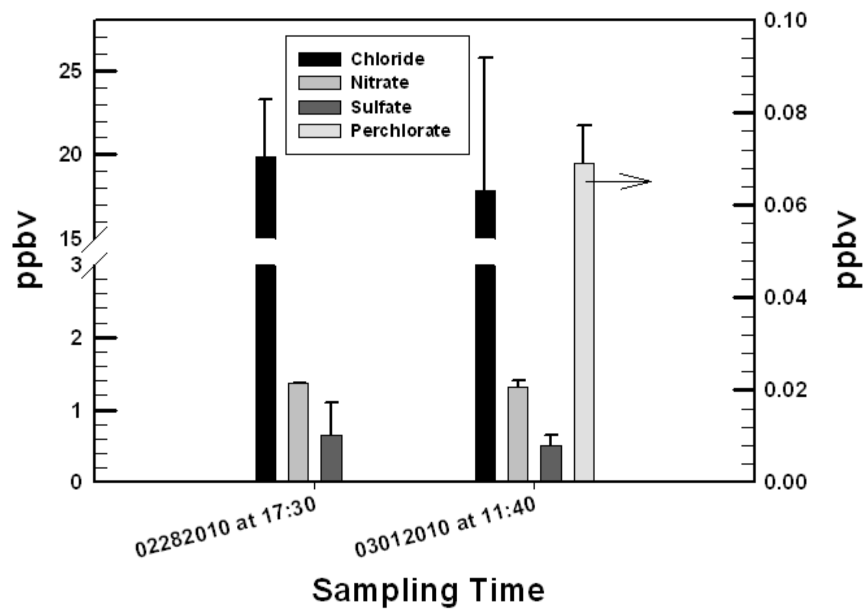
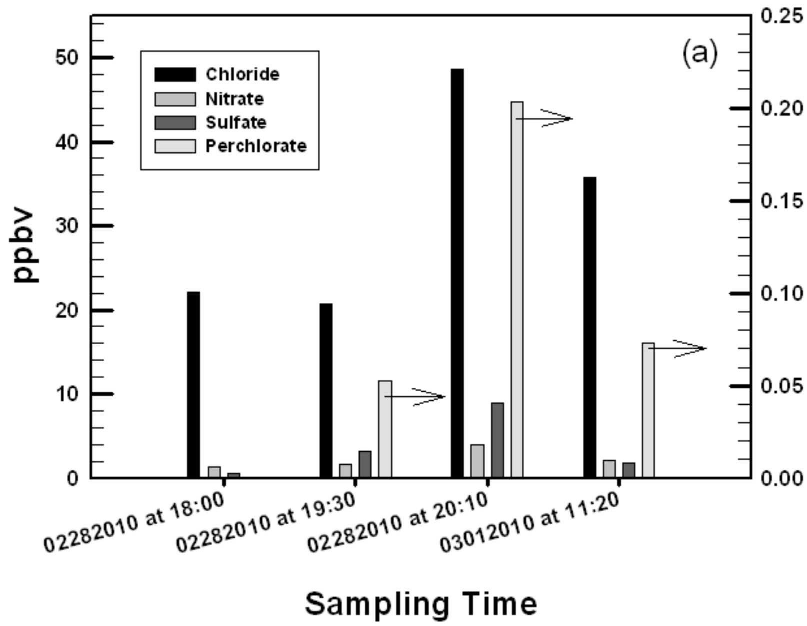
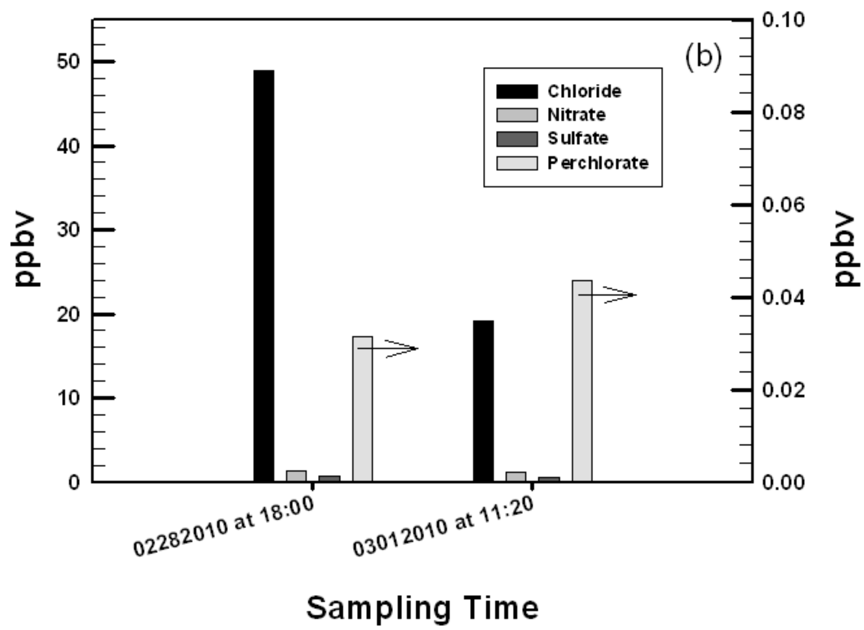


Figure 4-2. Concentration of anions in the air before and after the firework event at elementary school site. Experimental condition: Sampling flow rate= 0.25 L/min, sampling time: 20 min.

Figure 4-3 shows the time profile of concentration of anions in the air samples during the firework and firecracker festival at three different sampling sites at High school sport field. The left y-axis represents the concentration of chloride, nitrate and sulfate in the air and the right y-axis represents the concentration of the perchlorate in the air. The x-axis indicates the sampling time in the beginning, during the high time and the end of the event. The results show that the concentration of the perchlorate increased in all three sampling site during the event. At the site 1 (Figure 4-3a), the concentration of perchlorate increased from 0 ppbv to 0.20 ppbv from the beginning of the event to the high time of the event and then it decreased to 0.07 ppbv at the end of the event. At the site 3 (Figure 4-3c), it increased from 0.03 ppbv to 0.27 from the beginning of the event to the high time of the event and then it decreased to 0.06 ppbv at the end of the event. At the site 2 (Figure 4-3b), air samples were collected at the beginning and at the end of the event, it shows that the concentration of perchlorate after the event was about the same before the event. Therefore, it is found that during the event the concentration of perchlorate did increase at the sampling site and it would reach to initial level after the event was done.


(a)
Chloride
Nitrate
Sulfate
Perchlorate
ppbv
ppbv
0
10
20
30
40
50
0.00
0.05
0.10
0.15
0.20
0.25
02282010 at 18:00
02282010 at 19:30
02282010 at 20:10
03012010 at 11:20
Sampling Time


(b)
Chloride
Nitrate
Sulfate
Perchlorate
ppbv
ppbv
0
10
20
30
40
50
0.00
0.02
0.04
0.06
0.08
0.10
02282010 at 18:00
03012010 at 11:20
Sampling Time

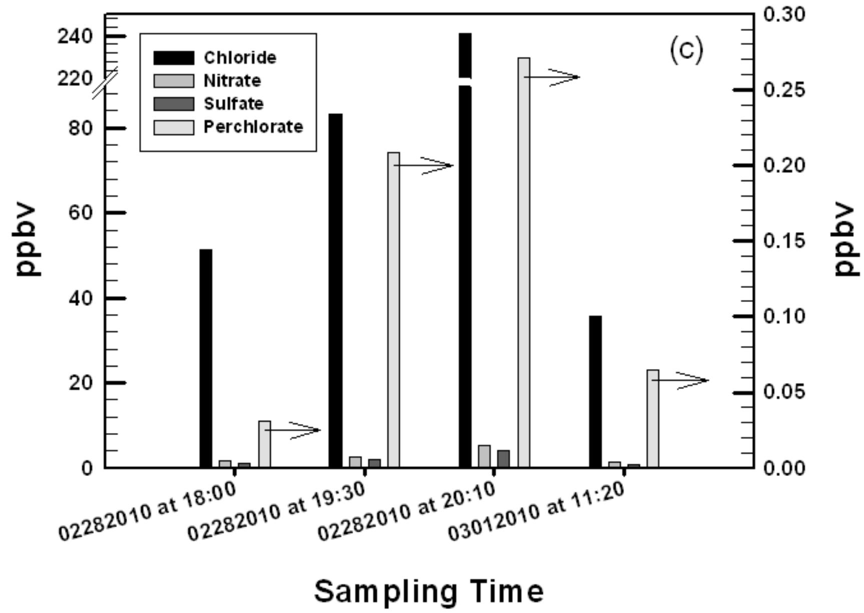


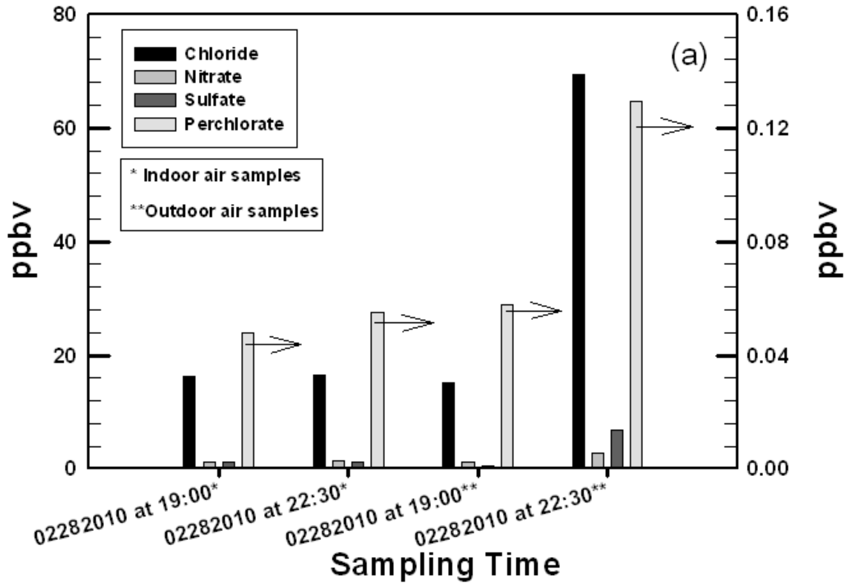
Figure 4-3. The anions (Cl^-, NO_3^-, SO_4^{2-}, ClO_4^-) concentrations of air – time profile during the fireworks/firecrackers events at nearby high school (a) sampling site 1, (b) sampling site 2 and (c) sampling site 3. Experimental condition: Sampling flow rate= 0.25 L/min, sampling time = 20 min.

Figure 4-4 compares the indoor and outdoor air quality during the fireworks/firecrackers events at three sites, that is, (a) Police station, (b) Resident A site and (c) Resident B site. Here we used the net emission percentage (δ) to represent the increase or decrease of the concentration of species after the events. Here is the equation for calculation of the emission percentage,

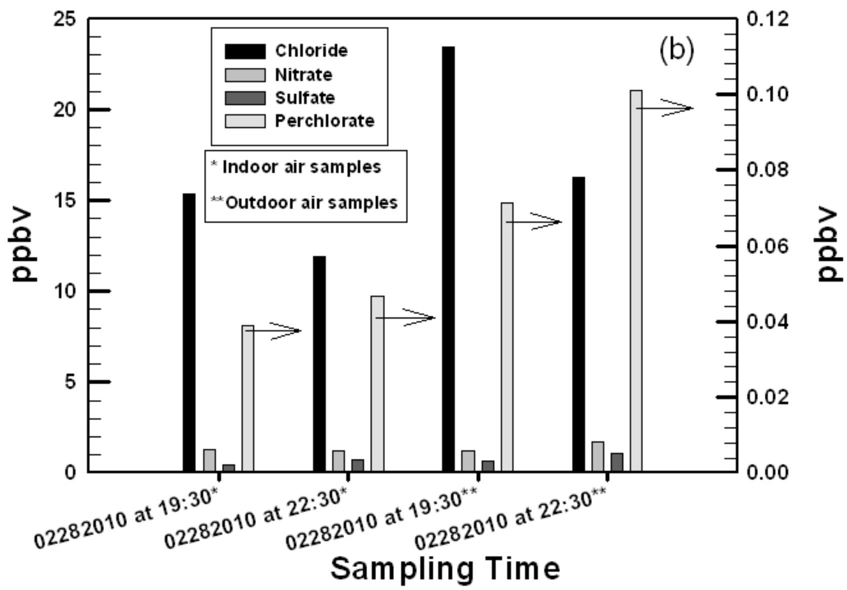
$$\delta(\%) = \frac{(C_a - C_i)}{C_i} \times 100(\%) \qquad \text{(Eq. 4-1)}$$

where C_a and C_i is the concentration of the anion at the end and the beginning of the fireworks events. The main event (fireworks) at the High school started at around

7:00PM. The parades started right after the main event with three parade routes and most of the township was in the range of the parades. Many fireworks were set up along the routes starting at 7:00PM, resulting in the detection of perchlorate at the beginning of the parades (Figure 4-4). At the Police station (Figure 4-4a) the emissions increased by 357% , 141%, 1327% and 124% for chloride, nitrate, sulfate and perchlorate, respectively, in the outdoor air. The outdoor air emissions at the private Residences A and B site showed that the concentration changed by -31%, 41%, 69% and 42% after fireworks event for chloride, nitrate, sulfate and perchlorate, respectively at the Resident A site and by 42%, -2.1%, -28%, and 12% for chloride, nitrate, sulfate and perchlorate, respectively at the Resident B site. For the indoor air samples at the three sampling sites, the emissions of chloride, nitrate sulfate and perchlorate ranged from -23% to 69% which is relatively stable compared to the outdoor air samples (See Table 4-1). It should be mentioned that during the event, most of the residences around the area closed their windows and doors to prevent the emission from the fireworks from entering the homes. However, the police station doors were kept open per police protocol. Despite this difference, the overall the concentration of anions in the indoor samples remained similar.



(a)
Chloride
Nitrate
Sulfate
Perchlorate
* Indoor air samples
**Outdoor air samples
ppbv
ppbv
0
20
40
60
80
0.00
0.04
0.08
0.12
0.16
02282010 at 19:00*
02282010 at 22:30*
02282010 at 19:00**
02282010 at 22:30**
Sampling Time



(b)
Chloride
Nitrate
Sulfate
Perchlorate
* Indoor air samples
**Outdoor air samples
ppbv
ppbv
0
5
10
15
20
25
0.00
0.02
0.04
0.06
0.08
0.10
0.12
02282010 at 19:30*
02282010 at 22:30*
02282010 at 19:30**
02282010 at 22:30**
Sampling Time

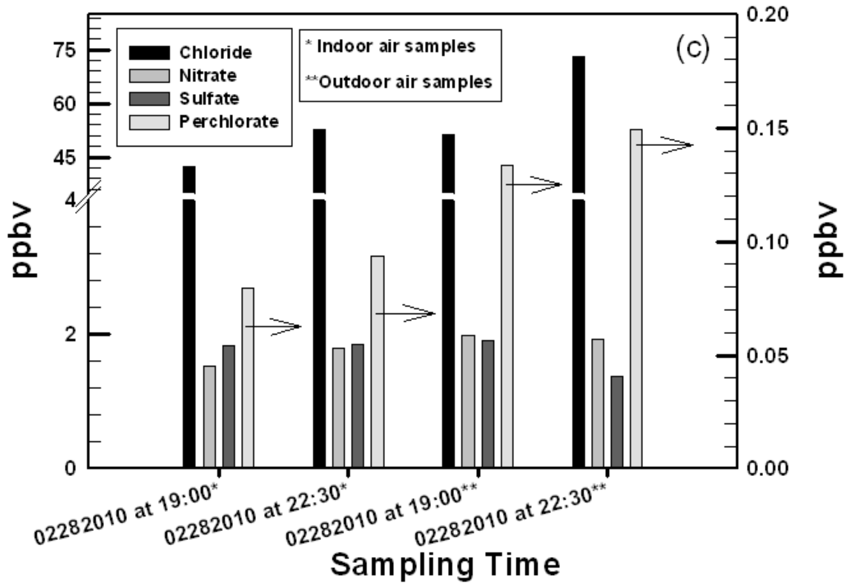


Figure 4-4. The anions (Cl^-, NO_3^-, SO_4^{2-}, ClO_4^-) concentrations of indoor and outdoor air – time profile during the fireworks/firecrackers events at nearby (a) Police station, (b) Resident A site and (c) Resident B site. Experimental condition: Sampling flow rate= 0.25 L/min, sampling time = 20 min.

Table 4-1. Net emission percentage of anions in the indoor and outdoor air samples after fireworks events at different sampling sites.

		Net Emission Percentage (%)			
Sampling Site	Air	Chloride	Nitrate	Sulfate	Perchlorate
Police Station	Indoor	1.3	15.5	2.3	14.1
	Outdoor	357.4	141.2	1326.5	123.7
Resident A	Indoor	-22.5	-4.1	67.4	19.8
	Outdoor	-30.5	41.3	68.7	41.5
Resident B	Indoor	24.0	16.7	1.4	18.0
	Outdoor	42.8	-2.1	-28.0	11.7

In summary, the results indicated clearly that during the high time of the fireworks event, the concentration of perchlorate increased dramatically in the air. The outdoor air quality was more deteriorate than the indoor air quality during the fireworks events. However, when the events ended after 12 hours, the anions concentration can be recovery to the original level. Unlike air samples, the anions concentrations in the soil increased after the fireworks events. The observation means that residuals of firecrackers or fireworks deposited on the ground after the event. Through the rainfall process, the anion on soil particle would be washed out and transported into groundwater bodies.

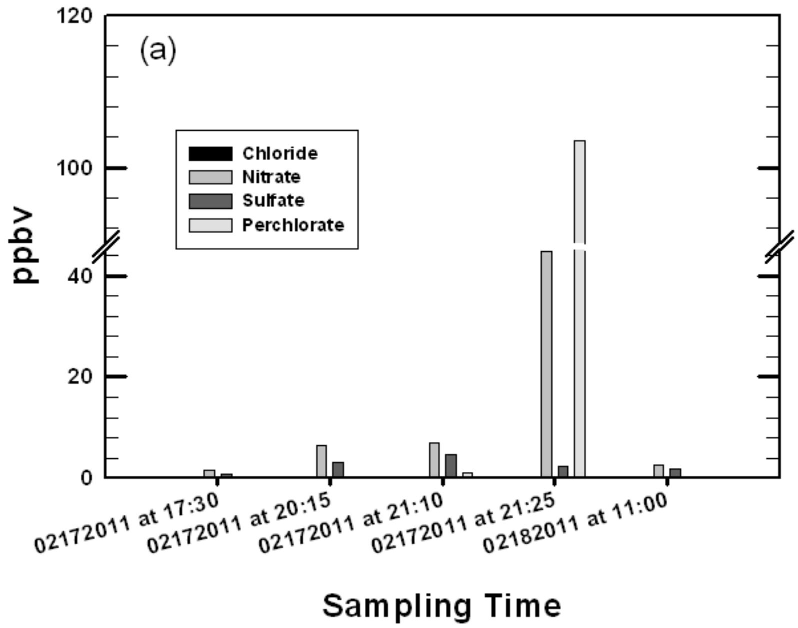
4.2 2011 Field Samples in Taiwan

The air and soil samples were collected in the year of 2011 during the fireworks/firecrackers events at the same site in Taiwan again. In addition the common anions analysis, such as chloride, nitrate, sulfate and perchlorate, the element analysis were also performed by ICP-OES.

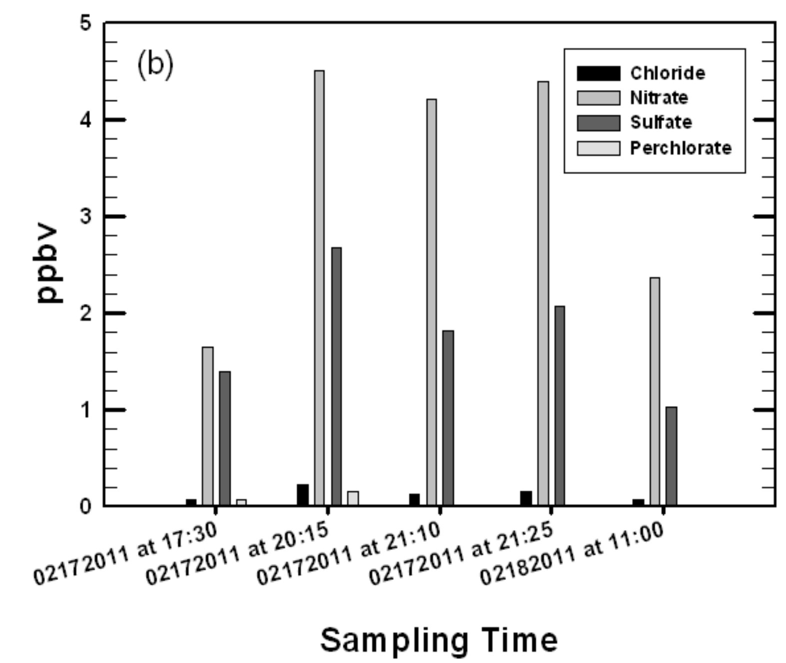
4.2.1 High School Region

4.2.1.1 Analysis of Air Samples

Figure 4-5 shows that the anions (Cl^-, NO_3^-, SO_4^{2-} and ClO_4^-) concentrations of air – time profile during the fireworks/firecrackers events at nearby high school. Total of 15 samples at three sites were collected before and after the fireworks events. At the sampling site 1 (Figure 4-5a), the concentration of perhclorate increased from 0 ppbv to 100.8 ppbv during the events at the mean time the concentration of nitrate increased from 1.6 ppbv to 40.7 ppbv. At the sampling site 2 (Figure 4-5b), the concentration of nitrate and sulfate during the fireworks event is about 2.7 and 1.9 folds higher than that before the firework event (2010/02/17 at 17:30). At the sampling site 3 (Figure 4-5c), the concentration of nitrate and sulfate during the fireworks event is about 2.3 and 6.5 folds higher than that at the beginning of the firework event. In addition, 0.4 ppbv of perchlorate was found at the sampling site 3. Therefore, the air quality around the fireworks event area was deteriorated during the fireworks period. The observation raised up the health concern for the people attending the fireworks events. However, after the fireworks events, the samples collected in the next day (sampled at 11:00 on 2010/02/18) at the three sites all showed the similar concentration of anions as that at the initial condition.



(a)
Chloride
Nitrate
Sulfate
Perchlorate
ppbv
120
100
40
20
0
02172011 at 17:30
02172011 at 20:15
02172011 at 21:10
02172011 at 21:25
02182011 at 11:00
Sampling Time



(b)
Chloride
Nitrate
Sulfate
Perchlorate
ppbv
5
4
3
2
1
0
02172011 at 17:30
02172011 at 20:15
02172011 at 21:10
02172011 at 21:25
02182011 at 11:00
Sampling Time

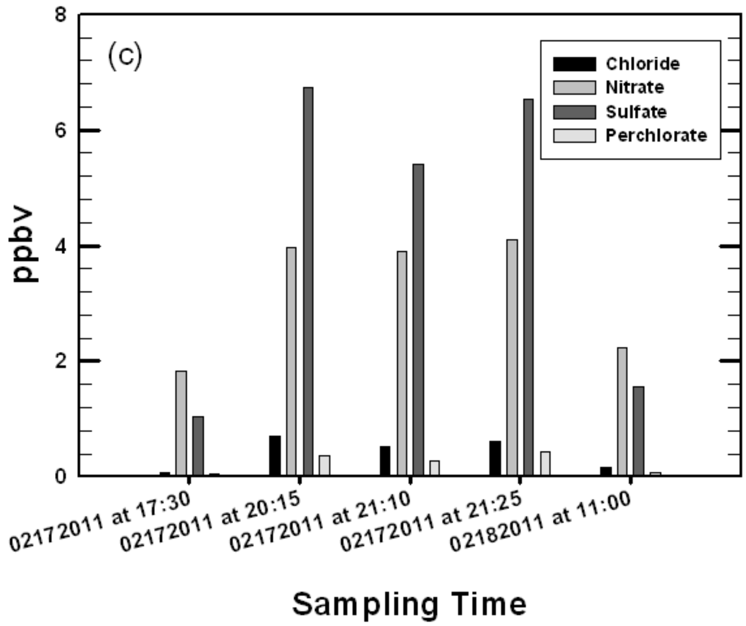


Figure 4-5. The anions (Cl^-, NO_3^-, SO_4^{2-}, ClO_4^-) concentrations of air – time profile during the fireworks/firecrackers events at nearby high school (a) sampling site 1, (b) sampling site 2 and (c) sampling site 3. Sampling condition - Flow rate: 0.25 L/min; Impinger water volume: 25 mL; Sampling time: 20 minutes for the background and final samples, 10 minutes for the samples before and during the main fireworks show.

Figure 4-6 shows that the metals concentrations of air – time profile during the fireworks/firecrackers events at nearby high school. At the first sampling site (Figure 4-6a1), the concentration of Ba(II), K(I), Na(I) and Sr(II) were 43.1, 30.5, 6.2 and 8.1 ppbv, respectively during the fireworks event. The concentration of Mg also increased from 0.1 ppbv to 1.5 ppbv (Figure 4-6a2). The element Ba(II), K(I), Sr(II) and Mg(II) are common chemical compositions, such as $Ba(NO_3)_2$, $KClO_3$,or $Sr(ClO_4)_2$) in the fireworks or firecrackers. It has been reported [34] that the concentrations of Mg(II), K(I), Pb(II), and Sr(II) in particulate matters during the firework periods were 10 times higher than those during the non-firework periods.

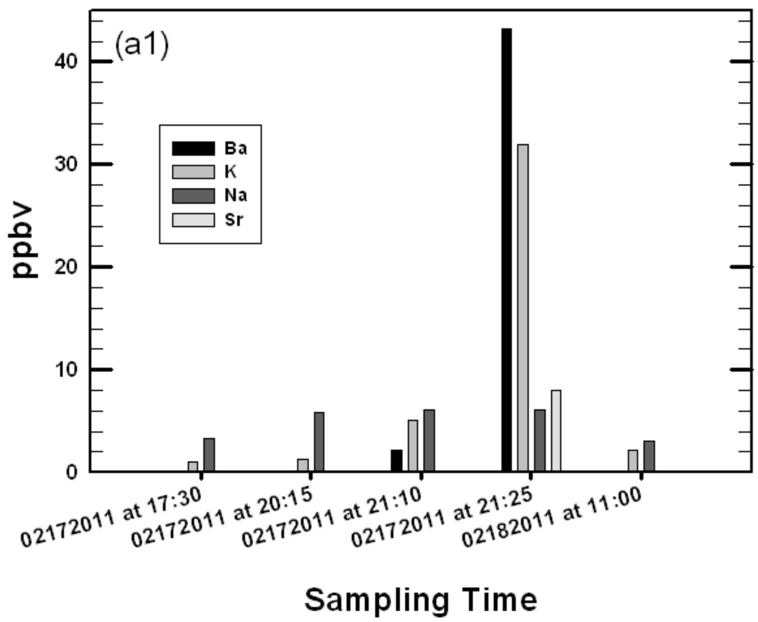
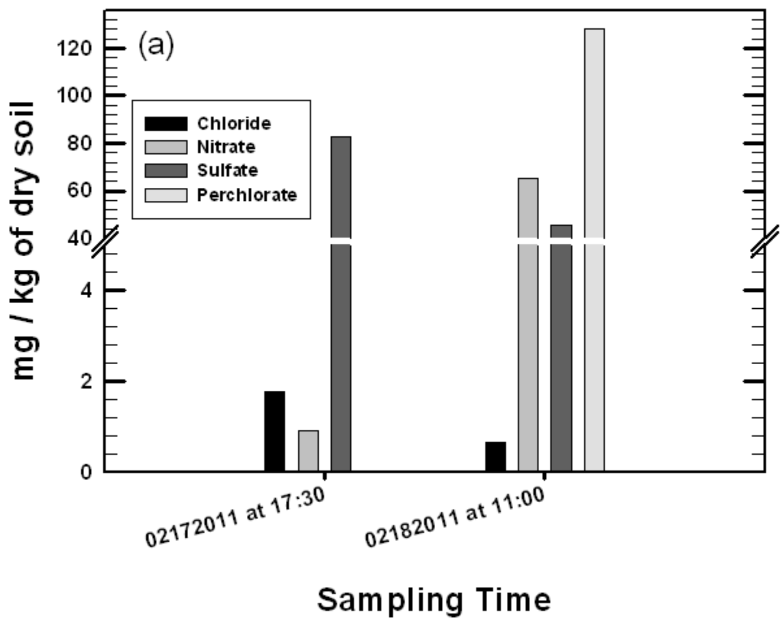


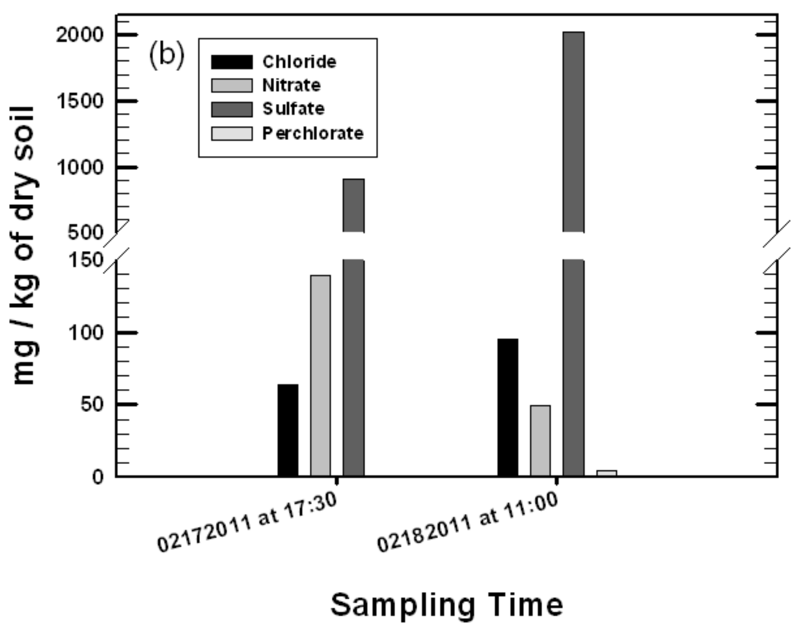
Figure 4-6. The metals concentrations of air – time profile during the fireworks/firecrackers events at nearby high school at nearby high school (a1-a2) sampling site 1, (b1-b2) sampling site 2 and (c1-c2) sampling site 3. Sampling condition. Sampling condition - Flow rate: 0.25 L/min; Sampling vial water volume: 25 mL; Sampling time: 20 minutes for the background and final samples, 10 minutes for the samples before and during the main fireworks show.

Also, during the Diwali holiday in India, the fireworks, firecrackers and sparklers display increased the concentration of Ba(II), K(I), Al(III) and Sr(II) in the air went up by 1091, 25, 18 and 15 times, respectively [27]. In similarity, Sarkar et al. reported during the firework festival in India that the concentration of Ba(II), K(I), Sr(II), Mg(II), Na(I), Al(III), Mn(IV) and Ca(II) were higher by factors of 264, 18, 15, 5.8, 5, 3.2, 2.7 and 1.6, respectively [35]. In this study, the concentration of Ba(II), K(I), Sr(II) and Mg(II) were more than 15 times higher than those in the beginning of the ireworks. At the sampling site 2 and sampling site 3, concentration of Ba(II), Sr(II) and K(I) also increased during the fireworks period. In the next day samples, the concentrations of the metals were remaining about the same as the non-fireworks event period.

4.2.1.2 Analysis of Soil Samples

Figure 4-7 reveals the anions concentrations of soil – time profile before and after the firework events at nearby high school. Results (Figure 4-7a) clearly indicated before the events the concentration of perchlorate in the soil in below detection limits. However, perchlorate was detected (128.4 mg/kg of dry soil) in the soil samples after the events. In addition, the concentration of nitrate increased from 0.8 to 65.4 mg/kg of dry soil. In the other two sampling sites (Figure 4-7b and 4-7c), perclorate was also detected at 9.2 mg/kg of dry soil and at 4.9 mg/kg of dry soil after the events. The observation implies that residuals of firecrackers or fireworks deposited on the ground after the event. Through rainfall or other precipitation process, the ions can be further transported to the groundwater bodies.


(a)
Chloride
Nitrate
Sulfate
Perchlorate
mg / kg of dry soil
120
100
80
60
40
4
2
0
02172011 at 17:30
02182011 at 11:00
Sampling Time


(b)
Chloride
Nitrate
Sulfate
Perchlorate
mg / kg of dry soil
2000
1500
1000
500
150
100
50
0
02172011 at 17:30
02182011 at 11:00
Sampling Time

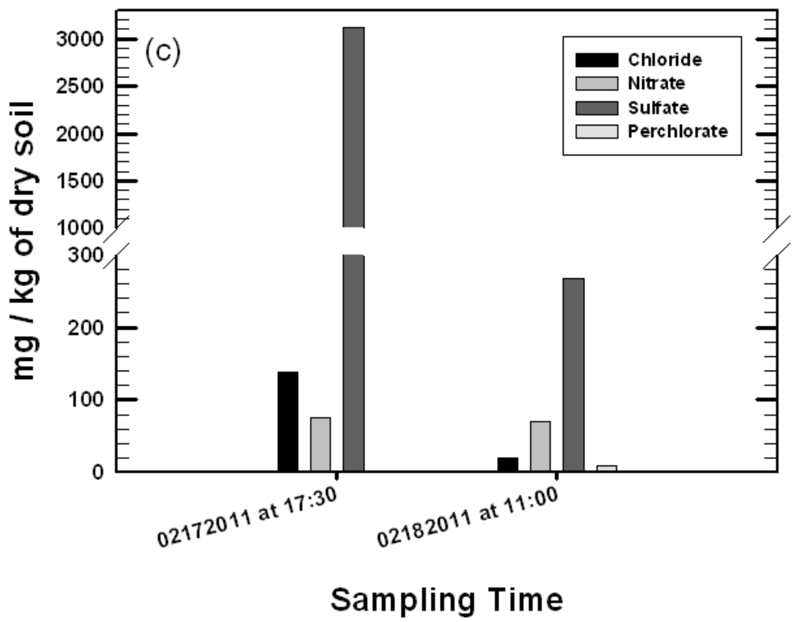
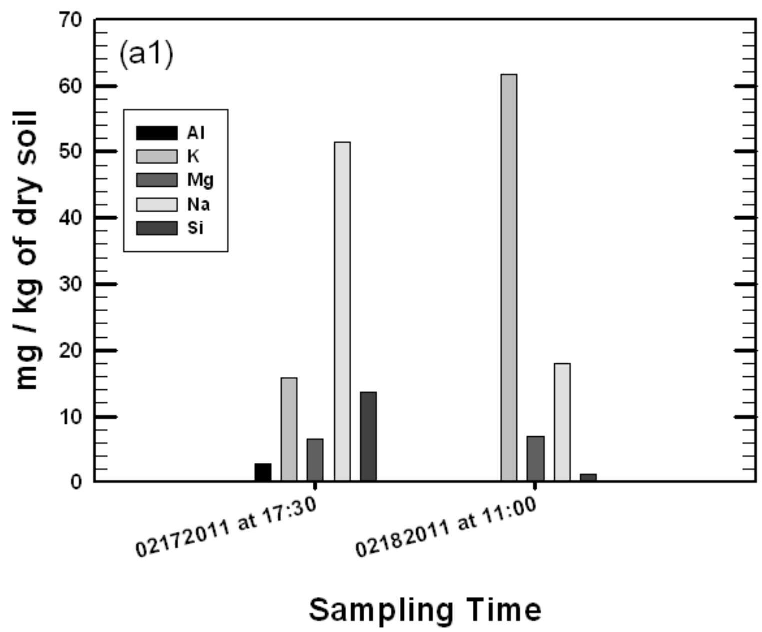
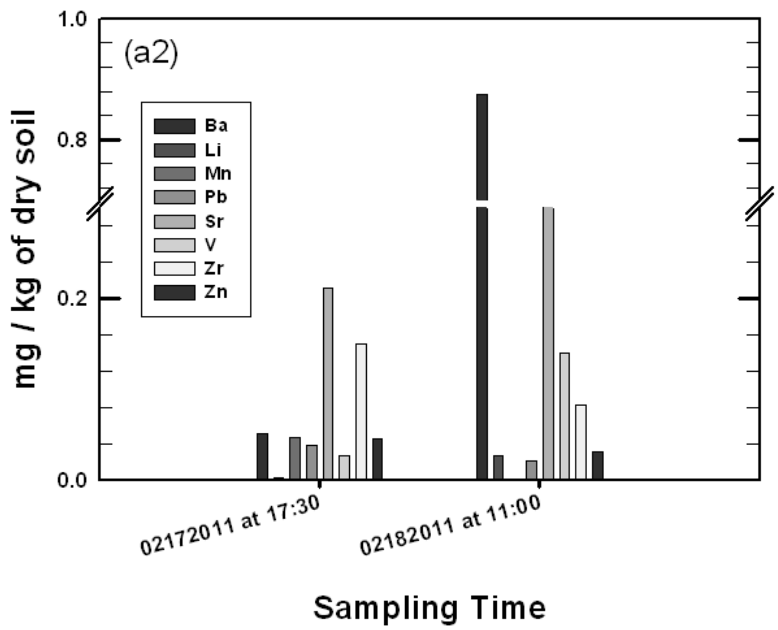


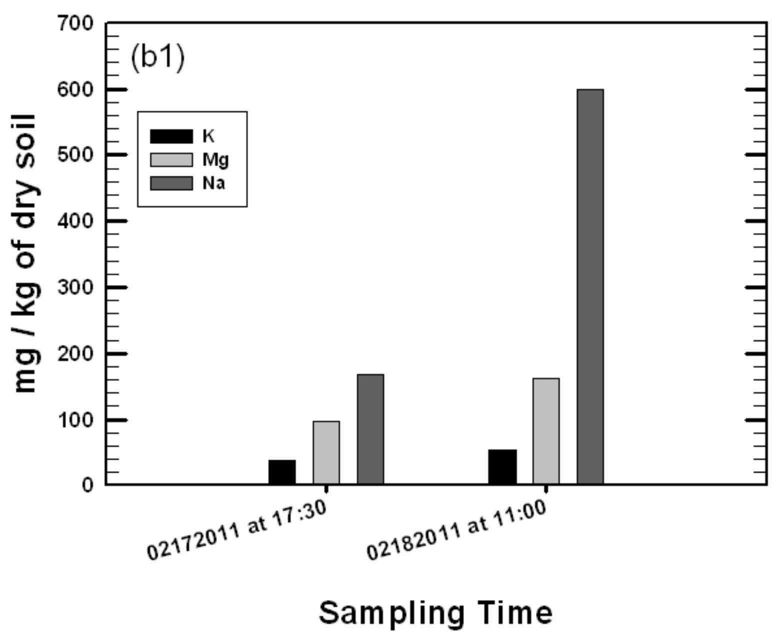
Figure 4-7.The anions (Cl^-, NO_3^-, SO_4^{2-}, ClO_4^-) concentrations of soil – time profile before/after the fireworks/firecrackers events at nearby high school (a) sampling site 1, (b)sampling site 2 and (c) sampling site 3. Sampling condition - Soil sample: 10 g.

Figure 4-8 shows that the cations concentrations of soil – time profile before and after the firework events at nearby high school. Total of 6 samples from 3 sites were collected before and after the events. The concentration of potassium ion in the soil sample increased significantly from 15.85 to 61.75 mg/kg of dry soil after the event (Figure 4-8a1). Also, the concentration of Ba(II) and Sr(II) increased 17.4, 2.3 times after the events (Figure 4-8a2). At sampling site 3, the concentration of Ba also increased from 0.01 to 0.07 mg/kg of dry soil (Figure 4-9c2). In addition, Na(I) and Mg(II) concentration in the soil also increased in the samples from the sampling site2 and 3. Again, the observation implies that residuals of firecrackers or fireworks deposited on the ground after the event.

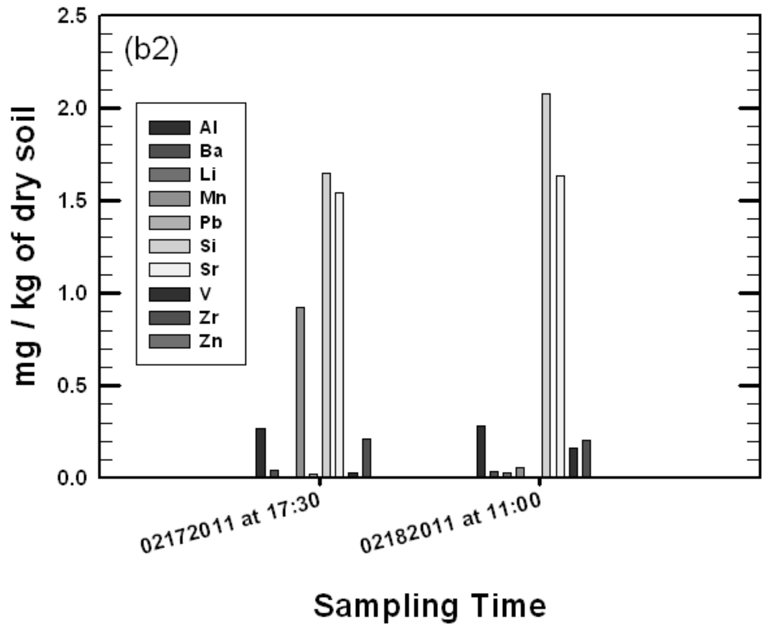




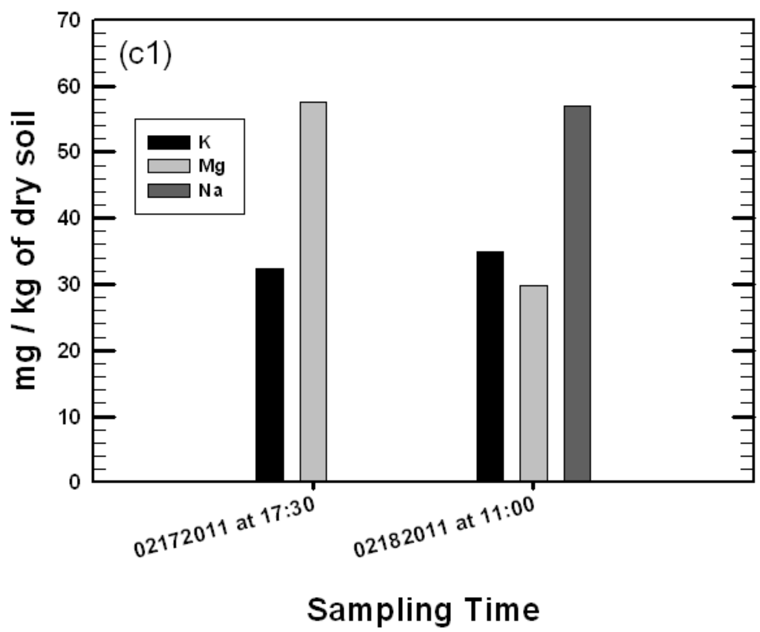
(a2)
Ba
Li
Mn
Pb
Sr
V
Zr
Zn
1.0
0.8
0.2
0.0
mg / kg of dry soil
02172011 at 17:30
02182011 at 11:00
Sampling Time



(b1)
K
Mg
Na
700
600
500
400
300
200
100
0
mg / kg of dry soil
02172011 at 17:30
02182011 at 11:00
Sampling Time



(b2)
mg / kg of dry soil
Al
Ba
Li
Mn
Pb
Si
Sr
V
Zr
Zn
0.0
0.5
1.0
1.5
2.0
2.5
02172011 at 17:30
02182011 at 11:00
Sampling Time



(c1)
mg / kg of dry soil
K
Mg
Na
0
10
20
30
40
50
60
70
02172011 at 17:30
02182011 at 11:00
Sampling Time

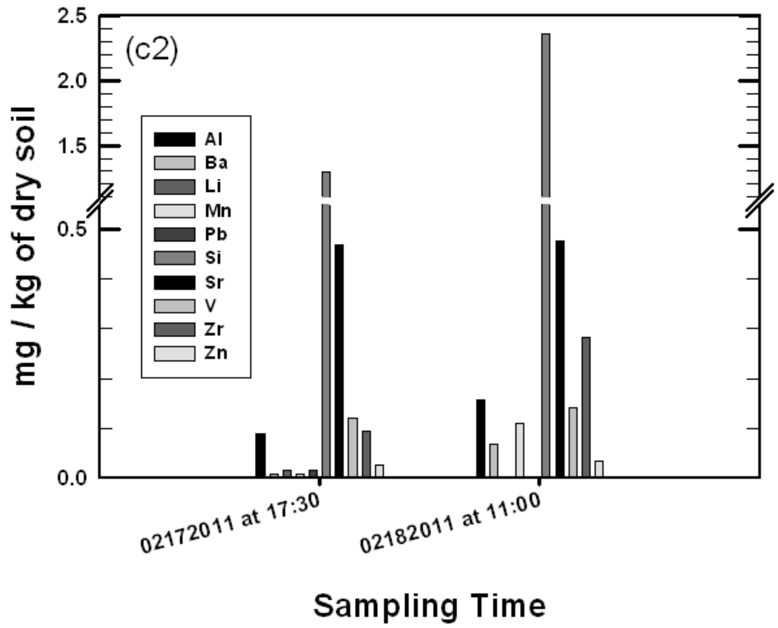


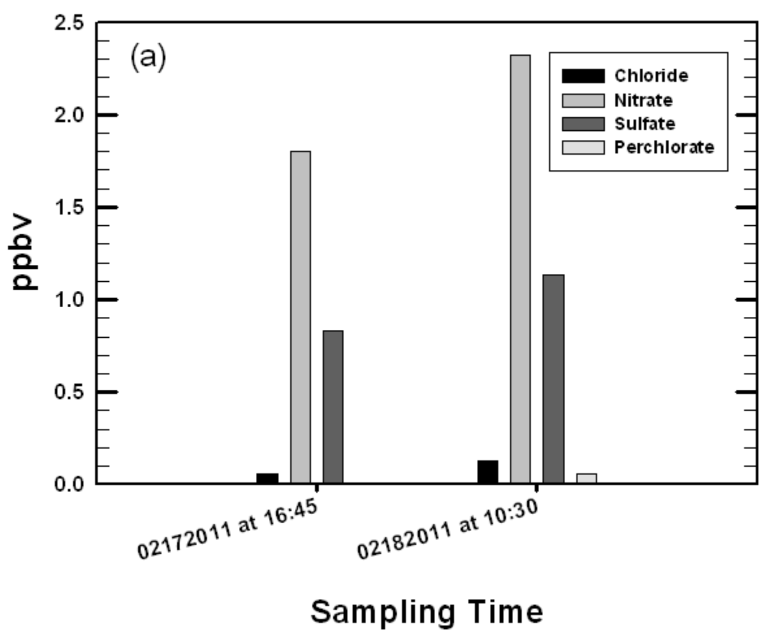
Figure 4-8. The metals concentrations of soil – time profile before/after the fireworks/firecrackers events at nearby high school (a1-a2) sampling site 1, (b1-b2) sampling site 2 and (c1-c2) sampling site 3. Sampling condition - Soil sample: 10 g.

4.2.2 Elementary School Region

As mention above, there were no fireworks or firecracker activities around the elementary school region. The samples collected here were used as the control groups. Figure 4-9 shows the anions concentrations of air and soil– time profile before and after the firework events at nearby elementary school. Only low concentration (0.06 ppbv)of perchlorate was observed in the air sample right after the event (Figure 4-9a). It is believed that the wind direction would spread the distribution of the perchlorate containing particles or aerosol in the air.

The concentration of anions in the soil samples remains constant before and after the events (Figure 4-9b). Figure 4-10 reveals the cations concentrations of air and soil – time profile before and after he firework events at nearby elementary school. No significant difference of the concentration of cations in both the air and soil samples was observed before and after the event.

Overall, the collected air and soil samples in the elementary school region show now significant change before and after the fireworks event. The observation is consistent with the observation in the previous year.



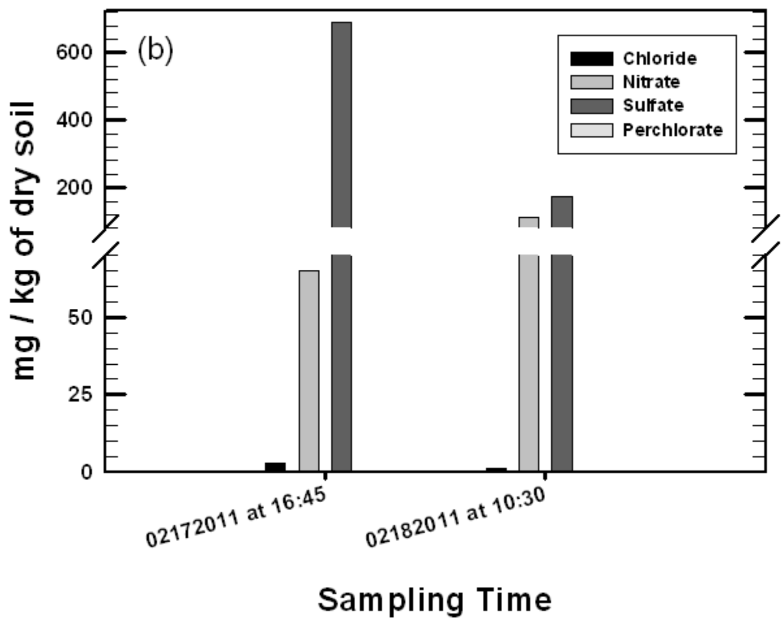
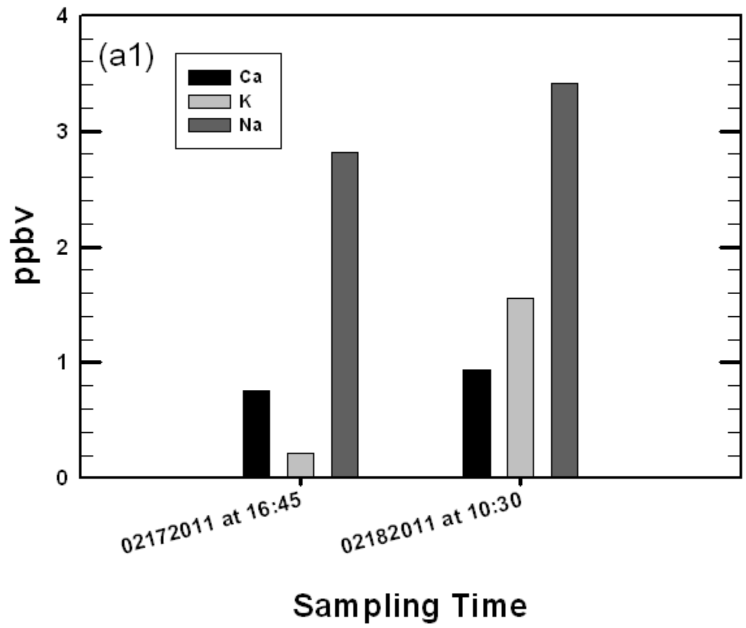
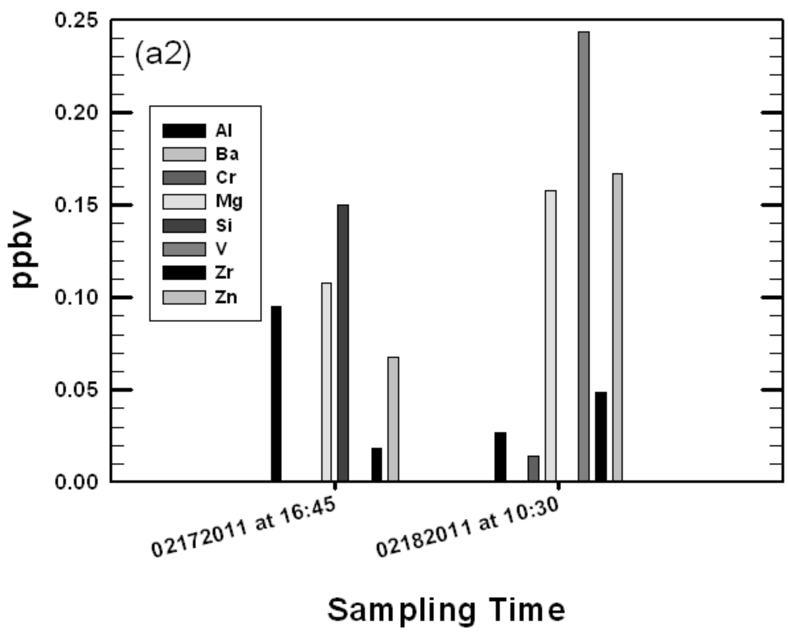


Figure 4-9. The anions (Cl^-, NO_3^-, SO_4^{2-}, ClO_4^-) concentrations of (a) air and (b) soil – time profile before/after the fireworks/firecrackers events at nearby elementary school. Sampling condition - Flow rate: 0.25 L/min; Impinger water volume: 25 mL; Sampling time: 20 minutes; soil sample: 10 g.


(a1)
Ca
K
Na
ppbv
4
3
2
1
0
02172011 at 16:45
02182011 at 10:30
Sampling Time


(a2)
Al
Ba
Cr
Mg
Si
V
Zr
Zn
ppbv
0.25
0.20
0.15
0.10
0.05
0.00
02172011 at 16:45
02182011 at 10:30
Sampling Time

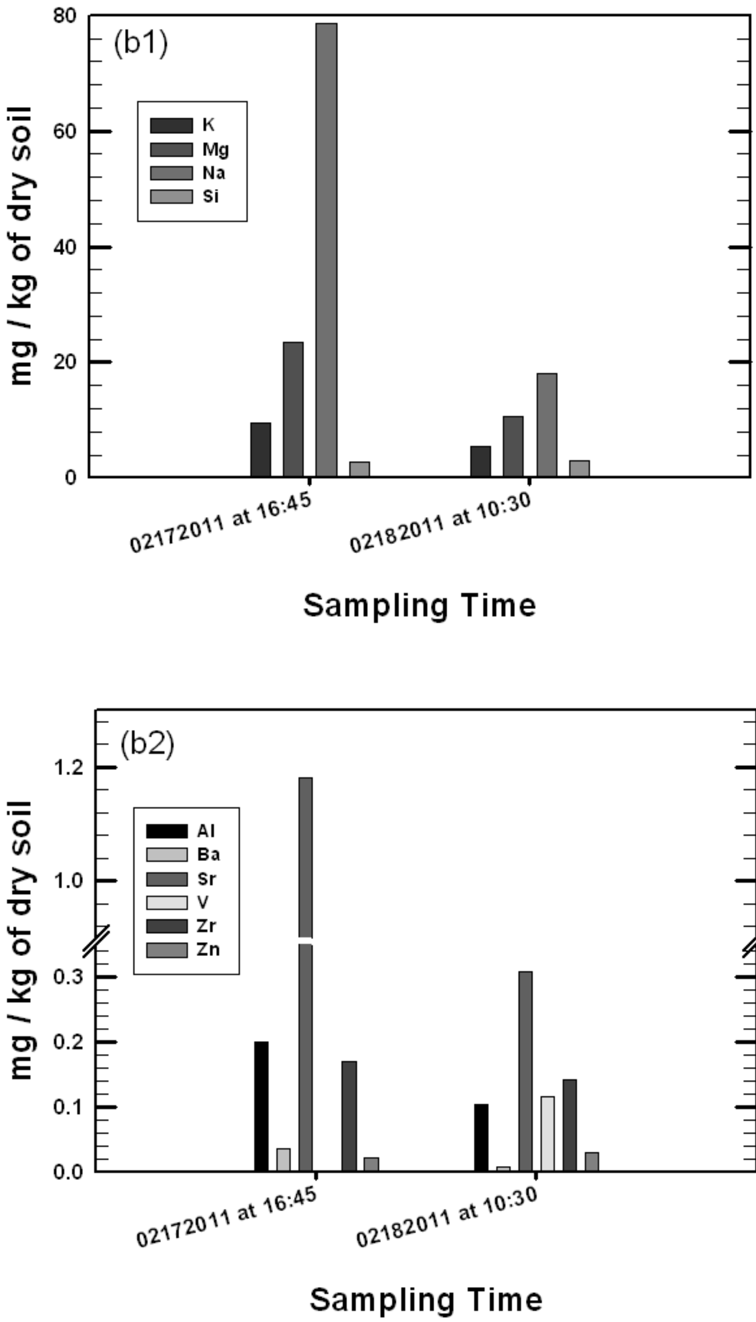
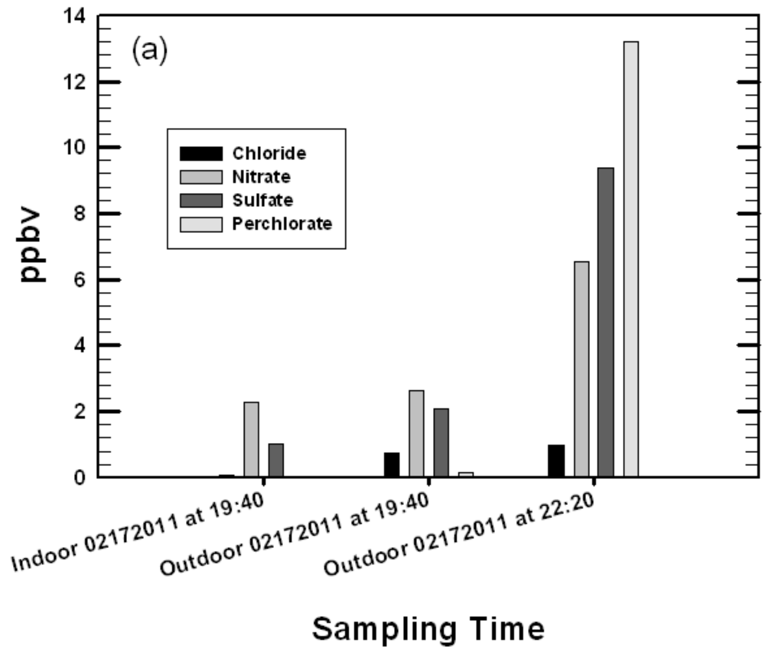


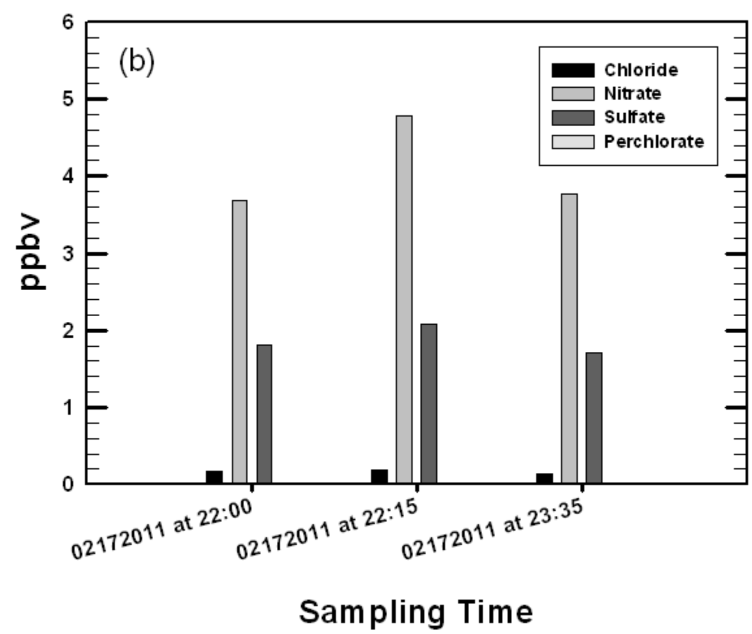
Figure 4-10. The metals concentrations of (a1-a2) air and (b1-b2) soil – time profile before/after the fireworks/firecrackers events at nearby elementary school. Experimental condition: soil sample= 10g.

4.2.3 Police Station Region

Figure 4-11 shows the anions concentrations of air time profile before and after the firework events at nearby police station. Total of 9 samples were collected in the three sites near the police station. Both indoor and outdoor air samples were collected at the police station during the fireworks events. Figure 4-11a reveals the air quality between the indoor and outdoor. After 40 minutes of fireworks events (sampling performed at 19:40 on 02/17/2011) at various locations across the township, 0.15 ppbv of perchlorate was already found in the outdoor samples while no perchlorate was detected in the indoor air samples. At the end of the fireworks period, perchlorate concentration in the air reached to 13.2 ppbv. The concentration of nitrate, sulfate also increased to 6.6 ppbv and 9.4 ppbv, respectively. The samples collected at the other two sites near police station were sampled at the end of the fireworks event (Figure 4-11b and 4-11c), and 0.7 ppbv of perchlorate was observed at the site 3. For the concentration of other anions (chloride, nitrate and sulfate), the results show no significant changes in the air.

Figure 4-12 shows the cations concentrations of air- time profile before and after the firework events at nearby police station. The concentration of Sr increased as from 0 ppbv to 0.202 ppbv in the outdoor samples after the fireworks event (Figure 4-12a). The cation concentration in the other two indoor air samples was not influenced by the events (Figure 4-12b and 4-12c). Overall, the observation indicates that the outdoor air quality was deteriorated by the event while the indoor air quality was stable.


(a)
ppbv
14
12
10
8
6
4
2
0
Chloride
Nitrate
Sulfate
Perchlorate
Indoor 02172011 at 19:40
Outdoor 02172011 at 19:40
Outdoor 02172011 at 22:20
Sampling Time


(b)
ppbv
6
5
4
3
2
1
0
Chloride
Nitrate
Sulfate
Perchlorate
02172011 at 22:00
02172011 at 22:15
02172011 at 23:35
Sampling Time

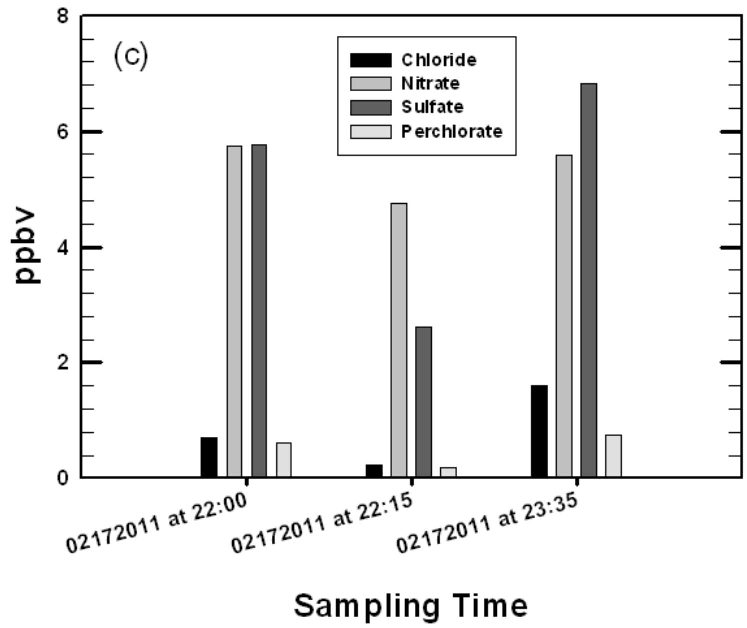
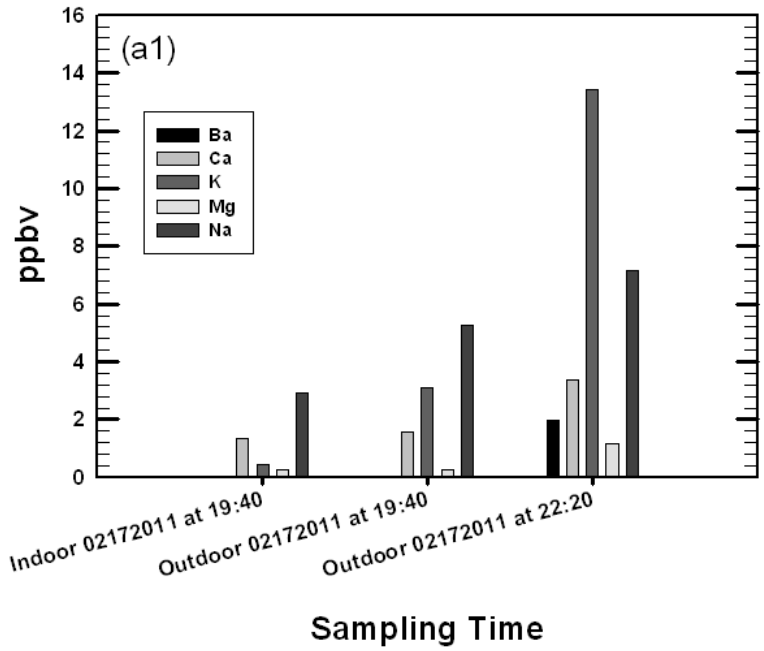
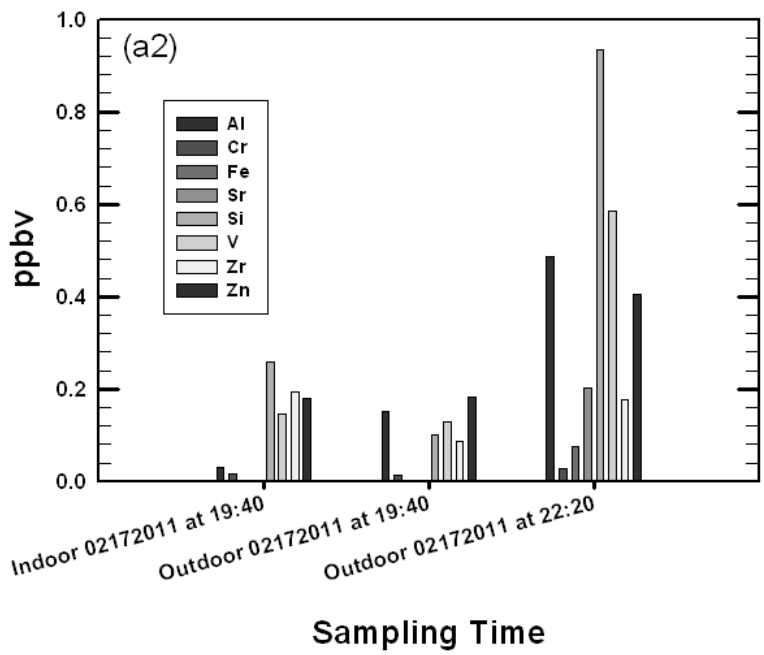
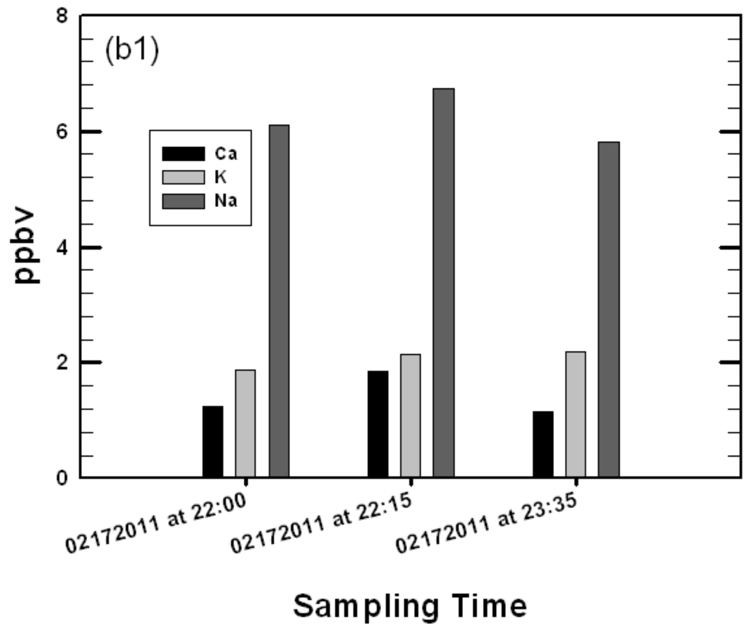
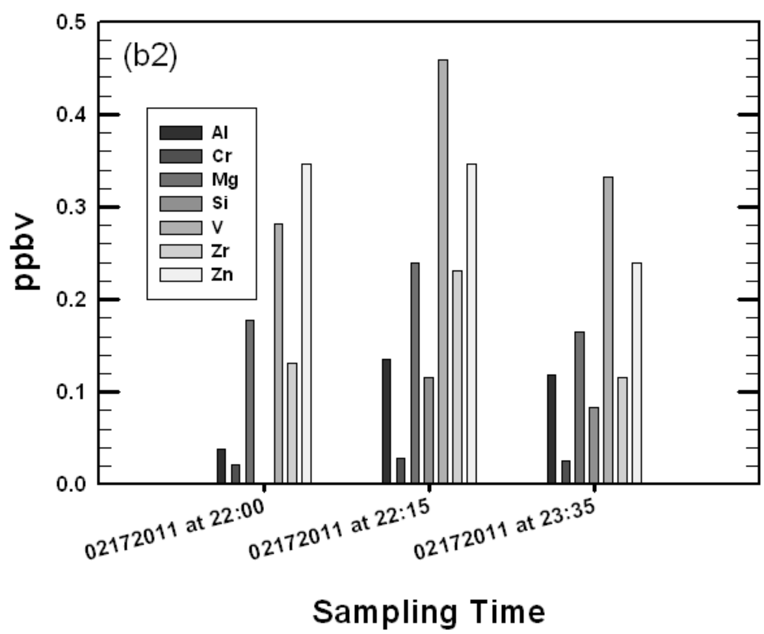


Figure 4-11. The anions (Cl^-, NO_3^-, SO_4^{2-}, ClO_4^-) concentrations of air – time profile before/after the fireworks/firecrackers events at nearby police station (a) indoor and outdoor air, (b) Site 1, indoor air and (c) Site 2, indoor air. Sampling condition - Flow rate: 0.25 L/min; Impinger water volume: 25 mL; Sampling time: 20/10 minutes.


(a1)
16
14
12
10
8
6
4
2
0
ppbv
Ba
Ca
K
Mg
Na
Indoor 02172011 at 19:40
Outdoor 02172011 at 19:40
Outdoor 02172011 at 22:20
Sampling Time


(a2)
1.0
0.8
0.6
0.4
0.2
0.0
ppbv
Al
Cr
Fe
Sr
Si
V
Zr
Zn
Indoor 02172011 at 19:40
Outdoor 02172011 at 19:40
Outdoor 02172011 at 22:20
Sampling Time


(b1)
Ca
K
Na
ppbv
8
6
4
2
0
02172011 at 22:00
02172011 at 22:15
02172011 at 23:35
Sampling Time


(b2)
Al
Cr
Mg
Si
V
Zr
Zn
ppbv
0.5
0.4
0.3
0.2
0.1
0.0
02172011 at 22:00
02172011 at 22:15
02172011 at 23:35
Sampling Time

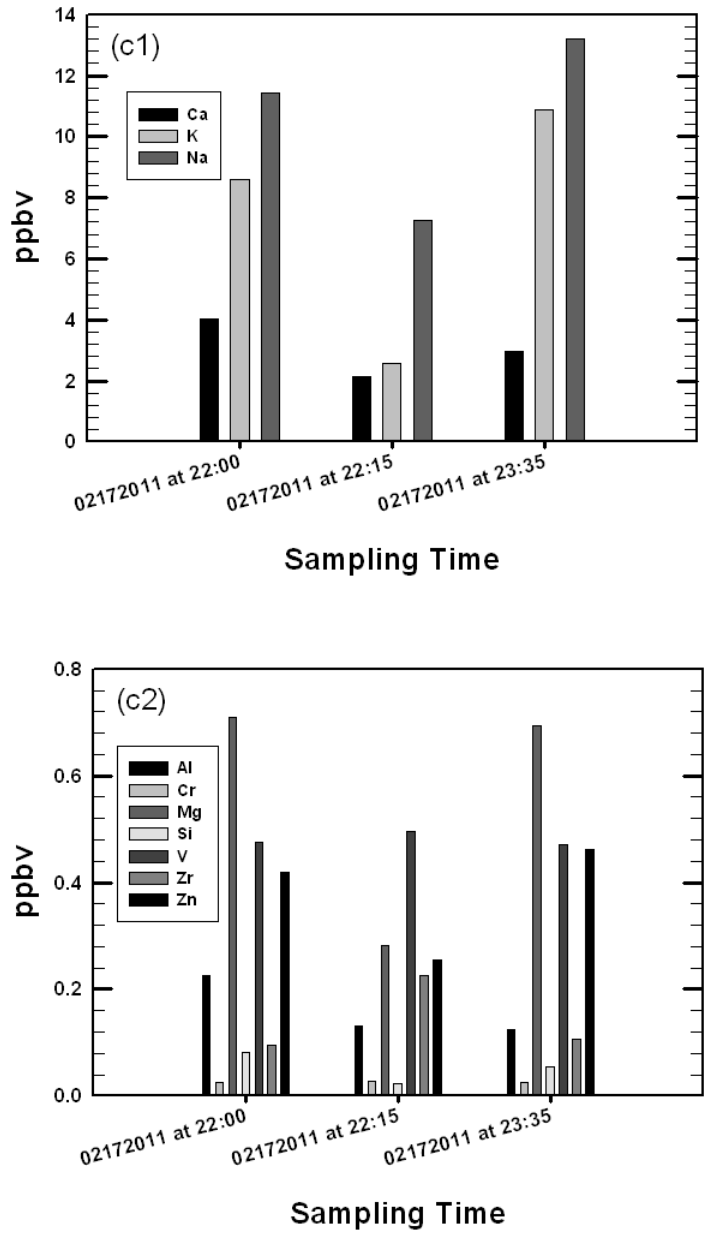


Figure 4-12. The metals concentrations of air – time profile before/after the fireworks/firecrackers events at nearby police station (a1-a2) indoor and outdoor,(b1-b2) Site 1 and (c1-c2) Site 2. Sampling condition - Flow rate: 0.25 L/min; Impinger water volume: 25 mL; Sampling time: 20 minutes.

4.2.4 Risk Assessment

Based on the above observation, the risk of exposure to the perchlorate during the fireworks/firecrackers events is going to discuss in this session. Here we consider perchlorate is a noncarcinogenic chemical and its risk could be characterized in terms of a hazard index. The hazard index is calculated as follows [36]:

$$HI = I_N \times Rfc \qquad \text{(Eq. 4-2)}$$

where HI = hazard index (dimensionless);

I_N = chronic daily intake of noncarcinogen (mg/(kg-day));

Rfc = reference concentration (mg/(kg-day))

From the definition of the hazard index, is simply the ratio of the intake dose from exposure to the reference concentration. If the reference dose is the maximum acceptable level of intake, then the risk is acceptable when the value of hazard index is less than 1.0.

In addition, chronic daily intake of noncarcinogen through inhalation process can be calculated with the following equation [36];

$$I_N = \frac{C \times CR \times EF \times ED \times RR \times Abs}{BW \times AT} \qquad \text{(Eq. 4-3)}$$

where C = concentration at exposure point (mg/m^3 in air);

CR = contact rate (m^3/day);

EF = exposure frequency (days/year);

ED = exposure duration (years);

RR = retention rate (decimal fraction);

Abs = absorption into bloodstream (decimal fraction);

BW = body weight (kg);

AT = average time (days);

Table 4-2 [36] lists the standard parameters for adults, child age between 6 to 12 years old, and child age between 2 to 6 years for calculation I_N. The duration of the exposure frequency is assumed as 2 day/year since these fireworks and firecracker events occurs two days (pre-event and main event) every year. And since the event is about 6 hours (6:00PM to 12:00AM), the total exposure frequency is 0.5 day. To assess the chronic effects associated with exposure to perchlorate as noncarcinogens, the averaging time is averaged over the exposure duration. The recommended reference dose (Rfd), 0.7 µg/kg-day for perchlorate set by the National Academy of Science was adapted for calculation here [20].

Table 4-2. Parameters for calculation of intake for different age group [36].

Parameters	Adults	Child age 6-12	Child age 2-6
Average body weight (kg)	70	29	16
Air breathed (m^3/hour)	0.83	0.46	0.25
Retention rate	100%	100%	100%
Absorption rate	50%	50%	50%
Exposure frequency (days/year)	0.5	0.5	0.5
Exposure duration (years)	30	6	4
Averaging Time (days)	10950	2190	1460

With Eq. 4-2 and Eq. 4-3, the HI values for each age group are present in Table 4-3, Table 4-4 and Table 4-5. Assuming people participate in the annual event constantly. For all the age group that are exposed perchlorate concentration at high school site 1 and police station site 2, the value of hazard index is in the range of 3.68 to 38.53. It implies that people who inhale perchlorate polluted air at this level (13.21 to 103.4 ppbv), the probability of having adverse health effect is relative higher than people who inhale perchlorate-free air. The value of hazard index for child age 6-12 and child age 2-6 at high school site 1 is 38.53 and 37.96, respectively. The numbers for these two groups are higher than 28.80 for adult. The calculated index numbers reveals that a younger child may have a higher risk than an adult when exposed to perchlorate during the fireworks/firecrackers events. In addition, the sampling site 1 at the high school is close to the main fireworks launching site. Workers who are operating the fireworks equipments might be exposed to high concentration of perchlorate in the air. Therefore, proper personal protective equipment would be necessary for both people who frequently attend and for those and who set up the fireworks/firecrackers in this annual event.

Table 4-3. Perchlorate Hazardous Index (HI) at different sites for adults.

	Exposure Conc.	Intake	HI
Sampling Site	mg/m^3	mg/kg of body wt.-day	Intake / Rfc
High School Site 1	103.4	2.02E-02	28.80
High School Site 2	0.162	3.16E-05	0.05
High School Site 3	0.429	8.36E-05	0.12
Elementary School	0.058	1.13E-05	0.02
Police Station Outdoor	0.147	2.86E-05	0.04
Police Station Site 1	0.744	1.45E-04	0.21
Police Station Site 2	13.21	2.57E-03	3.68

Table 4-4. Perchlorate Hazardous Index (HI) at different sites for child age 6 to 12.

Sampling Site	Exposure Conc. mg/m^3	Intake mg/kg of body wt.-day	HI Intake / Rfc
High School Site 1	103.4	2.70E-02	38.53
High School Site 2	0.162	4.23E-05	0.06
High School Site 3	0.429	1.12E-04	0.16
Elementary School	0.058	1.51E-05	0.02
Police Station Outdoor	0.147	3.83E-05	0.05
Police Station Site 1	0.744	1.94E-04	0.28
Police Station Site 2	13.21	3.44E-03	4.92

Table 4-5. Perchlorate Hazardous Index (HI) at different sites for child age 2 to 6.

Sampling Site	Exposure Conc. mg/m^3	Intake mg/kg of body wt.-day	HI Intake / Rfc
High School Site 1	103.4	2.66E-02	37.96
High School Site 2	0.162	4.17E-05	0.06
High School Site 3	0.429	1.10E-04	0.16
Elementary School	0.058	1.48E-05	0.02
Police Station Outdoor	0.147	3.77E-05	0.05
Police Station Site 1	0.744	1.91E-04	0.27
Police Station Site 2	13.21	3.39E-03	4.85

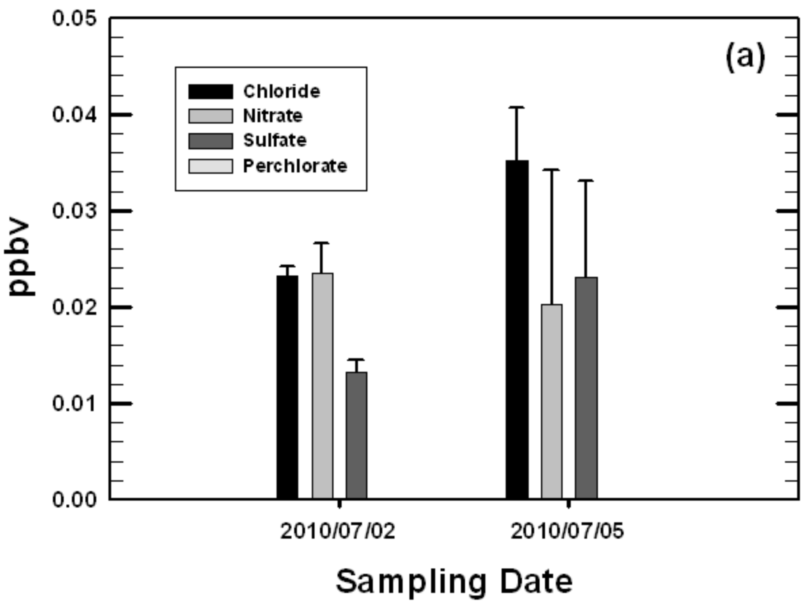
4.3 2010 Field Samples in USA

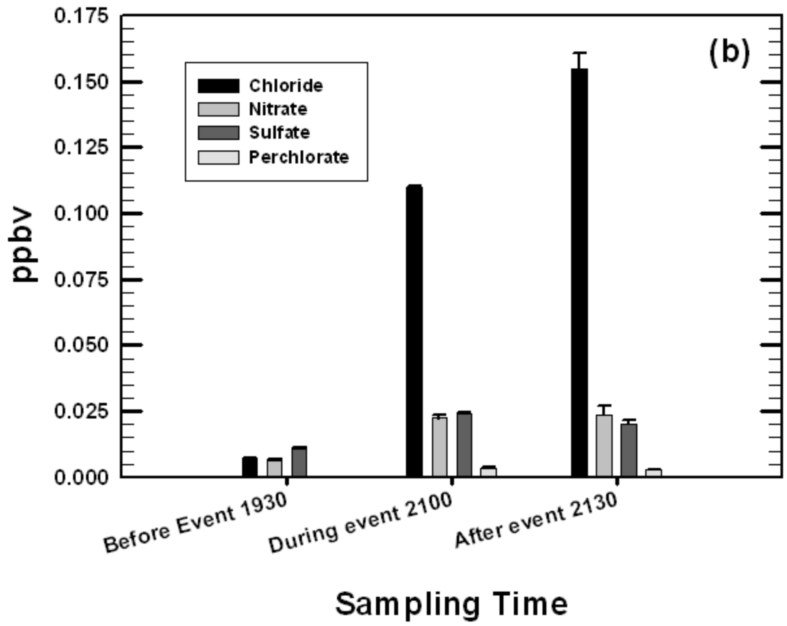
Unlike the samples from Taiwan that were collected during near-ground fireworks or firecrackers activities, the air samples presented in this section were collected during sky fireworks display event (see Figure 3-3). This observation site was chosen because it is where attendees of the local 4th of July celebration go to view the sky fireworks display. The concentration of anions and cations in the air and soil are compared from the two different types of firework activities.

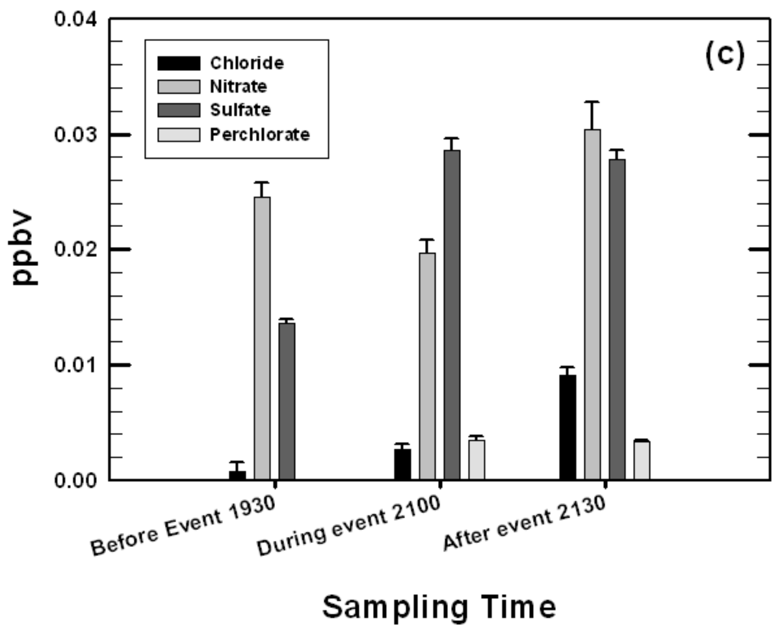
4.3.1 Analysis of Air Samples

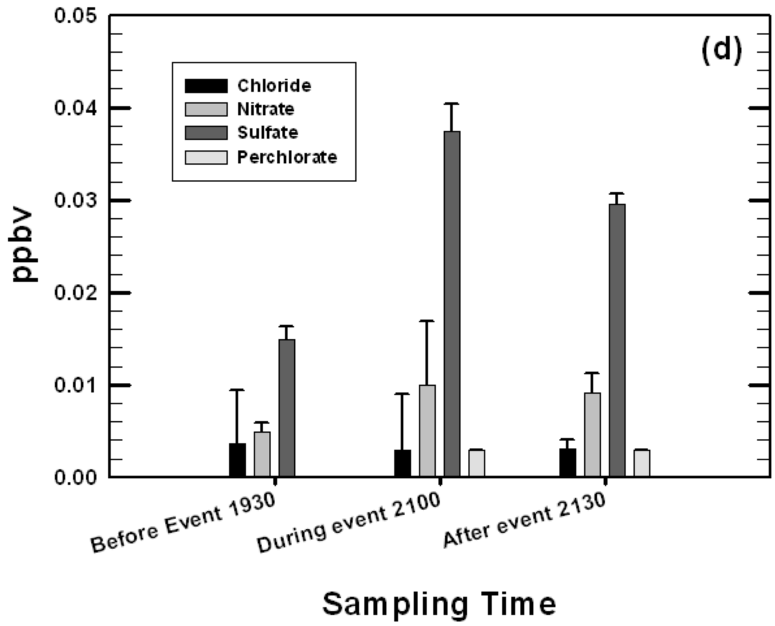
Figure 4-13e shows the concentration of anions in the air samples before (07/02/2010), during (07/04/2010) and a day (07/05/2010) after the fireworks display at fireworks observation area (Figure 3-3). Total of 17 samples were collected at 6 sites in the observation area. The data in the Figure 4-13a represents the background level of the air at the observation area. The concentration of chloride, nitrate and sulfate were all below 0.04 ppbv before and after the event. No perchlorate was detected in the background samples. Figure 4-13b shows the concentration perchlorate increased from 0 to 0.035 ppbv during the fireworks display period and the concentration still remained at 0.029 ppbv after the event. At mean time, the concentration of chloride, nitrate and sulfate showed the similar trend as the concentration of perchlorate. In addition, the concentration of perchlorate was about 0.003, 0.003, 0.004, and 0.003 ppbv at the sampling site 2, 3, 4 and 5, respectively (Figure 4-13c, 4-13d, 4-13e and 4-13f).

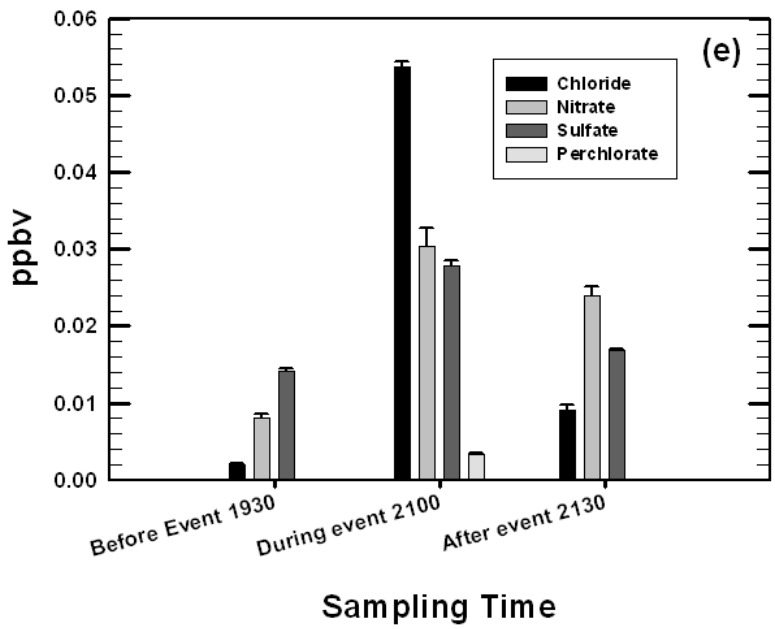
Overall, the concentration of perchlorate in the air during the sky fireworks event did increase. However, the concentration of perchlorate found in the near-ground fireworks event was found to be 2.5×10^3 (based on the highest observation value in Figure 4-7a) times higher than the concentration of perchlorate in the air during the sky fireworks. Hence, the health effect from inhaling the air during the sky fireworks display would be less harmful. However, Vella et al.[37] reported that perchlorate in dust fall ranged from 0.52 μg/g to 561 μg/g due to the fireworks usage in a small central Mediterranean island. Therefore, the perchlorate containing particles or aerosols would eventually deposit on the surface of soil or water.




(b)
Chloride
Nitrate
Sulfate
Perchlorate
ppbv
0.175
0.150
0.125
0.100
0.075
0.050
0.025
0.000
Before Event 1930
During event 2100
After event 2130
Sampling Time


(c)
Chloride
Nitrate
Sulfate
Perchlorate
ppbv
0.04
0.03
0.02
0.01
0.00
Before Event 1930
During event 2100
After event 2130
Sampling Time


(d)
Chloride
Nitrate
Sulfate
Perchlorate
ppbv
0.05
0.04
0.03
0.02
0.01
0.00
Before Event 1930
During event 2100
After event 2130
Sampling Time


(e)
Chloride
Nitrate
Sulfate
Perchlorate
ppbv
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Before Event 1930
During event 2100
After event 2130
Sampling Time

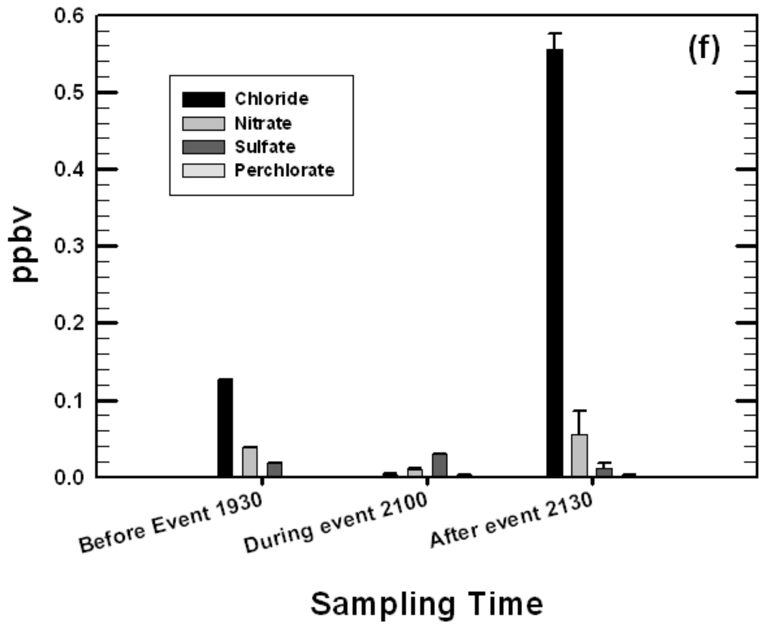
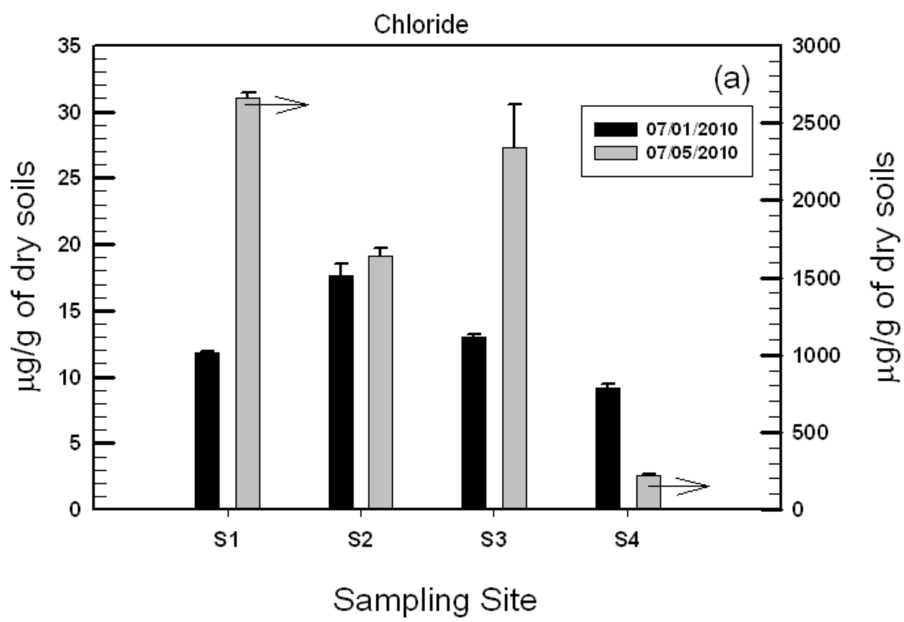
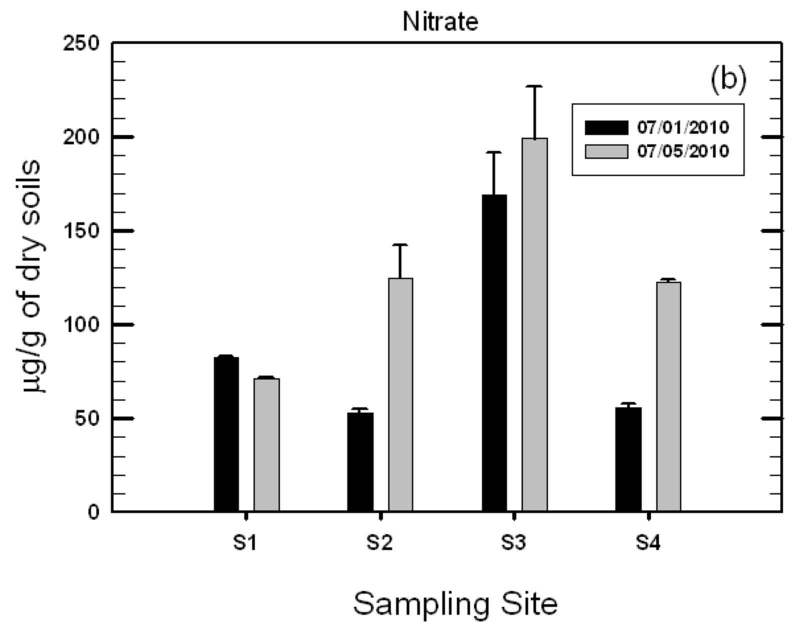


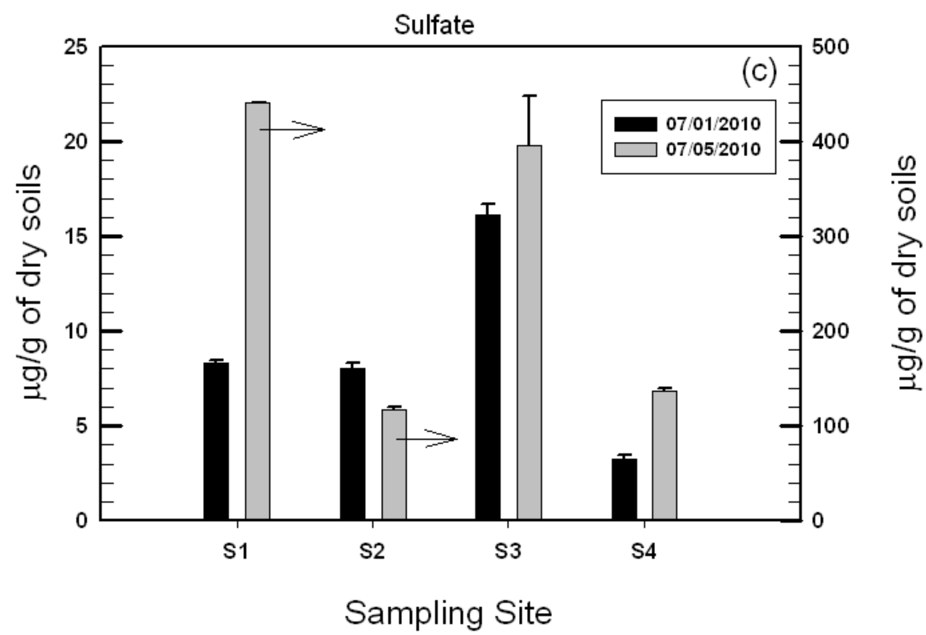
Figure 4-13. The anions concentrations in the air samples – time profile before, during and after the fireworks display at observation sites (a) Background samples; (b) Site 1; (c) Site 2; (d) Site 3; (e) Site 4 and (f) Site 5. Sampling condition - Flow rate: 0.25 L/min; Impinger water volume: 25 mL; Sampling time:20 minutes.

4.3.2 Analysis of Soil Samples

Figure 4-14 shows the concentration of anions (a) chloride, (b) nitrate, (c) sulfate and (d) perchlorate in the soil samples 3 days before (07/01/2010) and a day (07/05/2010) after the firework display at 4 sampling sites at fireworks launch area. The left y-axis and right y-axis in Figure 4-14a, 4-14c represents the concentration of anions in the air but are at the different scale. The concentration of chloride, nitrate and sulfate increased after the fireworks activities in 3 out of the 4 sampling sites. In Figure 4-13a, the concentration of chloride increase from 11.85 to 2659 μg/g of dry soil and from 9.2 to 161 μg/g of dry soil at the sampling site 1 and site4 after fireworks event, respectively. In Figure 4-14c , the concentration of sulfate increased from 8.3 to 440 8.0 to 117 μg/g of dry soil at the sampling site 1 and site2 after fireworks event, respectively. Also, 3 out of 4 sampling sites also show the concentration of pechlorate in the range of 2.4 to 3.7 μg/g of dry soil after the firework event (Figure 4-14d). It implies that the residuals of fireworks deposited on the ground after the event. Through rainfall or other precipitation process, the ions can be further transported to the groundwater bodies.




Nitrate
(b)
07/01/2010
07/05/2010
250
200
150
100
50
0
μg/g of dry soils
S1
S2
S3
S4
Sampling Site


Sulfate
(c)
07/01/2010
07/05/2010
25
20
15
10
5
0
500
400
300
200
100
0
μg/g of dry soils
μg/g of dry soils
S1
S2
S3
S4
Sampling Site

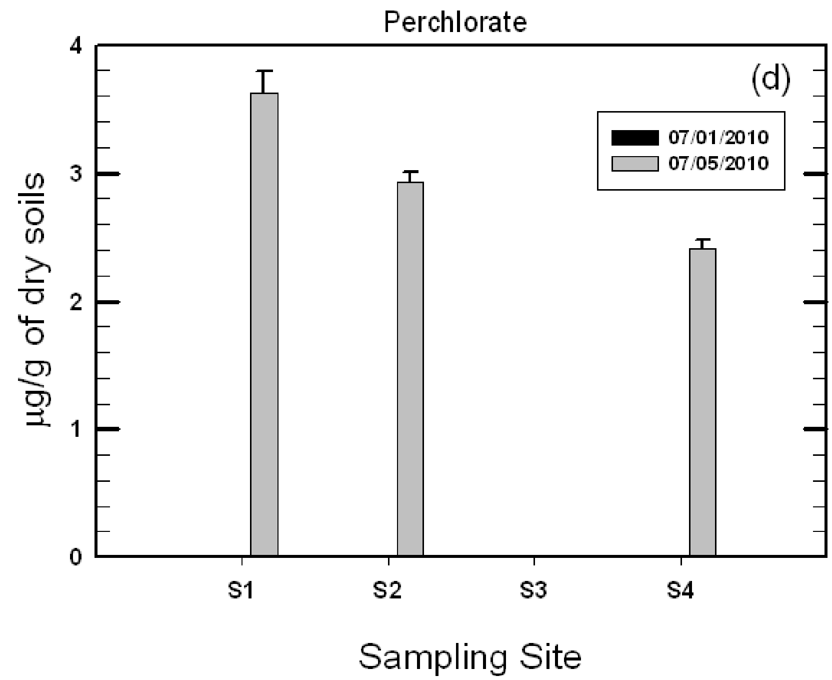


Figure 4-14. The anions (a) chloride; (b) nitrate; (c) sulfate and (d) perchlorate before/after the fireworks at launch site soil samples. Experimental condition: soil sample = 10 g.

CONCLUSIONS

Samples analyzed from near-ground fireworks and firecracker events demonstrate that during the peak time of the fireworks event, the concentration of perchlorate increased dramatically in the air. The outdoor air quality was more deteriorate than the indoor air quality during the fireworks events. However, when the events ended after 12 hours, both the anions and cations concentration in the air returned to baseline levels. Unlike the air samples, however, cation and anion concentrations in the soil increased after the fireworks events and remained elevated. This observation means that residuals of firecrackers or fireworks deposited in the ground after the event. Through the rainfall process, the anions in the soil would be washed out and transported into groundwater bodies.

Sample analysis from the sky fireworks display also showed the presence of perchlorate in the air and soil. However, the concentration of perchlorate during the sky fireworks was lower than during the near-ground fireworks. In addition, the concentration of cations, such as Ba(II), K(I), Na(I), Mg(II) and Sr(II) in the air and soil samples all increased as the concentration of perchlorate increased.

The risk of exposure to the perchlorate during the near-ground fireworks/firecrackers events is higher than that during the sky fireworks event. All age groups, adults, child age of 6-12, and child age of 2-6, were shown to have a high hazard index when exposed to perchlorate during the near-ground fireworks events. Given the pervasive presence of perchlorate during fireworks events, especially in the soil and during near ground explosions, protective gear and improved regulations may be necessary to help limit human exposure to perchlorate and prevent a number of potential adverse health effects.

REFERENCES

1. Stephenson, J.B., *EPA actions could reduce the availability of environmental information to the public*. 2007, United States Government Accountability Office.
2. Urbansky, E.T., *Perchlorate Chemistry: Implications for Analysis and Remediation.* Bioremediation Journal, 1998. **2**(2): p. 81 - 95.
3. Urbansky, E.T. and S.K. Brown, *Perchlorate retention and mobility in soils.* Journal of Environmental Monitoring, 2003. **5**(3): p. 455-462.
4. Dasgupta, P.K., et al., *The origin of naturally occurring perchlorate: The role of atmospheric processes.* Environmental Science & Technology, 2005. **39**(6): p. 1569-1575.
5. Rajagopaian, S., et al., *Perchlorate in Wet Deposition Across North America.* Environmental Science & Technology, 2009. **43**(3): p. 616-622.
6. Motzer, W.E., *Perchlorate: Problems, Detection, and Solutions.* Environmental Forensics, 2001. **2**(4): p. 301-311.
7. NRC, *Health Implications of Perchlorate Ingestion*. 2005, Washington, D. C.: National Academies Press.
8. Dyke, J.V., et al., *Perchlorate in Dairy Milk. Comparison of Japan versus the United States.* Environmental Science & Technology, 2007. **41**(1): p. 88-92.
9. Dyke, J.V., et al., *Sample processing method for the determination of perchlorate in milk.* Analytica Chimica Acta, 2006. **567**(1): p. 73-78.
10. Anderson, T.A. and T.H. Wu, *Extraction, cleanup, and analysis of perchlorate anion in tissue.* Bulletin of Environmental Contamination and Toxicology, 2002. **68**: p. 684-691.

11. Sanchez, C.A., et al., *Perchlorate in the feed-dairy continuum of the southwestern United States.* Journal of Agricultural and Food Chemistry, 2008. **56**(13): p. 5443-5450.
12. Kirk, A.B., et al., *Temporal patterns in perchlorate, thiocyanate, and iodide excretion in human milk.* Environmental Health Perspectives, 2007. **115**(2): p. 182-186.
13. Kirk, A.B., *Environmental perchlorate: Why it matters.* Analytica Chimica Acta, 2006. **567**(1): p. 4-12.
14. Greer, M.A., et al., *Health Effects Assessment for Environmental Perchlorate Contamination: The Dose Response for Inhibition of Thyroidal Radioiodine Uptake in Humans.* Environ Health Perspect, 2002. **110**(9).
15. Wolff, J., *Perchlorate and the thyroid gland.* Pharmacological Reviews, 1998. **50**(1): p. 89-105.
16. De Groef, B., et al., *Perchlorate versus other environmental sodium/iodide symporter inhibitors: potential thyroid-related health effects.* European Journal of Endocrinology, 2006. **155**(1): p. 17-25.
17. Blount, B.C., et al., *Perchlorate, Nitrate, and Iodide Intake through Tap Water.* Environmental Science & Technology, 2010. **44**(24): p. 9564-9570.
18. Cao, Y., et al., *Goitrogenic Anions, Thyroid-Stimulating Hormone, and Thyroid Hormone in Infants.* Environmental Health Perspectives 2010. **118**: p. 1332-1337.
19. Parker, D.R., *Perchlorate in the environment: the emerging emphasis on natural occurrence.* Environ. Chem., 2009. **6**: p. 10-27.
20. Kucharzyk, K.H., et al., *Development of drinking water standards for perchlorate in the United States.* Journal of Environmental Management, 2009. **91**(2): p. 303-310.
21. *Perchlorate treatment technology update, EPA 542-R-05-015*, USEPA, Editor. 2005. p. 84.

22. CDPH. *Perchlorate in Drinking Water*. 2014 [cited 2014 March 3rd]; Available from: http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Perchlorate.shtml.

23. MDEP. *Drinking Water Standard for Perchlorate*. 2006 [cited 2014 March 3rd]; Available from: http://www.mass.gov/eea/docs/dep/water/laws/i-thru-z/perchlorate-310cmr22-07282006.pdf.

24. USEPA. *Drinking Water: Regulatory Determination on Perchlorate*. 2011 [cited 2014 March 3rd]; 7762-7767]. Available from: http://www.gpo.gov/fdsys/pkg/FR-2011-02-11/pdf/2011-2603.pdf.

25. Greenhaw, K., *Rules to Watch (and Wait) for in 2014*. 2014 [cited 2014 March 3rd]; Available from: http://www.foreffectivegov.org/rules-watch-and-wait-2014.

26. *Fireworks Consumption Figures 2000-2013*. 2015 [cited 2015 March 20th]; Available from: http://www.americanpyro.com/industry-facts-figures.

27. Kulshrestha, U.C., et al., *Emissions and accumulation of metals in the atmosphere due to crackers and sparkles during Diwali festival in India.* Atmospheric Environment, 2004. **38**(27): p. 4421-4425.

28. Backus, S.M., et al., *Determination of perchlorate in selected surface waters in the Great Lakes Basin by HPLC/MS/MS.* Chemosphere, 2005. **61**: p. 834-843.

29. Wilkin, R.T., D.D. Fine, and N.G. Burnett, *Perchlorate behavior in a municipal lake following fireworks displays.* Environmental Science & Technology, 2007. **41**(11): p. 3966-3971.

30. Munster, J., et al., *The Fallout from Fireworks: Perchlorate in Total Deposition.* Water, Air, & Soil Pollution, 2009. **198**(1): p. 149-153.

31. Shi, Y., et al., *Effect of fireworks display on perchlorate in air aerosols during the Spring Festival.* Atmospheric Environment, 2011. **45**(6): p. 1323-1327.

32. Markowitz, M.M., *A basis for the prediction of the thermal decomposition products of metal perchlorates.* Journal of Inorganic and Nuclear Chemistry, 1963. **25**(4): p. 407-414.
33. Jacobs, P.W.M. and H.M. Whitehead, *Decomposition and combustion of ammonium perchlorate.* Chemical Reviews, 1969. **69**(4): p. 551-590.
34. Tsai, H.-H., et al., *Influences of fireworks on chemical characteristics of atmospheric fine and coarse particles during Taiwan's Lantern Festival.* Atmospheric Environment, 2012. **62**(0): p. 256-264.
35. Sarkar, S., et al., *Chemical speciation of respirable suspended particulate matter during a major firework festival in India.* Journal of Hazardous Materials, 2010. **184**(1-3): p. 321-330.
36. LaGrega, M.D., P.L. Buckingham, and J.C. Evans, *Hazardous Waste Management*. Second ed. 2001: McGraw-Hill.
37. Vella, A.J., et al., *Perchlorate in dust fall and indoor dust in Malta: An effect of fireworks.* Science of The Total Environment, 2015. **521**(0): p. 46-51.