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Levels, indoor–outdoor relationships and exposure risks of airborne particle-associated perchlorate and chlorate in two urban areas in Eastern Asia

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HIGHLIGHTS

- Fireworks display was a significant source of perchlorate in Jinan, China.
- Mass concentration ratios of chlorate/perchlorate exhibited large difference between Jinan and Kumamoto.
- Indoor accumulation of fireworks emission led to high indoor perchlorate pollution.
- Indoor perchlorate exposure risks to child in fireworks displays should be concerned.

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ABSTRACT

Indoor and outdoor concentrations of $PM_{2.5}$-associated perchlorate (ClO_4^-) and chlorate (ClO_3^-) were investigated in Jinan, China, and size-resolved perchlorate and chlorate were studied in Kumamoto, Japan. The average outdoor $PM_{2.5}$-associated concentrations of perchlorate and chlorate were 4.18 ng m^{-3} and 2.82 ng m^{-3}, respectively, in Jinan. Perchlorate and chlorate were mainly distributed in fine particles, and their approximate $PM_{2.5}$-associated concentrations were 0.04 ng m^{-3} and 4.14 ng m^{-3}, respectively, in Kumamoto. The ratios of ClO_3^-/ClO_4^- ranged from 18.72 to 360.22 in Kumamoto and from 0.03 to 7.45 in Jinan. The highest concentration of perchlorate (173.76 ng m^{-3}) was observed on Spring Festival Eve. This finding and the significant correlation between perchlorate and fireworks-related components (Cl^- and K^+) indicated that the fireworks display was a significant source of perchlorate in Jinan. The indoor concentrations of perchlorate and chlorate in Jinan were 3.54 ng m^{-3} (range, 0.14–125.14 ng m^{-3}) and 0.94 ng m^{-3} (range, 0.10–1.80 ng m^{-3}), respectively. In the absence of an indoor source of perchlorate, the occurrence of indoor concentrations higher than those found outdoors was a common effect of individual fireworks displays near the sampling sites, coupled with meteorological influences and poor indoor diffusion conditions. The exposure risks of perchlorate and chlorate indoors indicated that the potential risk of perchlorate exposure to children during fireworks displays is deserving of concern.

1. Introduction

Perchlorate and chlorate are newly emerging, persistent environmental pollutants that have high water solubility, mobility and stability and pose a potential health threat to humans (Motzer, 2001; Cañas et al., 2006). Perchlorate has been found to inhibit the uptake of iodine and disturb the synthesis of thyroid hormone

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(Greer et al., 2002; Bradford et al., 2005; Crump and Gibbs, 2005), which affect the development of the central nervous system in newborns (NAS, 2005). Chlorate also has thyroid-related effects similar to those of perchlorate (Hooth et al., 2001) and leads to dysfunction in red blood cells (Couri et al., 1982). In stratospheric chemistry, perchlorate is a possible important sink for chlorine (Jaeglé et al., 1996).

Perchlorate pollution in the environment has both anthropogenic and natural sources. Perchlorate is mainly used in military applications, fireworks, explosives and various additives (for example, rubber and lubricants) used in manufacturing industries (Urbansky, 1998; Rajagopalan et al., 2008). Natural sources of perchlorate include Chilean nitrate, in which perchlorate exists as an impurity, and atmospheric formation (Trumpolt et al., 2005). Chlorate is more active than perchlorate and has similar uses (Ader et al., 2001). The literature contains fewer studies of chlorate than of perchlorate. With the development of new techniques for the analysis of chlorate, a recent study of chlorate in precipitation suggested a possible atmospheric process of chlorate formation (Rao et al., 2010).

Human exposure to perchlorate and chlorate from drinking water has been reported (NAS, 2005; Kannan et al., 2009; WHO, 2011). Perchlorate in groundwater has been investigated in northwest Texas, eastern New Mexico and north-central New Mexico (Plummer et al., 2006; Rajagopalan et al., 2006). The results suggested that atmospheric deposition was most likely the source. Perchlorate and chlorate detected in lakes in the Antarctic were determined to be of atmospheric origin (Jackson et al., 2012). High concentrations of perchlorate in soil also carry potential risks to organisms (Hecht et al., 2009). An investigation of perchlorate in outdoor dust and soils in mainland China reported that perchlorate concentrations in settled dust samples were significantly higher ($p < 0.05$) than those in paired soil samples (Gan et al., 2014). From this we can infer that the higher perchlorate concentrations in dust were probably a result of atmospheric deposition. Thus far, very few studies of airborne particle-associated perchlorate and chlorate have been performed. Therefore, an investigation of airborne particle-associated perchlorate and chlorate contamination is desirable because atmospheric deposition is an important source of perchlorate and chlorate in water and soil.

Indoor air pollution has been a focus since the 20th century (Baek et al., 1997; Lee and Chang, 2000; Shoeib et al., 2004; Hassanvand et al., 2014). Because people spend at least 80–90% of their time in indoor environments, indoor pollutants likely have considerable harmful effects even at low concentrations. However, no information is available concerning perchlorate and chlorate levels in indoor environments.

In this study, we simultaneously collected atmospheric (outdoor) and indoor $PM_{2.5}$ samples in Jinan, China, and size-resolved samples in Kumamoto, Japan. The objectives of this study were to estimate the levels, sources and indoor–outdoor relationship of airborne particle-associated perchlorate and chlorate. China is a producer of fireworks, and setting off fireworks and firecrackers to celebrate important days is a tradition of the Chinese people; therefore, samples were also collected during the Spring Festival. To our knowledge, this is the first report of indoor concentrations of perchlorate and chlorate, and an estimation of the potential risks of exposure should prove helpful because humans spend most of their time indoors.

2. Experiments

2.1. Sites and sampling

The indoor and outdoor experiments concerning $PM_{2.5}$-associated perchlorate and chlorate were conducted in Jinan (36°40′N, 117°03′E), a typical heavily polluted city in inland China. The indoor and outdoor sampling sites were selected in a building of Shandong University, which is located in a mixed area with residential, commercial and transportation uses. Size-resolved perchlorate and chlorate were investigated in Kumamoto (32°48′N, 130°42′E), a typical moderately sized coastal city in western Japan. A sampling site on the roof of a nine-story building in Kumamoto University was selected. Fig. 1 shows detailed information on the indoor and outdoor sampling sites in Jinan and the site in Kumamoto. Table 1 gives detailed information on the samples from Jinan and Kumamoto.

2.2. Sample pre-treatment

Quartz filters were treated before sampling and weighed before and after sampling to calculate the $PM_{2.5}$ mass concentration following a method described in the literature (Yang et al., 2012). The filters were cut into pieces, 10 mL of ultrapure water was added for ultrasound-assisted extraction (two times for 20 min) and 20-mL extracts were obtained for each sample. After filtering through a 0.22-μm nylon filter, the liquid samples first were injected for ion chromatography for water soluble analysis, and IC-ESI–MS was then used for analysis of perchlorate and chlorate.

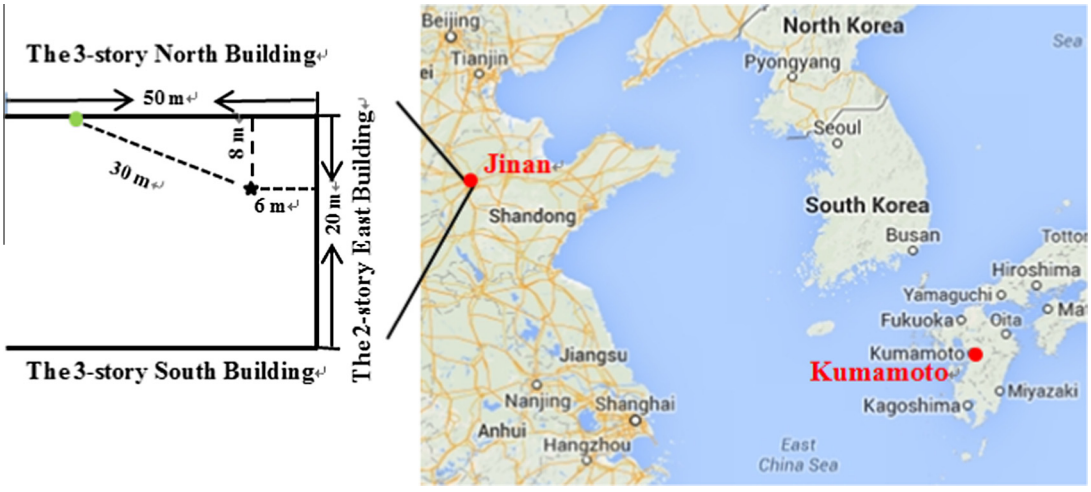

Fig. 1. Outdoor (marked with black star) – indoor (marked with green dot) sampling positions in Jinan, China and the site of Kumamoto, Japan. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Description of sampling in Jinan and Kumamoto.

Sites	Type	Sampler	Sampler position	Sampling period	Sampling time	Number of samples	Notes
Jinan, China	Indoor, $PM_{2.5}$	Medium volume intelligent $PM_{2.5}$ samplers (Wuhan Tianhong, China), 100 L min^{-1}	The indoor site was selected in a student lab (in the 2nd floor of the North Building, see Fig. 1); The sampler was placed on a lab table, with height of ~1.5 m from the sampler air inlet to the lab floor	January 12–February 4, February 9–11, 2013 (February 10 is spring festival)	Indoor–outdoor samples were simultaneously collected 3 times d^{-1}: 07:30–13:30, 14:00–20:00, 21:00–07:00	69	The lab has two windows (face north); Windows were usually closed but not sealed. The sampler is ~1.5 m from one of the windows
	Outdoor $PM_{2.5}$	RAAS 2.5–400 (Thermo) one channel with 7.33 L min^{-1}	The outdoor sampler was placed in a yard (20 m × 50 m, see Fig. 1); The sampler air inlet is ~1.5 m above the ground			70	The yard was surrounded by buildings (see Fig. 1)
Kumamoto, Japan	Outdoor, size-resolved particles	An eight-stage impactor (Tokyo dyrec AN-200, Japan), 28.3 L min^{-1}	The sampler was installed on a small desk, with height of ~1 m from the sampler air inlet to the ground of the roof	November 8–December 3, 2012	09:00–09:00; Each sample was collected for 72 h or 96 h	7 sets (21 in total)	Resolved sizes of particles: 100–11 μm (coarse), 3.3–2.1 μm (fine), <0.43 μm (ultrafine)

2.3. Analytical methods

Perchlorate and chlorate were analysed by ion chromatography (Ultimate 3000, Thermo Scientific) coupled with mass spectrometry (MSQ Plus, Thermo Scientific). After spiking with the labelled internal standard ($Cl^{18}O_4^-$ for perchlorate and $Cl^{18}O_3^-$ for chlorate), 500 μL of the sample was injected into the instrument through a guard column (AG16, Dionex) and a separation column (AS16, Dionex). The eluent was 100 mM KOH at a flow rate of 0.30 mL min^{-1} generated by an eluent auto generator (RFC30, Thermo Scientific). After it was passed through an electrolytic suppressor (ASRS-300-2 mm, Dionex) with a suppression current of 75 mA, the eluent was directed to the ESI–MS. Negative polarity ion monitoring (SIM) transitions were m/z 83 for chlorate and m/z 101 for perchlorate. The peaks for chlorate and perchlorate were detected at retention times of 7.5 min and 10.7 min, respectively.

External calibration standards were used for quantification of perchlorate and chlorate. The samples were prepared by dilution of certified standard solutions of chlorate and perchlorate to obtain a series of concentrations of 100, 500, 1000, 5000 and 10000 ng L^{-1}. The linear correlation coefficients (r^2) were 0.9999 for chlorate and 0.9996 for perchlorate. The limit of detection was 40 ng L^{-1} for chlorate and 20 ng L^{-1} for perchlorate. Each sample was measured twice, and the average concentration was obtained. The repeatability for chlorate was 3.10% ± 2.49% (0.1–11.7%), and that for perchlorate was 3.61% ± 3.51% (0.1–16.3%) in relative standard deviation. Laboratory blanks were analysed in the manner similar to that of the samples, and no targeted compounds were detected.

Detailed information on the water-soluble ion (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) analysis can be found elsewhere (Zhou et al., 2009).

3. Results and discussion

3.1. Atmospheric concentrations of perchlorate and chlorate in Jinan

The average atmospheric (outdoor) concentration of $PM_{2.5}$-associated perchlorate in Jinan was 4.18 ng m^{-3} (range, 0.23–173.76 ng m^{-3}). A previous study of PM_{10}-associated perchlorate was conducted in Lanzhou City and Yuzhong County (Shi et al., 2011). The concentrations of perchlorate ranged from less than the method's detection limit (<MDL) to 9.89 ng m^{-3} in Lanzhou and from < MDL to 4.97 ng m^{-3} in Yuzhong County. The average concentrations of perchlorate in Lanzhou and Yuzhong County were not calculated (Shi et al., 2011). To compare the perchlorate concentrations of these two sites with that of Jinan, we replaced the < MDL values with half of the MDL to calculate average concentrations of perchlorate for Lanzhou and Yuzhong County. The perchlorate concentrations of $PM_{2.5}$ in Jinan were 2.32 times and 5.81 times those of PM_{10}-associated perchlorate in Lanzhou (1.80 ng m^{-3}) and Yuzhong County (0.72 ng m^{-3}), respectively.

Time series of outdoor $PM_{2.5}$-associated perchlorate, chlorate and $PM_{2.5}$ concentrations in Jinan are shown in Fig. 2. The perchlorate concentration reached a low from February 1 to 4 and increased sharply to its highest value (173.76 ng m^{-3}) on Spring Festival Eve. According to the meteorological data (http://lishi.tianqi.com/jinan/201302.html), snow and rain fell from February 1 to 4 (light rain on February 1, heavy snow on February 3, and light snow on February 4), and the $PM_{2.5}$ concentrations also reached a low, which explained in part the lower concentrations of perchlorate. The highest concentration of perchlorate on Spring Festival Eve was affected by the intensive fireworks display. Perchlorate salts, such as $KClO_4$, are widely used as oxygen donors in fireworks and firecrackers. $KClO_4$ can be reduced to KCl and releases O_2

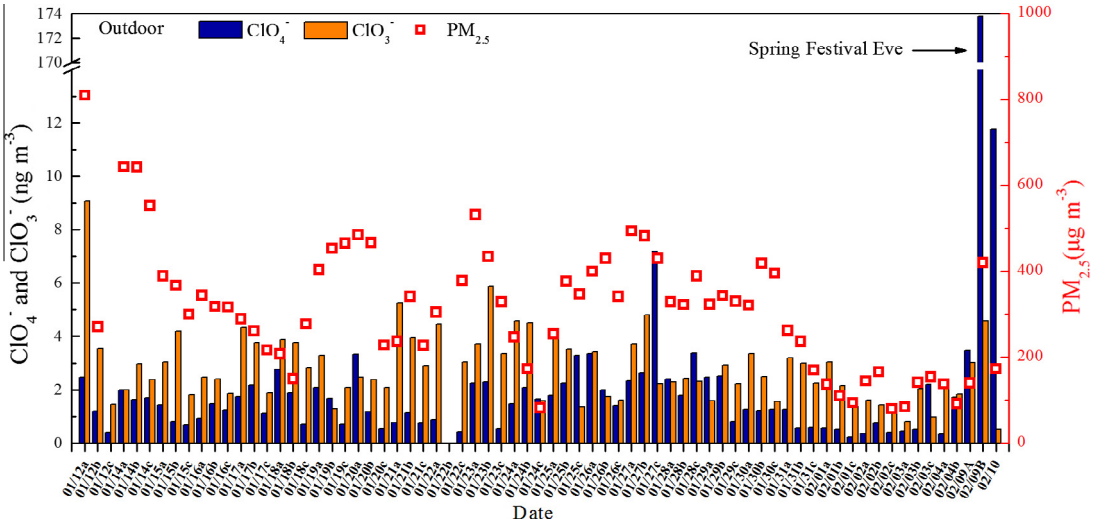

Fig. 2. Time series of atmospheric perchlorate, chlorate and $PM_{2.5}$ concentrations in Jinan. a: 07:30–13:30; b: 14:00–20:00; c: 21:00–07:00; A: 02/09 11:00–16:00; B: 02/09 17:00–02/10 09:00; 02/10: 02/10 12:30–02/11 12:30.

(Wang et al., 2007). Therefore, the highest concentration of Cl^- (78.81 μg m^{-3}) was also observed on Spring Festival Eve. Similar results were obtained in a study of the effects of fireworks displays on concentrations of perchlorate in particles during the Spring Festival in Lanzhou and Yuzhong County (Shi et al., 2011). The maximum concentrations of PM_{10}-associated perchlorate in Lanzhou (9.89 ng m^{-3}) and Yuzhong County (4.97 ng m^{-3}) were also observed on Spring Festival Eve. The maximum concentration of $PM_{2.5}$-associated perchlorate in Jinan was 17 times the concentration of PM_{10}-associated perchlorate in Lanzhou and 34 times that in Yuzhong County on Spring Festival Eve, indicating that the fireworks display in Jinan may have more serious effects. Therefore, the perchlorate pollution caused by the fireworks display in Jinan is worthy of our attention.

The average concentration of $PM_{2.5}$-associated chlorate in Jinan (2.82 ng m^{-3}; range, 0.52–9.07 ng m^{-3}) was comparable with that of perchlorate. Ours is the first report of airborne particle-associated chlorate. Lower concentrations of chlorate were also observed from February 1 to 4 due to the cleaning effect of snow and rain. The concentration of chlorate did not increase significantly on Spring Festival Eve, even though chlorate salts are also ingredients of fireworks, which indicates that chlorate decomposes more completely than perchlorate during fireworks displays because of its greater level of activity (Wu et al., 2011).

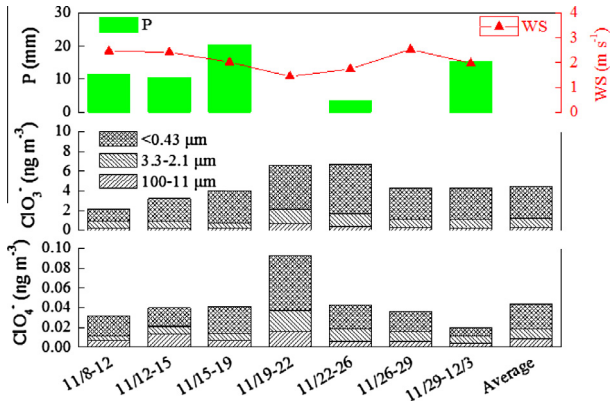

Fig. 3. Size distribution of perchlorate and chlorate concentrations and meteorological factors in Kumamoto. P: precipitation; WS: wind speed.

3.2. Atmospheric perchlorate and chlorate in Kumamoto

The concentrations of perchlorate and chlorate and the meteorological parameters in Kumamoto are shown in Fig. 3. The meteorological data were downloaded from http://www.jma.go.jp/jma/index.html. The average perchlorate concentrations in the size ranges 100–11 μm, 2.1–3.3 μm, and <0.43 μm were 0.01, 0.01, and 0.03 ng m^{-3}, respectively, indicating that perchlorate was mainly distributed in fine particles. A similar size distribution pattern was more obvious for chlorate: the average chlorate concentrations in the size ranges 100–11 μm, 2.1–3.3 μm, and <0.43 μm were 0.32, 0.93 and 3.21 ng m^{-3}, respectively. Meteorological factors usually play a significant role in air pollution. Higher concentrations of perchlorate and chlorate were observed with less precipitation and lower wind speeds (Fig. 3). For chlorate, coarse particles (100–11 μm) exhibited a higher correlation ($r = -0.77$) with precipitation than did fine particles (<0.43 μm, $r = -0.45$), which is consistent with the observation that rain can wash chlorate off coarse particles more efficiently than with smaller particles. Similar results were found with perchlorate and precipitation ($r = -0.68$ for particles between 2.1–3.3 μm, and $r = -0.47$ for those <0.43 μm).

To compare the concentrations of the target compounds in Kumamoto with those in Jinan, the ClO_3^-/ClO_4^- ratio was defined as the mass concentration of ClO_3^- to that of ClO_4^-. The ratios of ClO_3^-/ClO_4^- ranged from 18.72 to 360.22 in Kumamoto. However, the ClO_3^-/ClO_4^- ratios ranged from 0.03 to 7.45 in Jinan. This unusual pattern was probably a result of high levels of ClO_4^- in Jinan. We sum the concentrations between 2.1–3.3 μm and <0.43 μm to approximately indicate the $PM_{2.5}$-associated concentrations for perchlorate and chlorate in Kumamoto. The concentrations of $PM_{2.5}$-associated perchlorate and chlorate in Kumamoto were 0.04 ng m^{-3} and 4.14 ng m^{-3}, respectively. The chlorate concentration of $PM_{2.5}$ in Kumamoto was comparable with that in Jinan (2.82 ng m^{-3}). However, the perchlorate concentration of $PM_{2.5}$ in Kumamoto was far lower than that in Jinan (4.18 ng m^{-3}). Thus, the level of atmospheric perchlorate pollution in Jinan is deserving of attention.

3.3. Relationships between atmospheric perchlorate, chlorate and related species

The relationships between atmospheric concentrations of perchlorate, chlorate and related species in Jinan and Kumamoto were

Table 2
Correlation coefficients (r) between ClO_4^-, ClO_3^- and related species in Jinan and Kumamoto.

Site		ClO_3^-	Cl^-	NO_3^-	SO_4^{2-}	K^+	NH_4^+	O_3	$PM_{2.5}$
Jinan	ClO_4^-	.152	.864**	−.027	.145	.982**	−.013	−.214	.100
	ClO_3^-	1	.161	.387**	.126	.155	.200	−.304*	.409**
	n	70	70	70	70	70	70	44	69
Kumamoto (n = 21)	ClO_4^-	.749**	−.322	.302	.540*	.589**	.598**		
	ClO_3^-	1	−.180	.723**	.872**	.876**	.924**		

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

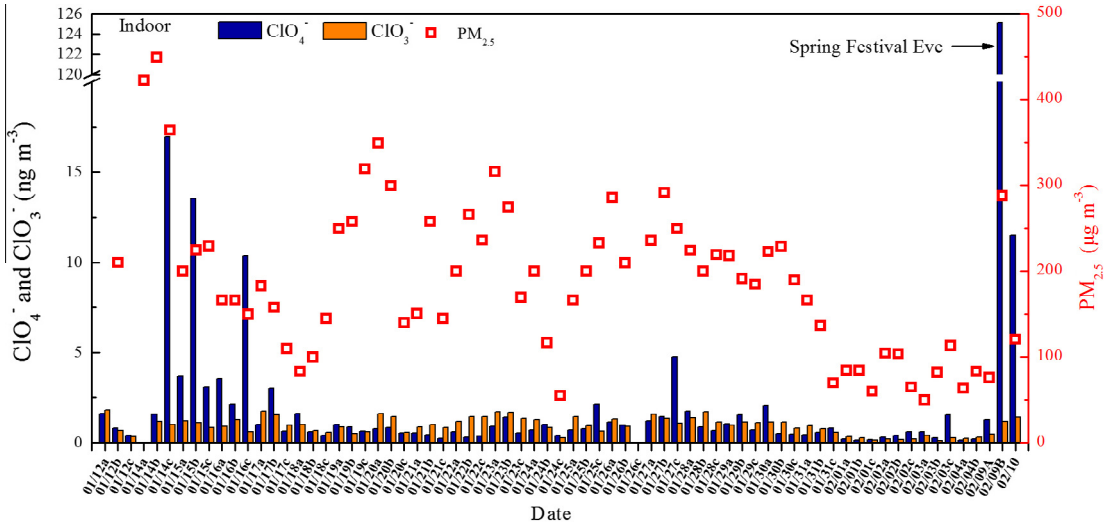

Fig. 4. Time series of indoor perchlorate, chlorate and $PM_{2.5}$ concentrations in Jinan. a: 07:30–13:30; b: 14:00–20:00; c: 21:00–07:00; A: 02/09 11:00–16:00; B: 02/09 17:00–02/10 09:00; 02/10: 02/10 12:30–02/11 12:30.

examined with Pearson correlation analysis, and the results are shown in Table 2. The correlation coefficients are labelled in the table to note the significance levels ($p < 0.01$ or $p < 0.05$). From Table 2, it can be seen that the concentrations of ClO_4^- and ClO_3^- were not related in Jinan, indicating that ClO_4^- and ClO_3^- in Jinan came from different sources. However, a significant correlation ($p < 0.01$, $r = 0.749$) was obtained between ClO_4^- and ClO_3^- in Kumamoto, indicating that they likely had the same source.

A previous laboratory experiment demonstrated that Cl^- could be oxidised into ClO_4^- when exposed to a high concentration of O_3 (Kang et al., 2008). In our study, no significant relationship was observed between the concentrations of ClO_4^- and O_3 in Jinan, which may indicate that O_3 did not play a key role in ClO_4^- oxidative formation due to the low concentration of O_3 in winter. However, the concentration of ClO_4^- was significantly related to that of Cl^- ($p < 0.01$, $r = 0.864$) in Jinan. In addition, the concentration of ClO_4^- exhibited a significant correlation with that of K^+ ($p < 0.01$, $r = 0.982$) in Jinan. The concentrations of Cl^- and K^+ were also strongly correlated ($p < 0.01$, $r = 0.899$) in Jinan, and fireworks are a common source of Cl^- and K^+ (Wang et al., 2007; Joly et al., 2010). Therefore, we deduced that fireworks were an important source of ClO_4^- in Jinan. Different results were obtained in Kumamoto: no significant relationship between ClO_4^- and Cl^- was seen, indicating that the concentration of ClO_4^- in Kumamoto was rarely affected by fireworks displays in the sampling period. NO_3^-, SO_4^{2-} and NH_4^+ are typical secondary pollutants formed from atmospheric oxidative processes. K^+ is obtained exclusively from primary sources. Strong correlations were observed between concentrations of ClO_3^- and NO_3^-, SO_4^{2-}, NH_4^+ and K^+ ($p < 0.01$, $r = 0.723$–0.924) in Kumamoto (Table 2). Therefore, we deduced that ClO_3^- is likely related to atmospheric oxidative processes and primary sources in Kumamoto.

3.4. Indoor perchlorate and chlorate

3.4.1. Temporal variation of indoor concentrations of perchlorate and chlorate

Fig. 4 describes the time series of indoor concentrations of perchlorate, chlorate and $PM_{2.5}$ in Jinan. The average indoor concentrations of perchlorate and chlorate were 3.54 ng m^{-3} (range, 0.14–125.14 ng m^{-3}) and 0.94 ng m^{-3} (range, 0.10–1.8 ng m^{-3}), respectively. Low indoor concentrations of perchlorate and chlorate were observed during February 1–4, which was consistent with those found outdoors. The highest indoor concentration of perchlorate was also identified during the time of fireworks (Spring Festival Eve) in Jinan (Fig. 4), indicating that the indoor concentrations of perchlorate were strongly affected by outdoor sources. On Spring Festival Eve, the indoor concentrations of $PM_{2.5}$-associated perchlorate reached 125.14 ng m^{-3}, which was 12 and 25 times that of PM_{10} reported in Lanzhou and Yuzhong County, respectively (Shi et al., 2011), which suggests that significant indoor perchlorate pollution occurred via infiltration from the fireworks display even though the windows were closed. Therefore, remaining indoors is not the optimal way to avoid exposure to perchlorate, and the control of fireworks displays is an urgent issue.

The average concentration of perchlorate indoors (3.54 ng m^{-3}) was similar to that outdoors (4.18 ng m^{-3}) because some individual indoor readings were very high (Fig. 4). At first, we expected to find indoor sources of perchlorate, for instance, stored fireworks or chemical reagents containing perchlorate. However, no such indoor sources were found. Therefore, we suspect that there were individual fireworks displays near the sampling sites. A detailed discussion is presented in the next section.

3.4.2. Relationship of indoor and outdoor concentrations of perchlorate and chlorate

The indoor to outdoor (*I*/*O*) ratio, defined as mass concentration of indoor to that of outdoor, is widely used to directly describe the relationship between indoor and outdoor particle concentrations (Jones et al., 2000; Matson, 2005; Custódio et al., 2014). In the absence of an indoor source of a target compound, the *I*/*O* ratio is usually less than 1. In our study, 67 pairs of $PM_{2.5}$ indoor–outdoor samples were obtained in Jinan. The *I*/*O* ratios of $PM_{2.5}$ were always less than 1 (range, 0.40–0.91). Similar results were obtained for *I*/*O* ratios for chlorate (range, 0.05–0.70). However, the *I*/*O* ratios of perchlorate ranged from 0.12 to 16.47, and the *I*/*O* ratios of 19.4% of the samples were greater than 1. Because no obvious indoor source of perchlorate was identified, two possible explanations were proposed for the occurrence of indoor concentrations of perchlorate that were higher than those outdoors. One source was the individual fireworks displays near the sampling sites. The sampling sites were surrounded by residential and commercial areas, and setting off fireworks to celebrate important days (weddings, birthdays, opening ceremonies) is common for Chinese people. In addition, the indoor diffusion conditions were poorer than those found outdoors, which allowed perchlorate to accumulate easily and to remain at high concentrations.

Table 3 provides examples of indoor measurements of perchlorate that were affected by suspected outdoor individual fireworks displays near the sampling sites. OC (organic carbon) was analysed by a thermal-optical carbon aerosol analyser (Sunset Laboratory); a detailed description of the method can be found in our previous study (Wang et al., 2011). As shown in Table 3, the concentrations of Cl^- and K^+ were higher than average. K^+ is an indicator of biomass burning or fireworks displays. Biomass burning events were commonly identified by high concentrations of K^+ and sharp increases in the $OC/PM_{2.5}$ ratio (Saarikoski et al., 2007). However, $OC/PM_{2.5}$ ratios of 1/16c-O and 1/14c-O were near the average-O level. Therefore, those high concentrations of K^+ were inferred to be caused by fireworks displays. We suppose that individual fireworks displays near the sampling sites and meteorological conditions played key roles.

Meteorological data were estimated from a local website (http://rp5.ru/history data). We found that northeast and east winds were dominant in the period during which the 19.4% of samples with an *I*/*O* ratio greater than 1 were collected. The laboratory room in which the indoor sampler was placed was located on the second floor of the North Building. It was noted that the windows of the room faced north and that the outdoor sampling site was surrounded by three linked buildings (Fig. 1). When there were individual fireworks displays near the sampling site, especially to the northeast and east, airflow that contained a high concentration of perchlorate was transported indoors through the windows and was interrupted by the three-story North Building (Fig. 1). Therefore, the outdoor concentrations of perchlorate in this case were lower than those found indoors.

A Pearson correlation analysis was also applied to determine the relationship between the outdoor and indoor target compounds (ClO_4^- and ClO_3^-) and with other $PM_{2.5}$-related species. A significant correlation were observed between the indoor and outdoor concentrations of ClO_4^- ($p < 0.01$, $r = 0.983$) and ClO_3^- ($p < 0.01$, $r = 0.559$). SO_4^{2-} has been proposed as a good marker for indoor particles of outdoor origin (Chithra and Shiva Nagendra, 2013), and strong correlations were exhibited between SO_4^{2-} found outdoors and that found indoors ($p < 0.01$, $r = 0.923$), as well as $PM_{2.5}$, Cl^- and K^+ ($p < 0.01$, $r > 0.900$), indicating that indoor particles and their related species primarily originated from outdoor aerosols.

3.4.3. Exposure evaluation

We estimated the daily intake (DI) of indoor perchlorate and chlorate in children and adults. Three routes of exposure were considered: (a) direct inhalation; (b) ingestion due to particle deposition; and (c) dermal absorption. The assessment method is described in detail elsewhere (Gan et al., 2014), and the calculation parameters were suggested by the US EPA (EPA, 2001).

The results showed that the average and maximum DIs of perchlorate via direct inhalation and dermal absorption did not exceed the reference dose of perchlorate of 0.7 $\mu g\ kg^{-1}\ d^{-1}$ for children and adults (EPA, 2005), nor did the average DI of perchlorate through ingestion. However, the maximum DI of perchlorate via ingestion (1.60 $\mu g\ kg^{-1}\ d^{-1}$) in children was higher than the reference dose, which suggests that the risk of exposure to perchlorate in children from fireworks displays is worthy of consideration. The tolerable DI (TDI) of chlorate was 30 $\mu g\ kg^{-1}\ d^{-1}$ (MHLW, 2003), and the maximum DIs of chlorate for both children (0.35 $\mu g\ kg^{-1}\ d^{-1}$) and adults (0.17 $\mu g\ kg^{-1}\ d^{-1}$) were far lower than the suggested dose. Therefore, the potential risk of exposure to chlorate is negligible for residents of Jinan.

Table 3
Typical examples of indoor perchlorate affected by individual fireworks displays near the sampling sites.

Sample	ClO_4^- ng m^{-3}	Cl^- mg m^{-3}	K^+ μg m^{-3}	OC μg m^{-3}	$PM_{2.5}$ μg m^{-3}	$OC/PM_{2.5}$ (%)
1/14c-I	16.95	4.20	5.06	–	364.3	–
1/14c-O	1.71	14.04	5.14	46.07	552.8	8.3
1/16c-I	10.36	3.15	10.50	–	149.7	–
1/16c-O	1.23	10.33	14.62	32.94	316.8	10.4
Average-I[a]	1.61	2.57	2.81	–	190.4	–
Average-O[a]	1.58	9.08	3.80	32.09	316.5	10.1

c: 21:00–07:00.
I: indoor; O: outdoor.
OC: organic carbon.
[a] Data obtained in intensive fireworks display were excluded to calculate the average concentrations of related species.

4. Conclusions

Indoor and outdoor concentrations of $PM_{2.5}$-associated perchlorate and chlorate were investigated in Jinan, China, and size-resolved perchlorate and chlorate were studied in Kumamoto, Japan. The mean outdoor concentration of $PM_{2.5}$-associated perchlorate in Jinan was 4.18 ng m^{-3} (range, 0.23–173.76 ng m^{-3}), which was several times the concentration of PM_{10}-associated perchlorate in other Chinese cities (Shi et al., 2011). The highest outdoor concentration of perchlorate (173.76 ng m^{-3}) was observed on Spring Festival Eve as a result of the intensive fireworks display. The outdoor concentration of $PM_{2.5}$-associated chlorate in Jinan was 2.82 ng m^{-3} (range, 0.52–9.07 ng m^{-3}). Perchlorate and chlorate were mainly distributed in fine particles, and the approximate concentrations of $PM_{2.5}$-associated perchlorate and chlorate in Kumamoto were 0.04 ng m^{-3} and 4.14 ng m^{-3}, respectively. The ratios of ClO_3^-/ClO_4^- ranged from 18.72 to 360.22 in Kumamoto and from 0.03 to 7.45 in Jinan. This unusual pattern was probably a result of high levels of ClO_4^- in Jinan.

O_3 did not play a role in the formation of perchlorate during winter in Jinan, possibly due to the low concentrations of O_3 in winter. The concentrations of perchlorate were significantly related to fireworks-related compounds (Cl^- and K^+; $p < 0.01$; $r = 0.864$ and 0.982 for Cl^- and K^+, respectively) in Jinan. Thus, fireworks displays were a significant source of perchlorate in Jinan. Chlorate exhibited strong correlations with secondary pollutants (SO_4^{2-}, NO_3^- and NH_4^+; $p < 0.01$; $r = 0.723$–0.876) and primary contaminants (K^+; $p < 0.01$; $r = 0.876$), indicating the atmospheric oxidative process and primary emission of chlorate in Kumamoto.

Indoor concentrations of perchlorate and chlorate were first reported in this study. The average indoor concentrations of perchlorate and chlorate were 3.54 ng m^{-3} and 0.94 ng m^{-3}, respectively. The highest indoor concentration of perchlorate (125.14 ng m^{-3}) was observed on Spring Festival Eve. A significant correlation was observed between outdoor and indoor concentrations of perchlorate ($p < 0.01$, $r = 0.983$) and concentrations of ClO_3^-, Cl^-, SO_4^{2-} and $PM_{2.5}$ ($p < 0.01$; $r = 0.559$–0.949). The occurrence of higher concentrations of perchlorate indoors than outdoors was a combined effect of outdoor fireworks displays, meteorological conditions and the specific indoor and outdoor sampling positions. The residents of Jinan have little potential risk of exposure to perchlorate and chlorate; however, the risk of exposure to perchlorate in children during fireworks celebrations is worthy of attention. It should be noted that our study was at a disadvantage due to limited data. Seasonal variations were not investigated, and further long-term studies are needed.

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