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ORIGINAL PAPER

Spatial and long-term temporal assessment of organic hazardous air pollutants and their comparative health risks

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Abstract This study investigated the spatial and long-term temporal characteristics of 13 selected organic hazardous air pollutants and the health risks associated with inhalation exposure over a recent 6-year period. Regional types selected for this study included a residential–commercial complex, traffic junction, petrochemical industry, iron and metal industry, and background areas in Korea. Toluene was generally the most abundant pollutants in all areas. The petrochemical industrial area had the highest median concentrations of six pollutants (benzene, ethyl benzene, *o*-xylene, *m*,*p*-xylene, styrene, and chloroform), followed by the residential–commercial complex, traffic junction, iron and metal industry, and background area. The residential–commercial complex and traffic junction areas showed the highest and second highest toluene concentrations, respectively. Two pollutants (1,1-dichloroethane and 1,3-butadiene) were present in similar concentrations among the five areas. In addition, the temporal trends in the annual mean concentrations exhibited unpredictable behavior depending on both the area and the type of pollutants. At the residential–commercial complex and traffic junction areas, six aromatic compounds showed significant correlations among themselves. In most cases, three important meteorological parameters (relative humidity, temperature, and wind speed) were not significantly correlated with ambient pollutant concentrations. Benzene was the only pollutant that exceeded the cancer risk levels of 1×10^{-6}, and this excess was only observed at certain areas.

Keywords Residential–commercial · Traffic junction · Petrochemical · Iron and metal · Long-term characteristics · Meteorological parameters

Introduction

Hazardous air pollutants (HAPs) are airborne toxins that have the potential to increase population health risks of cancer and reproductive, immunological, developmental, and neurological disorders (USEPA 2010). HAPs and other volatile organic compounds can also easily photochemically react with hydroxyl radicals and other oxidants in the atmosphere to produce secondary toxic oxidants such as ozone and aldehydes and secondary organic aerosols (Stroud et al. 2008). These characteristics of HAPs necessitate that their atmospheric concentrations be managed. In the USA, the federal Clean Air Act Amendments of 1990 authorized the United States Environmental Protection Agency (USEPA) to regulate emissions of 188 HAPs. Similarly, there has been growing public concern regarding HAPs in Korea, particularly in urban areas, which has led the Korean Ministry of Environment (KME) to regulate their emissions (KME 2008; Shin and Yang 2010). Initially, 16 HAPs were regulated by the KME in 1978, and 48 HAPs are currently regulated (Shin and Yang 2010). Developing effective regulation and control strategies to reduce health risks associated with population exposure to HAPs requires the identification and quantification of individual HAPs. Accordingly, the KME developed a monitoring program for 13 volatile organic compounds

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(VOCs) and seven polycyclic aromatic hydrocarbons. These compounds have been monitored monthly in several Korean urban and suburban areas by the KME since 1995. Even though the increased national concern regarding air pollutants in Korea has led to significant investment in pollution control measures, the effects of these measures on atmospheric air quality have not yet been properly evaluated (Yoo et al. 2008).

Several risk analysis studies essential to the establishment of HAPs regulation strategies have been conducted based on data obtained during monitoring of ambient HAPs (Touma et al. 2006; McCarthy et al. 2009). Different areas can exhibit different distributions of ambient HAPs, resulting in different health risks (Khoder 2007; Hoque et al. 2008). However, even though data describing atmospheric HAP concentrations in areas with different characteristics in Korea are available, they have not yet been properly incorporated to provide valuable information for assessment of health risks associated with population exposure. Moreover, the HAPs emission strength of many anthropogenic sources can change over long-term periods, which is reflected in the concentrations of atmospheric HAPs (Blanchard et al. 2010).

Therefore, the present study was conducted to investigate the spatial and long-term temporal characteristics of 13 selected organic HAPs and the health risks associated with inhalation exposure over a recent 6-year period. Regional types selected for this study included a residential–commercial complex, traffic junction, petrochemical industry, iron and metal industry, and background areas. The target HAPs are primarily released into urban atmospheres from anthropogenic sources such as motor vehicle exhaust and other combustion processes utilizing fossil fuels, petroleum storage and distribution, solvent usage, and other industrial processes (Badol et al. 2008). These compounds have acute and/or chronic adverse health effects (USEPA 2010), as well as the potential to form secondary toxic air pollutants via photochemical reactions with OH radicals and other oxidants (Carter and Seinfeld 2012). Cancer risks associated with chronic inhalation exposure were estimated using unit risks (URs), while hazard quotients (HQs) for acute inhalation exposure were calculated using reference concentrations (RfCs) or reference exposure levels (RELs).

Materials and methods

Study protocol

Five areas with different characteristics that were selected for investigation of selected organic HAPs from 2006 to 2011 are presented in Fig. 1. The survey areas were as follows: RCS, residential–commercial complex area at Seoul, which is the capital of Korea and has a population of ca. 9.63 million and an area of 605 km^2; TJS, traffic junction area in Seoul; PIU, petrochemical industries-concentrated area in Ulsan, which has a population of ca. 1.07 million and an area of 1059 km^2; IMP, iron and metal industries-concentrated area at Pohang, which has a population of ca. 0.51 million and an area of 1128 km^2; and BAP, background area at suburban Padolee, Chungnam, which has a population of ca. 0.04 million and an area of 505 km^2. At each area, the 24-h resolution VOC concentrations were determined by averaging the concentrations of eight 3-h VOC samples (2-h sampling and 1-h analysis) collected at flow rates of 10–40 ml min^{-1}. One sample every month was collected from each monitoring station. These measurements were taken according to the Korean standard method for VOC measurements. Ambient VOC sampling was conducted on the roofs of 3- to 5-storey buildings by drawing air through a stainless steel trap with a 1/4 in. outside diameter and length of 10 cm that contained Tenax TA. A coupled on-site thermal desorption system (Unity/Air Server, Markes) and GC/Deans switch/dual-flame ionization detector system (Varian 3800) with a capillary column (Restek RTX-1, 60 m × 0.32 mm × 3 μm) or a coupled TDS (Ultra TD Auto Sampler, Markes) and GC/mass selective detector system (Varian Saturn 2000) were utilized to measure ambient target VOCs. The target compounds were selected based on their prevalence in ambient air and toxic effects. The target compounds included benzene (BZ), toluene (TL), ethyl benzene (EB), *o*-xylene (OX), *m*,*p*-xylene (MPX), styrene (ST), chloroform (CF), methyl chloroform (MCF), trichloroethylene (TCE), perchloroethylene (PCE), 1,1-dichloroethane (11DCE), carbon tetrachloride (CT), and 1,3-butadiene (13BT). For quality control, gas-phase calibration mixtures of the target compounds with the concentration range of 0.01–100 ppb and field as well as laboratory blanks (Tenax TA traps without injecting calibration mixtures) were introduced to the analytical system in the same way as for ambient air samples. Once the data were quality assured, the information was transferred to the Air Quality Management Bureau of the KME. We chose to begin our study with data from 2006 because the data have been quality assured since this year. VOC concentrations of measurements below the method detection limits (MDLs) were set to half of the MDLs of the respective VOCs for the conservative calculations of statistical values using SAS software (Su et al. 2013). The MDLs of the target compounds ranged from 0.01 to 0.08 ppb.

Health risk analysis

The target VOCs were classified into two sub-categories based on whether they were carcinogenic or non-

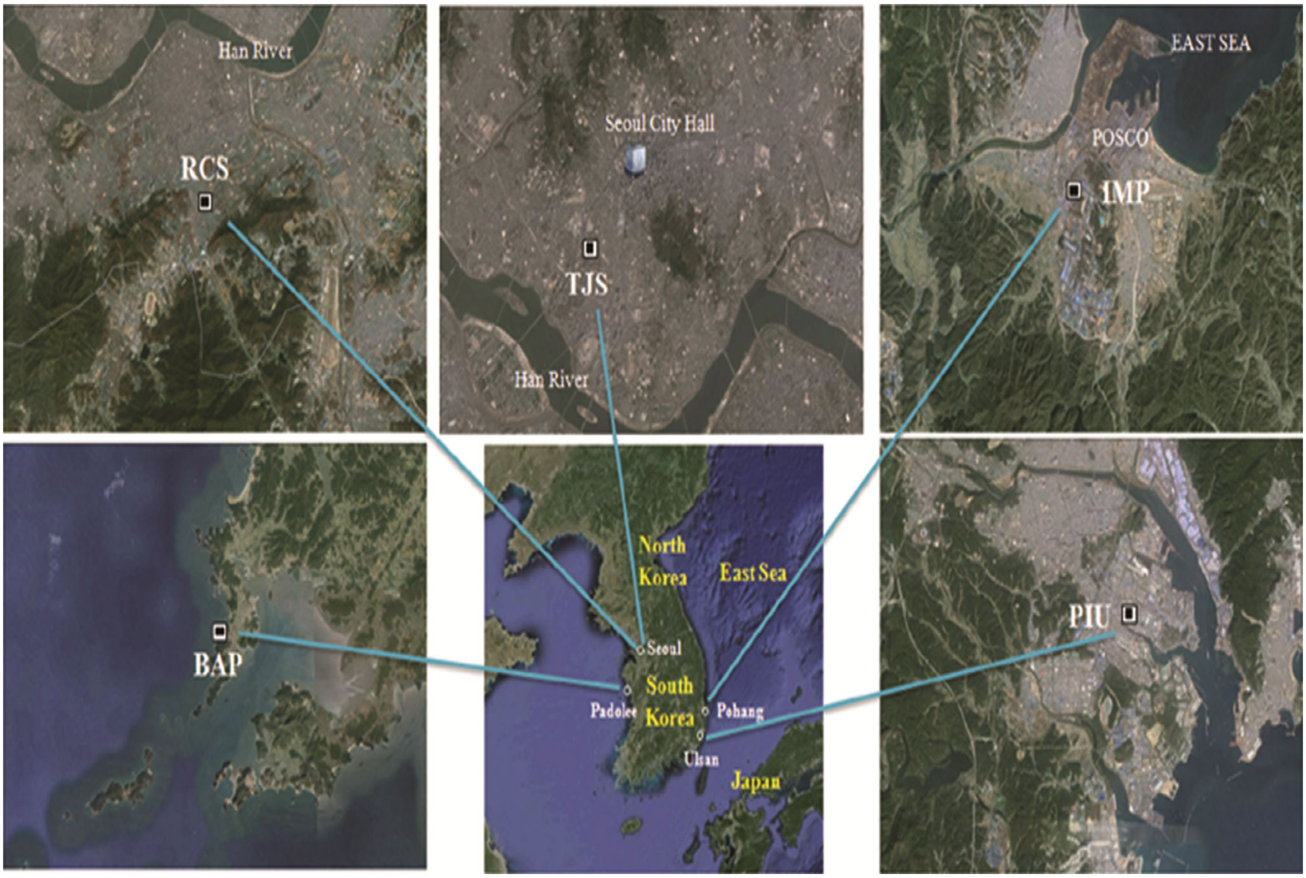


Fig. 1 Map of monitoring areas. *RCS* residential–commercial complex at Seoul, *TJS* traffic junction area at Seoul, *PIU* petrochemical industries-concentrated area at Ulsan, *IMP* iron and metal industries-concentrated area at Pohang, *BAP* background area at Padolee, Chungnam

carcinogenic to estimate their health risks. The expected excess cancer risks (R_cs) and non-carcinogenic health risks as HQs were estimated using published URs and inhalation RfCs or RELs, respectively, as follows (Tam and Neumann 2004; Barregard et al. 2009):

$$[R_c = C_{VOC} \times UR] \qquad (1)$$

$$[HQ = C_{VOC}/RfC\,\mathrm{or}\,REL] \qquad (2)$$

where C_{VOC} is the measured median concentration; UR is the inhalation unit risk, which is the upper-bound excess lifetime cancer risk calculated to result from exposure to specified VOCs at a concentration of 1 ppb; RfC is the maximum acceptable inhalation concentration of a specified VOC set by the USEPA; and REL is the occupational exposure limit recommended by the United States NIOSH and OSHA for adoption as a permissible exposure limit of a specified VOC. Four VOCs (BZ, CL, CT, and 13BT) had both unit risk values and RfC or REL values available, while only RfC or REL values were available for the nine remaining VOCs (TL, EB, OX, MPX, ST, MCF, TCE, PCE, and 11DCE) (USEPA 2010).

Results and discussion

Characteristics of ambient HAPs by area

The characteristics of long-term ambient organic HAP concentrations monitored at five different areas were investigated. Figure 2 summarizes the 24-h average concentrations of 13 selected HAPs obtained from five monitoring stations (RCS, TJS, PIU, IMP, and BAP) from 2006 to 2011. The mean values were generally higher than the median values, indicating that HAP concentrations were not normally distributed. Therefore, a normality test (Shapiro–Wilk statistical test) was conducted, and the results indicated that the HAP concentrations showed a lognormal distribution. Accordingly, median concentration values were utilized to nominate the HAP concentrations. The median concentrations of individual HAPs monitored in the five areas from 2006 to 2011 are shown in Table 1. Toluene was generally the most abundant HAP for all areas, likely due to the highest emission rate of this pollutant (Na and Kim 2007). As anticipated, BAP (suburban area) displayed the lowest atmospheric concentrations for most

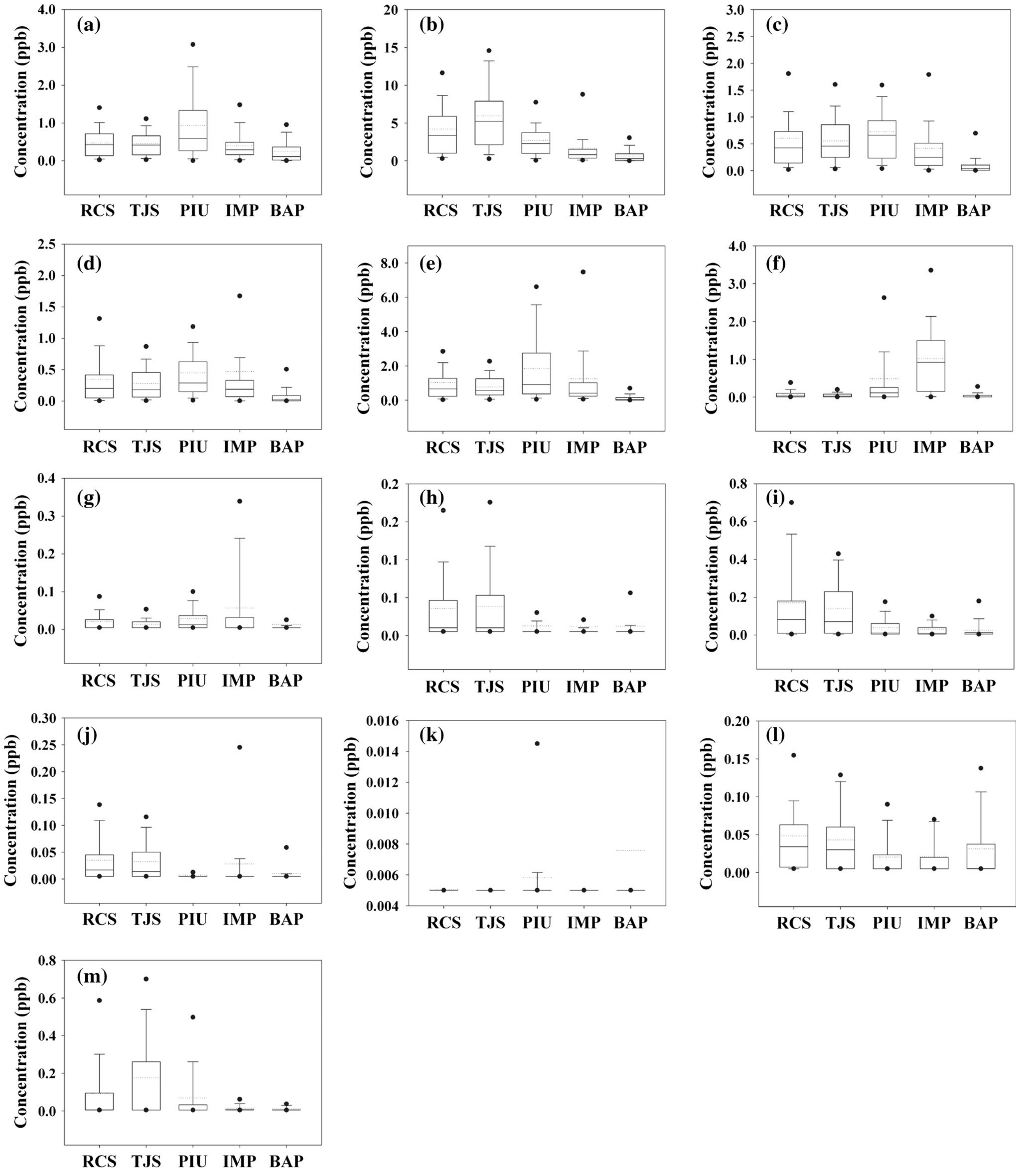


Fig. 2 Box plots of average HAP concentrations (ppb) obtained from five monitoring stations (RCS, TJS, PIU, IMP, and BAP) from 2006 to 2011: **a** BZ; **b** TL; **c** EB; **d** OX; **e** MPX; **f** ST; **g** CF; **h** MCF; **i** TCE; **j** PCE; **k** 11DCE, **l** CT; **m** 13BT. The *bottom* and *top lines* represent the 10th and 90th percentiles, respectively, the *bottom* and *top circles* represent the 5th and 95th percentiles, and the *dotted line* represents the mean value

HAPs. It should be noted that the PIU revealed the highest median concentrations for six HAPs (BZ, EB, OX, MPX, ST, and CF), which was attributed to emissions from petroleum refining, oil production, solvent storage, and other handling processes (Axelsson et al. 2010). For these compounds, the RCS and TJS, which showed similar

Table 1 Median values of average HAP concentrations (ppb) obtained at five monitoring stations from 2006 to 2011

HAPs	RCS	TJS	PIU	IMP	BAP
BZ	0.424	0.414	0.592	0.289	0.115
TL	3.345	5.210	2.281	0.823	0.281
EB	0.424	0.458	0.659	0.250	0.039
OX	0.205	0.182	0.289	0.190	0.020
MPX	0.669	0.560	0.911	0.409	0.040
ST	0.030	0.024	0.114	0.020	0.005
CF	0.005	0.005	0.013	0.005	0.005
MCF	0.010	0.010	0.005	0.005	0.005
TCE	0.082	0.071	0.010	0.010	0.005
PCE	0.017	0.014	0.005	0.005	0.005
11DCE	0.005	0.005	0.005	0.005	0.005
CT	0.034	0.030	0.005	0.005	0.005
13BT	0.006	0.005	0.005	0.005	0.005

RCS residential–commercial complex at Seoul, *TJS* traffic junction area at Seoul, *PIU* petrochemical industries-concentrated area at Ulsan, *IMP* iron and metal industries-concentrated area at Pohang, *BAP* background area at Padolee, Chungnam

concentrations to each other, had the second highest median values, followed by the IMP and BAP. These results were ascribed to higher emissions from motor vehicles at RCS (residential–commercial complex area) and TJS (traffic junction area) in Seoul compared to the IMP (Pohang) and BAP (suburban area) with less populations. The major atmospheric sources of five of the six HAPs (BZ, EB, OX, MPX, and ST) were petrochemical handling processes and motor vehicles (Leuchner and Rappenglück 2010). The RCS and TJS showed the highest and second highest toluene concentrations, respectively, as well as higher concentrations of the other four HAPs (MCF, TCE, PCE, and CT) relative to the rest of the survey areas. These differences were likely due to greater solvent use in Seoul, because these chemicals are contained in a variety of solvents, including dry cleaners (Na and Kim 2007). CF is also emitted from drinking or waste water treatment plants (Oskouie et al. 2008; Chu et al. 2011). In addition, two HAPs (11DCE and 13BT) showed similar concentrations among the five survey areas.

Long-term temporal variation

Long-term temporal variations in the ambient concentrations of six HAPs (BZ, TL, EB, OX, MPX, and 13BT), which were selected based on high concentrations or toxicity, were further investigated. Figure 3 shows the annual trends in average concentrations of the six selected HAPs in the five areas from 2006 to 2011. The long-term trends in the annual mean HAP concentrations exhibited unpredictable behavior that varied by area and type of HAP. Specifically, the mean HAP concentrations observed at three areas (RCS, PIU, and IMP) fluctuated without showing any patterns. Additionally, 13BT did not show any patterns in average concentrations. For example, the average concentrations of 13BT for RCS were 0.007, 0.006, 0.007, 0.008, 0.007, and 0.007 ppb for 2006, 2007, 2008, 2009, 2010, and 2011, respectively. Consequently, the variations in annual HAP concentrations observed in many cases cannot be reasonably explained without further information; therefore, the annual trends obtained from this study are not likely to be useful in determining whether previous HAP control measures applied to the five areas were successful or not. Exceptionally, the mean HAP concentrations for IMP showed an increasing trend from 2006 to 2010, while those for BAP displayed a decreasing trend since 2007. The increasing trend in mean HAP concentrations for IMP was most likely due to the gradual increase in metal production activities, while the decreasing trend for BAP was ascribed to effective control measures implemented at the suburban area. The MPX concentration at sites RCS and TJS gradually increased in the years 2006, 2007, 2008 and then rapidly decreased to very low levels in 2009, 2010, and 2011. The increasing pattern over the former 3-year period was attributed to the gradual increase in traffic emissions due to the increase in the number of motor vehicles, while the increasing pattern over the latter 3-year period was likely due to the enforcement of emission control policy for motor vehicles since 2009.

Figure 4 shows the seasonal trends in the average concentrations of the six selected HAPs for each investigated area. The seasonal concentrations varied with pollutant types as well as by area. Specifically, toluene concentrations, which displayed the most abundant HAP in all areas, were highest for the three areas (RCS, TJS, and PIU) during winter, while they were highest for IMP and BAP during spring and autumn, respectively. According to the Korean Petroleum Institute, the proportion of aromatic constituents in gasoline sold in Korea ranges from 20 to 35 %, with benzene accounting for 1.0 to 3.0 %, toluene 10 to 20 %, ethyl benzene 3 to 5 %, and xylenes 6 to 7 %. The fuel blends of these constituents varied little with seasons. Since traffic emissions are a primary source of organic HAPs in Korea (Na et al. 2005), the highest concentration of toluene among the target HAPs was attributed to the highest proportion of toluene in gasoline. One possible cause of the higher benzene and toluene concentrations during winter relative to summer could have been the lower combustion efficiency of gasoline, causing higher VOC concentrations in the roadway air due to incomplete combustion. This assertion was supported by Deng et al. (2011), who reported that high tailpipe emissions from motor vehicles are associated with cold ambient temperature. In addition, the highest amount of heating fuel is

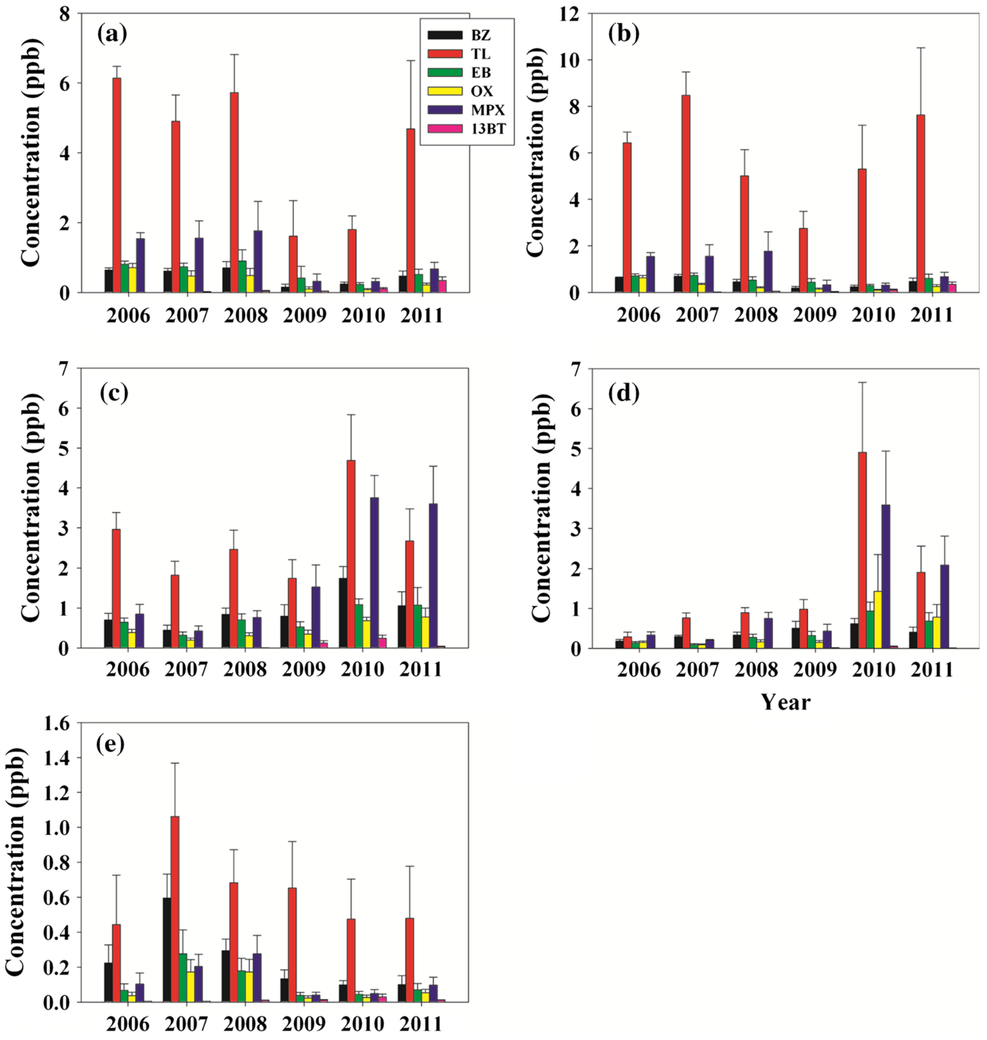


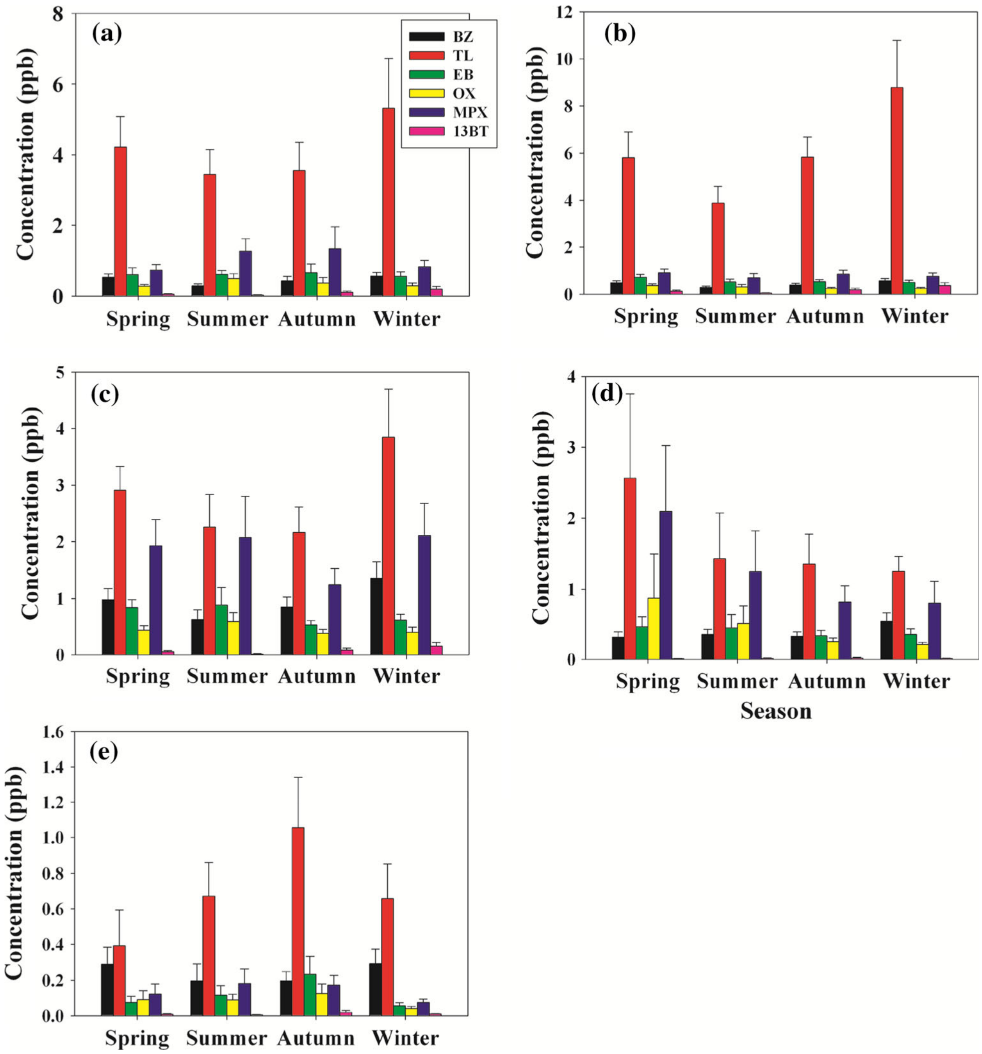
Fig. 3 Annual average concentrations (ppb) and standard errors of six selected HAPs (BZ, TL, EB, OX, MPX, and 13BT) for five areas: **a** RCS; **b** TJS; **c** PIU; **d** IMP; and **e** BAP

typically consumed in Korean urban areas during winter, which elevates the ambient air pollutant levels in these regions (Lee et al. 2006). Higher atmospheric stability is also generally observed in Korea during winter due to the more frequent occurrence of low inversion heights, which elevate ground-level air pollution (Lee et al. 2008). Moreover, seasonal rain fronts typically occur in Korea during the summer months, which increase the wet deposition of atmospheric toluene (Vu et al. 2011). Vehicle evaporation emissions may also be higher during summer than winter due to increased evaporation of gasoline constituents from fuel tanks and engines in summer (Yurdakul et al. 2013). Nevertheless, the higher atmospheric toluene concentration during winter suggests that the winter low combustion efficiency effect would overweigh the summer high evaporation effect on ambient toluene concentrations in RCS, TJS, and PIU. In addition, the other target HAPs exhibited different seasonal variations depending on area. These results were likely a result of seasonal variations in meteorological factors, such as wind speed, humidity, and mixing height, as well as long-range transport of HAPs.

Correlation among selected HAPs

Table 2 shows the correlation coefficients of the atmospheric HAPs monitored at the five categorical areas from 2006 to 2011. For two monitoring areas (RCS and TJS), six aromatic HAPs (BZ, TL, EB, OX, MPX, and ST) were significantly correlated among themselves. These results were ascribed to high traffics as a common source of the aforementioned compounds at the residential–commercial complex and traffic junction in Seoul, since these pollutants are markers of motor vehicle emissions. Similarly, Parra et al. (2006) found high correlations among all of six HAPs except for ST in northern Spain. However, it is notable that styrene and BTEX compounds in industrial area may show an insignificant correlation, possibility due to ST emissions from industrial activities. Other studies (Na et al. 2005; Nguyen et al. 2009)

Fig. 4 Seasonal average concentrations (ppb) and standard errors of six selected HAPs (BZ, TL, EB, OX, MPX, and 13BT) for five areas: **a** RCS; **b** TJS; **c** PIU; **d** IMP; and **e** BAP



have also revealed significant correlations among aromatic hydrocarbons in Seoul, although the location of HAP monitoring areas differed between this and previous studies. One chlorinated HAP (CF) was also significantly correlated with the six aromatic HAPs, which was attributed to the combined effects of traffic and petrochemical handling processes in the petrochemical industry-concentrated area in Ulsan. However, there was no significant correlation among other chlorinated HAPs, suggesting that their emission sources are not same. At IMP and BAP, certain aromatic HAPs were significantly correlated with each other, suggesting that these areas were at least partially influenced by traffic emissions. Meanwhile, both 13BT and BTEX are important motor vehicle-emission marker and thus, there should be a statistical significant correlation between them. Nevertheless, in the present study there was no significant correlation between BTEX compounds and 13BT. These results are most likely due to low concentrations of 13BT with little variation in the average range of 0.005–0.006 ppb (Table 1).

Relationship of HAP concentrations with meteorological parameters

The correlation of the concentrations of individual HAPs with three important meteorological parameters (relative humidity, temperature, and wind speed) is shown in Table 3. The meteorological data were obtained from the meteorological offices of each city because area-specific meteorological data were unavailable. In most cases, the three meteorological parameters were not significantly correlated with HAP concentrations, although a few cases revealed a significant correlation. In addition, based on our preliminary study (data not shown), there was no significant correlation between wind direction and VOC concentrations. These results were not consistent with those of previous atmospheric polycyclic aromatic hydrocarbon studies (Karar and Gupta 2006; Tham et al. 2008). Strong wind speed could exert a dilution effect on atmospheric concentrations (Karar and Gupta 2006), while high temperature could increase the photochemical reactions of

Table 2 Correlation between target HAPs according to area

Area	VOCs	BZ	TL	EB	OX	MPX	ST	CF	MCF	TCE	PCE	11DCE	CT	13BT
RCS	BZ	1												
	TL	0.82*	1											
	EB	0.71*	0.73*	1										
	OX	0.58*	0.56*	0.78*	1									
	MPX	0.63*	0.56*	0.83*	0.92*	1								
	ST	0.46*	0.49*	0.63*	0.63*	0.57*	1							
	CF	0.14	0.13	0.06	0.16	0.12	0.13	1						
	MCF	0.13	0.07	0.06	0.19	0.15	0.05	0.15	1					
	TCE	0.12	0.16	0.15	0.11	0.13	0.12	0.17	0.19	1				
	PCE	0.14	0.15	0.17	0.18	0.13	0.14	0.18	0.12	0.18	1			
	11DCE	−0.01	−0.06	−0.05	−0.06	−0.04	0.01	−0.08	−0.08	−0.1	−0.08	1		
	CT	0.17	0.12	0.18	0.15	0.13	0.19	0.16	0.15	0.18	0.16	0.04	1	
	13BT	0.21	0.17	0.15	0.13	0.11	0.16	0.13	−0.04	0.15	0.19	0.13	0.14	1
TJS	BZ	1												
	TL	0.71*	1											
	EB	0.53*	0.68*	1										
	OX	0.55*	0.48*	0.72*	1									
	MPX	0.71*	0.63*	0.80*	0.84*	1								
	ST	0.37**	0.54*	0.39**	0.55*	0.49*	1							
	CF	0.16	0.08	0.18	0.03	0.15	0.07	1						
	MCF	0.07	0.05	0.13	0.15	0.21	0.15	0.14	1					
	TCE	0.11*	0.06	0.07	0.05	0.19	0.14	0.13	0.07	1				
	PCE	0.08	0.19	0.17	0.23	0.08	0.13	0.08	0.14	0.12	1			
	11DCE	0.2	0.06	0.18	0.14	0.22	0.09	−0.11	−0.09	−0.01	0.22	1		
	CT	0.16	0.12	0.18	0.16	0.12	0.07	0.12*	0.20	0.16	0.13	−0.06	1	
	13BT	0.09	0.05	0.19	0.13	0.15	0.22	0.21	−0.06	0.17	0.18	−0.08	0.19	1

Table 2 continued

Area	VOCs	BZ	TL	EB	OX	MPX	ST	CF	MCF	TCE	PCE	11DCE	CT	13BT
PIU	BZ	1												
	TL	0.51*	1											
	EB	0.31***	0.59*	1										
	OX	0.33***	0.56*	0.84*	1									
	MPX	0.54*	0.57*	0.77*	0.82*	1								
	ST	0.33**	0.32**	0.36**	0.24***	0.22	1							
	CF	0.44**	0.35**	0.13	0.14	0.25***	−0.03	1						
	MCF	0.07	0.11	0.04	0.07	0.03	−0.03	−0.04	1					
	TCE	0.18	0.21	0.11	0.17	0.12	−0.07	0.20	0.16	1				
	PCE	0.18	0.05	−0.08	−0.04	−0.03	−0.04	0.07	−0.02	0.02	1			
	11DCE	0.18	0.11	0.06	0.14	0.19	−0.03	0.21	0.04	0.2	0.05	1		
	CT	0.21	0.14	0.15	0.15	0.12	0.01	0.14	0.01	0.13	0.04	0.18	1	
	13BT	0.17	0.11	0.21	0.16	0.11	0.21	0.14	−0.03	0.19	0.07	0.15	0.11	1
IMP	BZ	1												
	TL	0.49*	1											
	EB	0.43**	0.63*	1										
	OX	0.10	0.44**	0.72*	1									
	MPX	0.34**	0.77*	0.8*	0.85*	1								
	ST	−0.06	−0.12	−0.19	−0.09	−0.13	1							
	CF	−0.02	−0.13	−0.12	−0.09	−0.14	0.13	1						
	MCF	0.1	0.03	0.04	0.02	0.02	0.04	−0.08	1					
	TCE	0.23	0.09	0.12	0.05	0.05	−0.03	−0.04	0.68*	1				
	PCE	−0.02	−0.04	−0.07	−0.02	−0.05	0.02	−0.06	−0.03	0.05	1			
	11DCE	0.11	−0.05	−0.06	−0.04	−0.05	−0.13	−0.06	−0.03	0.01	−0.05	1		
	CT	0.12	0.13	0.11	0.13	0.19	−0.13	−0.19	0.12	0.11	−0.1	0.05	1	
	13BT	0.15	0.21	0.13	0.14	0.15	−0.1	−0.16	0	0.21	−0.08	0.03	0.12	1

Table 2 continued

Area	VOCs	BZ	TL	EB	OX	MPX	ST	CF	MCF	TCE	PCE	11DCE	CT	13BT
BAP	BZ	1												
	TL	0.37**	1											
	EB	0.24	0.68*	1										
	OX	0.23	0.58*	0.86*	1									
	MPX	0.27***	0.67*	0.81*	0.8*	1								
	ST	0.27***	0.36***	0.37**	0.35***	0.56*	1							
	CF	0.21	0.18	0.04	0	0.05	0.02	1						
	MCF	−0.03	0.02	0.03	0.2	0.09	0.16	0	1					
	TCE	0.16	0.11	0.13	0.16	0.18	0.23	0.02	0.15	1				
	PCE	−0.12	0.03	0.2	0.12	0.15	0.11	0.02	0.13	0.22	1			
	11DCE	−0.12	−0.09	−0.07	0.05	−0.08	0.17	−0.01	0.19	−0.04	0.11	1		
	CT	0.16	0.15	0.19	0.11	0.15	0.15	0.09	0.19	0.15	0.14	0.22	1	
	13BT	−0.12	−0.04	−0.07	−0.01	−0.08	−0.01	−0.04	0.1	−0.02	0.12	0.13	0.02	1

Statistical significance: * $p < 0.0001$; ** $p < 0.005$; *** $p < 0.05$

HAPs, thereby reducing HAP concentrations (Stroud et al. 2008). In contrast to the present study, Parra et al. (2006) reported a positive correlation between relative humidity and the concentrations of certain aromatic HAPs. The reason for this difference remains unclear; therefore, further studies to address this issue are warranted. Meanwhile, it is noteworthy that, although information on mixing heights is unavailable in the present study, mixing heights can be highly correlated with VOC concentrations (Sangiorgi et al. 2011; Yuan et al. 2013). It is also interesting to note that there was no significant correlation between four aromatic VOCs (BZ, TL, EB, and MPX) and 13BT, which are all markers for vehicle emissions. These results are ascribed to trivial variation in concentrations of 13BT. Meanwhile, it is noted that mixing height may be highly correlated with HAP concentrations. Nevertheless, we could not collect all necessary data because of limited logistics, which is a limitation of this study.

Risk assessment

Table 4 shows the cancer risks and the hazard quotients (HQs) for non-carcinogenic health effects of the selected HAPs monitored in the five study areas. BZ was the only HAP that exceeded the cancer risk levels of 1×10^{-6}, and this excess only occurred at RCS, TJS, and PIU, where cancer risk levels of 1.06×10^{-6}, 1.04×10^{-6}, and 1.48×10^{-6}, respectively, were observed. In addition, the cancer risk level for IMP was close to 1×10^{-6}, whereas the cancer risk level for BAP was much lower. BZ exposure has often been associated with adverse genetic effects and increased cancer risks (Snyder 2002; Pyatt and Hays 2010). Chronic exposure to BZ can also cause bone marrow depression, which is characterized by leukocytopenia, thrombocytopenia, granulocytopenia, and pancytopenia (Snyder 2002). In addition, the cancer risk levels associated with 13BT exposure were close to 1×10^{-6} in all five areas. Environmental exposure to this pollutant is closely associated with lymphohematopoietic cancers (Divine and Hartman 2001) and leukemia (Delzell et al. 2001) in industrial environments. This pollutant can also cause other non-cancerous health hazards such as adverse reproductive and developmental effects (USEPA 2010). However, no HAPs exhibited HQ levels that exceeded 1 for any areas. It should be noted that these HQ values would be somewhat underestimated because acute REL values were utilized to evaluate chronic toxicities of HAPs. Nevertheless, the results obtained in the present study suggested that HAPs control strategies should be focused on BZ and 13BT to reduce the risk of cancer posed to residents in four (RCS, TJS, PIU, and IMP) of the five study areas. Additionally, the cancer risk levels observed in this study were lower than the results obtained in Portland, OR, USA (Tam and Neumann 2004). In the aforementioned

Table 3 Pearson correlation of HAP concentrations with meteorological parameters for five areas

HAPs	Region	Absolute humidity		Temperature		Wind speed	
		R^2	*p* Value	R^2	*p* Value	R^2	*p* Value
BZ	RCS	0.047	0.153	0.037	0.203	0.023	0.318
	TJS	0.078	0.056	0.061	0.096	0.001	0.873
	PIU	0.031	0.249	0.031	0.245	0.030	0.249
	IMP	0.069	0.086	0.146	0.010	0.000	0.988
	BAP	0.020	0.391	0.011	0.520	0.031	0.278
TL	RCS	0.003	0.711	0.000	0.963	0.042	0.179
	TJS	0.000	0.970	0.011	0.488	0.026	0.284
	PIU	0.031	0.248	0.049	0.144	0.058	0.107
	IMP	0.117	0.020	0.114	0.021	0.008	0.544
	BAP	0.037	0.240	0.046	0.189	0.042	0.202
EB	RCS	0.016	0.408	0.040	0.190	0.049	0.145
	TJS	0.066	0.082	0.102	0.029	0.022	0.321
	PIU	0.009	0.529	0.008	0.568	0.001	0.809
	IMP	0.103	0.039	0.144	0.013	0.002	0.788
	BAP	0.030	0.303	0.038	0.246	0.052	0.159
OX	RCS	0.085	0.055	0.100	0.037	0.120	0.020
	TJS	0.038	0.196	0.057	0.109	0.035	0.207
	PIU	0.007	0.601	0.013	0.457	0.000	0.993
	IMP	0.085	0.067	0.093	0.056	0.000	0.986
	BAP	0.052	0.194	0.072	0.124	0.041	0.211
MPX	RCS	0.056	0.119	0.075	0.069	0.064	0.094
	TJS	0.009	0.524	0.038	0.187	0.039	0.186
	PIU	0.040	0.185	0.049	0.140	0.013	0.460
	IMP	0.132	0.013	0.131	0.013	0.011	0.483
	BAP	0.069	0.112	0.069	0.112	0.004	0.704
ST	RCS	0.063	0.096	0.043	0.174	0.120	0.020
	TJS	0.008	0.543	0.003	0.716	0.063	0.096
	PIU	0.001	0.859	0.002	0.763	0.004	0.695
	IMP	0.133	0.013	0.088	0.046	0.072	0.071
	BAP	0.001	0.836	0.000	0.943	0.002	0.800
CF	RCS	0.003	0.733	0.004	0.678	0.000	0.968
	TJS	0.019	0.354	0.008	0.547	0.001	0.807
	PIU	0.137	0.011	0.218	0.001	0.069	0.078
	IMP	0.021	0.335	0.033	0.228	0.044	0.160
	BAP	0.016	0.437	0.016	0.437	0.021	0.373
MCF	RCS	0.006	0.608	0.012	0.466	0.009	0.536
	TJS	0.027	0.274	0.020	0.342	0.012	0.477
	PIU	0.003	0.728	0.001	0.803	0.042	0.173
	IMP	0.074	0.067	0.049	0.138	0.016	0.407
	BAP	0.064	0.117	0.040	0.216	0.033	0.260
TCE	RCS	0.014	0.431	0.001	0.847	0.027	0.284
	TJS	0.001	0.801	0.002	0.764	0.003	0.702
	PIU	0.001	0.842	0.001	0.846	0.002	0.773
	IMP	0.028	0.265	0.021	0.337	0.001	0.828
	BAP	0.060	0.129	0.045	0.189	0.042	0.202

Table 3 continued

HAPs	Region	Absolute humidity		Temperature		Wind speed	
		R^2	*p* Value	R^2	*p* Value	R^2	*p* Value
PCE	RCS	0.002	0.748	0.014	0.435	0.002	0.795
	TJS	0.048	0.141	0.038	0.188	0.004	0.694
	PIU	0.061	0.099	0.017	0.383	0.000	0.935
	IMP	0.171	0.004	0.125	0.016	0.027	0.277
	BAP	0.091	0.059	0.068	0.103	0.014	0.466
11DCE	RCS	0.001	0.842	0.001	0.861	0.000	0.956
	TJS	0.001	0.807	0.000	0.952	0.002	0.753
	PIU	0.000	0.935	0.004	0.663	0.062	0.096
	IMP	0.016	0.406	0.025	0.295	0.005	0.644
	BAP	0.023	0.354	0.033	0.264	0.044	0.192
CT	RCS	0.000	0.901	0.004	0.675	0.052	0.134
	TJS	0.003	0.713	0.000	0.888	0.028	0.274
	PIU	0.008	0.555	0.016	0.396	0.070	0.077
	IMP	0.009	0.540	0.002	0.786	0.007	0.581
	BAP	0.006	0.622	0.000	0.947	0.006	0.639
13BT	RCS	0.005	0.639	0.001	0.824	0.011	0.498
	TJS	0.043	0.163	0.037	0.193	0.000	0.961
	PIU	0.026	0.287	0.033	0.229	0.079	0.059
	IMP	0.066	0.084	0.081	0.055	0.002	0.754
	BAP	0.000	0.978	0.000	0.986	0.056	0.140

Table 4 Unit risks and median cancer risks (R_cs) for carcinogenic effect and RfC (or REL) and median hazard quotients (HQs) for non-carcinogenic health effects of the target HAPs for five areas

HAP	Unit risk (per ppb)[a]	R_cs, RCS/TJS/PIU/IMP/BAP $\times 10^6$	RfC or REL (ppb)	HQs, RCS/TJS/PIU/IMP/BAP
BZ	2.5×10^{-6}	1.06/1.04/1.48/0.72/0.29	9[b]	0.05/0.05/0.07/0.03/0.01
TL	NA	NA	80[c]	0.04/0.07/0.03/0.01/<0.01
EB	NA	NA	231[b]	<0.01/<0.01/<0.01<0.01<0.01
OX	NA	NA	23[b]	0.01/0.01/0.01/0.01/<0.01
MPX	NA	NA	23[b]	0.03/0.02/0.04/0.02/<0.01
ST	NA	NA	212[c]	<0.01/<0.01/<0.01<0.01<0.01
CF	4.7×10^{-6}	0.02/0.02/0.06//0/02/0.02	69[c]	<0.01/<0.01/<0.01<0.01<0.01
MCF	NA	NA	184 [c]	<0.01/<0.01/<0.01<0.01<0.01
TCE	0.4×10^{-6}	0.03/0.03/<0.01/<0.01/<0.01	112[c]	<0.01/<0.01/<0.01<0.01<0.01
PCE	0.9×10^{-6}	0.02/0.01/<0.01/<0.01/<0.01	5[c]	<0.01/<0.01/<0.01<0.01<0.01
11DCE	NA	NA	NA	NA
CT	7.1×10^{-6}	0.26/0.21/0.04/0.04/0.04	6[c]	0.01/0.01/<0.01<0.01<0.01
13BT	127×10^{-6}	0.76/0.64/0.64/0.64/0.64	1[b]	0.01/0.01/0.01/0.01/0.01

NA not available; R_cs or HQs RCS/TJS/PIU/IMP/BAP represent R_c or HQ values estimated for five areas (RCS, TJS, PIU, IMP, and BAP), respectively

[a] Unit risk is the upper limit increased lifetime cancer risk of an individual who is exposed for a lifetime to 1 ppb in air (USEPA 2010)

[b] RfC is the inhalation reference concentration that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA 2010)

[c] REL is the recommended exposure limit at which no adverse health effects are anticipated for a specified exposure period (USEPA 2010)

study, the nominal cancer risk levels of BZ, CF, TCE, PCE, CT, and 13BT were 15.3×10^{-6}, 5.71×10^{-6}, 4.41×10^{-6}, 4.61×10^{-6}, 42.7×10^{-6}, and 38.3×10^{-6}, respectively. However, the cancer risk levels in Portland may have changed owing to implementation of different HAPs control measures since the study was conducted.

Conclusion

In this study, the spatial and long-term temporal characteristics of selected organic HAPs and the health risks associated with inhalation exposure to HAPs in five different areas over a recent 6-year period were investigated. The highest concentrations for six of 13 HAPs were observed in a petrochemical industries-concentrated area. For these compounds, residential–commercial complex and traffic junction areas, which showed similar concentrations to each other, had the second highest median values, followed by an iron and metal industries-concentrated area. As anticipated, the background area displayed the lowest atmospheric concentrations for most HAPs. However, the temporal trends in HAP concentrations exhibited unpredictable behavior that depended on both the area and the type of HAPs. Considering the annual increase in the number of motor vehicles and industrial activities, a steady increase in the annual HAP concentrations was expected. However, the fluctuated temporal trend in HAP concentrations indicates that there was no steady HAP concentration increase, likely due to the HAP emission control measures taken in Korea. Meteorological parameters (relative humidity, temperature, and wind speed) did not reveal any significant correlations with HAP concentrations. Additionally, BZ was the only HAP that exceeded the cancer risk levels of 1×10^{-6}, and this excess was only observed in three areas. The cancer risk levels associated with 13BT exposure were also close to 1×10^{-6} for all five areas. Overall, the results of this study suggest that HAPs control strategies should focus on BZ and 13BT to effectively reduce the risk of cancer posed to residents in urban areas.

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