Chemosphere 94 (2014) 128–134

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Levels, profiles and gas–particle distribution of atmospheric PCDD/Fs in vehicle parking lots of a South China metropolitan area

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HIGHLIGHTS

- Diesel truck park held higher air TSP and PCDD/F level than LPG bus/gasoline car park.
- LPG-fueled vehicle in operation can also emit PCDD/Fs for the presence of Cl and Cu.
- 2,3,7,8-PCDD/F congener profiles of parks and tailpipe exhaust studies were identical.
- Unlike tailpipe study, park air show distinct gaseous and particulate PCDD/F profiles.
- PCDD/F pollution in diesel-truck park is noteworthy for exceeding the air TEQ limit.

ARTICLE INFO

Article history:
Received 24 May 2012
Received in revised form 14 September 2013
Accepted 21 September 2013
Available online 28 October 2013

Keywords:
Persistent organic pollutants (POPs)
Doxins and furans
Vehicle exhaust
Heavy-duty diesel-trucks
Liquefied petroleum gas (LPG)

ABSTRACT

Vehicle exhaust is one important PCDD/F source in urban areas. In this study, occurrence and inhalation of atmospheric PCDD/Fs in three enclosed/semi-enclosed large-scale vehicle parks were investigated. The park for heavy-duty diesel-trucks exhibited the highest atmospheric 2,3,7,8-PCDD/F concentrations (17.7 ± 4.3 pg m^{-3}, 0.818 ± 0.264 pg I-TEQ m^{-3}), followed sequentially by those for liquefied petroleum gas-buses and for unleaded gasoline-cars. High-chlorinated congeners/homologues dominated 2,3,7,8-PCDD/F profiles. Principal component analysis indicated their similarities with tailpipe studies. More than 70% of PCDD/Fs were particle-bound and their congener/homologue patterns differed from those of gaseous PCDD/Fs. In all studied parks logarithms of the gas/particle partitioning coefficients (K_ps) of PCDD/F homologues were linearly correlated with those of their sub-cooled vapor pressures (p_Ls). Daily PCDD/F doses inhaled by park-workers were estimated to be between 0.099–0.227 pg I-TEQ kg^{-1} d^{-1}. Their probabilistic incremental lifetime cancer risks were 1.08×10^{-5}–2.07×10^{-5}, which were in the acceptable range (1.0×10^{-4}–1.0×10^{-6}). However, all data from the diesel-truck park significantly exceeded the upper limit for PCDD/Fs in ambient air of Japan (0.6 pg TEQ m^{-3}). Hence, air pollution and adequate ventilation should be considered during the design and construction of such enclosed/semi-enclosed parks.

1. Introduction

Polychlorinated dibenzo-*p*-dioxin/furans (PCDD/Fs) are carcinogenic, teratogenic, mutagenic and ubiquitous pollutants; mainly derived from incomplete combustion processes (Lohmann and Jones, 1998). Many publications have shown that vehicle exhaust is an important PCDD/F source in urban areas (Yu et al., 2006; Chuang et al., 2010), especially in high traffic areas (Grochowalski et al., 1995; Miyabara et al., 1999; Lee et al., 2004). A survey by U.S. Environmental Protection Agency (EPA) showed that heavy-duty diesel-engine exhaust was the sixth largest PCDD/F source in the U.S. and accounted for 4.6% of total emissions in 2000 (USEPA, 2006). PCDD/Fs in exhaust are mainly associated with particulate matters emitted from automobiles (Chuang et al., 2010). These contain fine respirable particles with the peak diameter between 0.1 and 0.2 μm (Kleeman et al., 2000). Some evidence suggests that mobile sources, in particular diesel-powered vehicles, might be the major source of human dioxin exposure (Jones, 1995). In view of their adverse health effects and sharply increasing vehicle numbers worldwide, PCDD/Fs from automobile exhaust have aroused much attention (Chuang et al., 2010).

Researches about PCDD/Fs' releases from vehicles have focused on tailpipe emissions (Gullett and Ryan, 1997, 2002; Chuang et al., 2010) and ambient air in high traffic areas, e.g. highway tunnels (Chang et al., 2004) and road intersections (Grochowalski et al.,

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http://dx.doi.org/10.1016/j.chemosphere.2013.09.061

1995; Ryan and Gullett, 2000). Summarizing published data, PCDD/F emission factors are typically in the range of 0.36–9500 pg I-TEQ km^{-1} (7.0–27440 pg I-TEQ L^{-1}) (Chang et al., 2004) and are correlated with engine type, load and age, fuel type and quality, driving mode, etc. (Gullett and Ryan, 1997, 2002; Miyabara et al., 1999; Kim et al., 2003; Heeb et al., 2007). Low load rates and idle conditions reportedly greatly increase dioxin emission from diesel-vehicles (Kim et al., 2003; Chang et al., 2004). High traffic areas showed significantly higher atmospheric PCDD/F levels than their surrounding areas (Grochowalski et al., 1995; Deng et al., 2011). Consequently, workers in such areas, e.g. traffic policemen, tollbooth attendants, taxi/bus drivers, likely are exposed to higher PCDD/F inhalation risks.

Nowadays, due to the rapidly increasing numbers of vehicles and dwindling available space in urban areas, many parking lots and bus stations/terminals are constructed underground or in buildings to save space and reduce parking-related traffic jams. But this approach makes the parks enclosed/semi-enclosed and concentrates related exhaust. To date, however, few rules and data on air quality in such areas are available. Guangzhou is a metropolitan area located in South China (area: 7434 km^2; population: 12.7 million). It was home to 1.83 million vehicles in 2006, including 22,430 liquefied petroleum gas (LPG)-powered buses/taxies. By the end of 2010 the number of total vehicles increased to 2.15 million. Atmospheric PCDD/F levels in Guangzhou were reported higher than those of many other cities worldwide and traffic was one of the most important sources (Yu et al., 2006; Yu, 2007). In this situation, three large-scale Guangzhou parks for unleaded gasoline-cars, LPG-buses and heavy-duty diesel-vehicles (HDDVs) respectively, were selected for air-sampling and PCDD/F analysis. The two aims were: (1) to investigate their atmospheric levels, congener/homologue profiles and gas–particle distribution of PCDD/Fs; (2) to assess potential PCDD/F inhalation exposure of park-workers.

2. Material and methods

2.1. Samples collection

The three studied parks are all open 24-h and located in the central area of Guangzhou. Park SY is located beneath a shopping mall in the most thriving commercial center of Guangzhou. It consists of two floors, with >1500 standard parking spaces and is equipped with a ventilation system that operates daily from 9:00 to 23:00. About 90% of the vehicles parked are unleaded gasoline-powered cars. The average traffic rate is about 1000 cars h^{-1}. The SY site sampled was in the middle of the first floor. Park GJ is a single-story bus terminal located under the square of the second biggest railway station of Guangzhou (area: 17,000 m^2). It is equipped with a ventilation system that operates daily from 6:00 to 23:00. During the sampling period, 26 bus lines connected and about 5000 buses per day entered and departed from it, and >90% of these were LPG-propelled. The GJ site sampled was in the middle of the park. The HY Park was built for a centralized freight transport market. Therein, more than 1000 transport routes connect and the daily goods trading volume is >6000 tons. It is an outdoor but semi-enclosed area (60,000 $m^{2,}$ >300 park spaces) surrounded by storehouses (10–15 m high) with only two entrances being left. Vehicles parked here are mainly HDDVs and the daily average in-out flow volume is >10,000. The sampling site was located 2 m inside away from one entrance tollgate.

Short consecutive sampling campaigns of about two weeks were conducted at each park between August 23 and November 11, 2006, using high-volume air samplers operating at 1.05 m^3 · min^{-1}. Glass fiber filter (GFF, 20.3 cm × 25.4 cm, Whatman) and polyurethane foam (PUF, 90 mm × 65 mm i.d.) plugs were used to collect total suspended particulate (TSP) and gaseous organic compounds, respectively. A total of 8, 10 and 10 samples were obtained for SY, GJ and HY, respectively. After sampling, the filters and PUFs were separately stored at ⩽−20 °C until analyzed.

2.2. Analysis

2.2.1. Chemicals

All native and ^{13}C-labeled PCDD/F standards were obtained from Cambridge Isotope Laboratories Inc. (Andover, USA). The solvents and reagents used were HPLC or pesticide grade from Merck (Darmstadt, Germany) or J.T. Baker (Phillipsburg, USA). Silica gel (70–230 mesh, Aldrich, USA) and Florisil (60–100 mesh, Merck, Germany) were Soxhlet-extracted with dichloromethane for 24 h, vacuum-dried, and were respectively activated at 180 °C for 5 h and 135 °C for 24 h before use.

2.2.2. Clean-up procedures

PCDD/F analysis followed U.S. EPA Method 1613 and is described briefly here: ^{13}C-labeled PCDD/Fs were added to filters and PUF plugs and Soxhlet-extracted with toluene for 48 h. Each extract was sequentially cleaned through acid silica gel bed, multi-layer silica gel column and Florisil column. The final eluent was concentrated to 20 μL under a gentle high-purity nitrogen stream and spiked with internal standards.

2.2.3. Instrumental analysis

The analysis of PCDD/Fs was performed with a HRGC-HRMS (Thermo Finnigan MAT95 XP, Germany) running in EI^+ and selected ion monitoring mode at a resolution >10000. A DB-5 MS fused silica capillary column (60 m × 0.25 mm i.d., 0.25 μm, J&W Scientific, CA) was used. The GC temperature program was: 90 °C (1.0 min) 76 °C min^{-1} 200 °C (7.0 min) 1.2 °C min^{-1} 275 °C 1.7 °C min^{-1} 300 °C. Carrier gas was helium (0.8 mL min^{-1}). Temperatures of injection port, ion source and transfer line were 260 °C, 250 °C and 305 °C, respectively. A 1 μL sample was injected in splitless mode. Electron emission energy: 55 eV; filament current: 0.80 mA.

2.3. Quality assurance and quality control

Prior to use, the filters were heated at 450 °C for 4 h and sealed in aluminum foil, the foam plugs were Soxhlet-extracted with methanol, dichloromethane, toluene and acetone for 24 h respectively, then were vacuum-dried and sealed in pre-cleaned amber glasses. All samples were spiked with $^{13}C_{12}$-labeled PCDD/Fs to evaluate the clean-up procedures, recoveries of which ranged in 56–133%. One field GFF/PUF blank, experimental blank, standard-spiked blank/matrix samples were analyzed for each twelve samples. No detectable or quantifiable 2,3,7,8-PCDD/F congeners were found in blank samples. Recoveries of the spiked standards were 49–120%.

2.4. Calculation

In our study, in addition to seventeen 2,3,7,8-PCDD/F congeners, concentrations of PCDD/F homologues (tetra- to octa-) including 2,3,7,8-subtituted and non-2,3,7,8-substituted congeners were also calculated through Xcalibar HRMS Software. The method detection limits were 0.5–5.0 pg μL^{-1} for PCDD/Fs. Concentrations were not recovery- or blank-corrected and values below the detection limits were regarded as nil. The statistical significance was defined as $p < 0.05$ and the mean value ± standard deviation were calculated for each set of samples.

3. Results and discussion

3.1. Concentrations of TSP and PCDD/Fs

Concentrations of TSP, 2,3,7,8-PCDD/Fs (I-TEQ) and total PCDD/Fs (tetra- to octa-) were 180 ± 56 μg m^{-3}, 3.99 ± 2.09 pg m^{-3} (0.167 ± 0.077 pg I-TEQ m^{-3}) and 11.9 ± 4.0 pg m^{-3} for SY; 427 ± 69 μg m^{-3}, 7.51 ± 2.69 pg m^{-3} (0.370 ± 0.174 pg I-TEQ m^{-3}) and 18.0 ± 6.7 pg m^{-3} for GJ; and 1026 ± 222 μg m^{-3}, 17.7 ± 4.3 pg m^{-3} (0.818 ± 0.264 pg I-TEQ m^{-3}) and 43.4 ± 11.0 pg m^{-3} for HY, respectively (Fig. 1). For power and security reasons, outside air samples near the three parks were unavailable for comparison. But we collected air samples at a typical urban site (TH) about 4 km away from the three parks weekly for one year (Jan–Dec, 2005) and analyzed them for PCDD/Fs (Yu, 2007). The average annual TSP and 2,3,7,8-PCDD/F concentrations (TEQ) were 227 μg m^{-3} and 5.30 pg m^{-3} (0.240 pg I-TEQ m^{-3}) with values in August being the lowest (TSP: 161 μg m^{-3}; PCDD/Fs: 2.54 pg m^{-3}/0.102 pg I-TEQ m^{-3}) (Yu, 2007). Results of HY and GJ were significantly higher than TH annual levels (*t*-test, $p = 0.000–0.039 < 0.05$), and values of SY were higher than TH's levels in August, the corresponding sampling month in SY. All results indicate local emission sources in the parks. The changing trend of HY > GJ > SY suggests greater TSP and PCDD/F pollution in the HDDV park than the parks for LPG- and gasoline-powered vehicles.

The occurrence of PCDD/Fs in automotive exhaust has been investigated by previous researchers (Turrio-Baldassarri et al., 2005), and HDDVs are reported to emit more PCDD/Fs than gasoline-powered or diesel passenger vehicles (Hagenmaier et al., 1990; Geueke et al., 1999; Miyabara et al., 1999; Chang et al., 2004; Chuang et al., 2010). Usage of unleaded gasoline instead of leaded gasoline was reported to lower PCDD/F emission by 1- to 2-orders of magnitude (Hagenmaier et al., 1990). Therefore, fuel and vehicle type might be the most important reasons for the lower pollution in SY. In addition, the mechanical ventilation in SY may also effectively diffuse the pollutants. In contrast at HY, passive natural air-exchange together with busy surrounding roads lowers its air quality.

To date, however, there are no published reports about PCDD/Fs emitted from LPG-propelled vehicles. LPG is regarded as cleaner fuel than diesel or gasoline, emitting less greenhouse gases, particulate matters, ozone precursors, and polycyclic aromatic hydrocarbons (Chang et al., 2001; Ristovski et al., 2005; Lim et al., 2007; Yang et al., 2007; Adam et al., 2011), and is currently widely used in buses and taxies in China (Ou et al., 2010). About 5000 buses and 9300 taxies in Guangzhou were LPG-powered in 2005 and the numbers increased to 6430 and 16000 in 2006, respectively. However, some on-road studies demonstrated that differences between LPG- and gasoline-vehicle emissions were not statistically significant owing to the large variations between vehicles (Ristovski et al., 2005), e.g., intensive use and poor maintenance of LPG-vehicles resulted in exceedances of emission standards (Ning and Chan, 2007; Lau et al., 2011). Unmatched engines and incomplete combustion of LPG could also offset its potential benefits (Lai et al., 2009; Adam et al., 2011). Emissions from the LPG-fleet in Guangzhou were found to increase more than those from the gasoline-fleet during morning and evening rush hours, as well as noontime break (Lai et al., 2009). Volatile organic compounds emitted by LPG-vehicles were higher than those from diesel- and gasoline-fueled vehicles (Wang et al., 2006). Formation of PCDD/Fs in vehicle engines requires both incomplete combustion process and presence of chlorine (UNEP, 2003), which may arise from Cl^- in airborne particulates (Deng et al., 2011). Furthermore Cu, a catalyst for PCDD/F formation (Heeb et al., 2007), was also found in residue formed in the fuel supply system of LPG-vehicles for the usage of copper pipeline (Gao et al., 2007). Our data suggested that PCDD/Fs emitted from LPG-buses might be lower than HDDVs, but higher than gasoline-powered cars. Further tailpipe exhaust

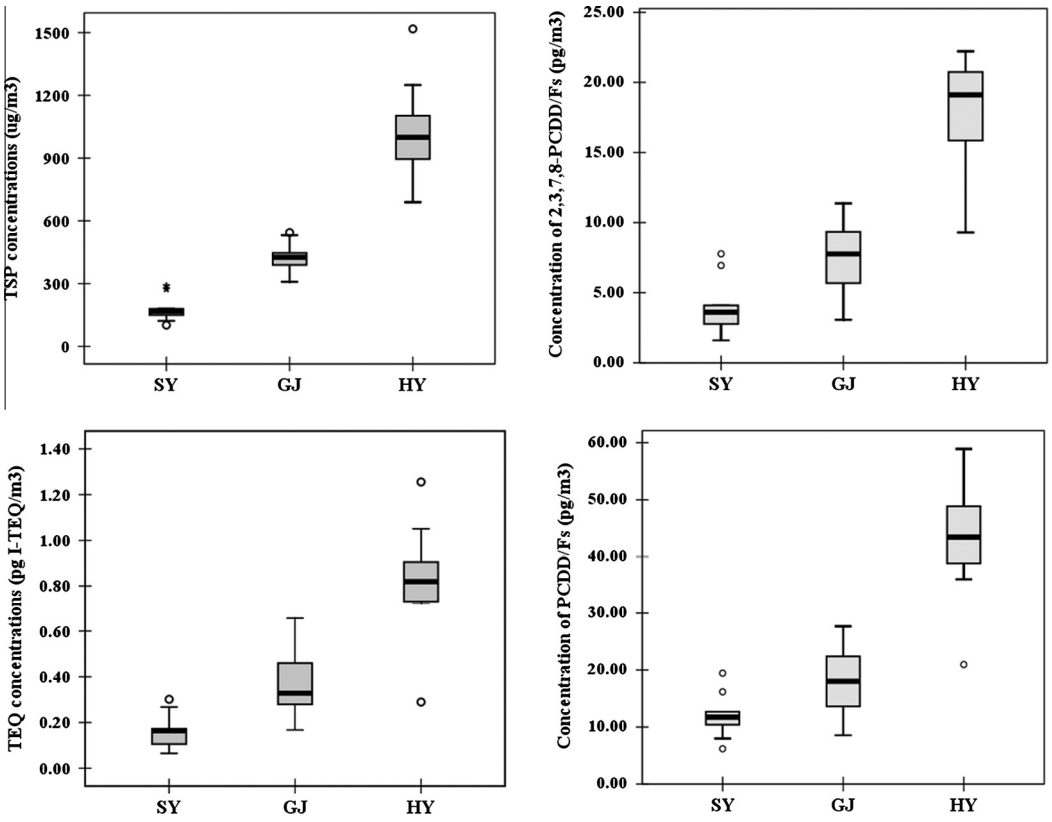

Fig. 1. Atmospheric concentrations of TSP, 2,3,7,8-PCDD/Fs, total PCDD/Fs and TEQs in three enclosed or semi-enclosed vehicle parks (SY, GJ and HY).

investigations are needed to clarify their emission factors and formation mechanisms.

Published data on atmospheric 2,3,7,8-PCDD/Fs in high traffic areas are summarized in Table 1. Air samples collected from a heavy traffic crossroad in Cracow, Poland in March, 1995 showed the highest ever-reported 2,3,7,8-PCDD/F concentration, i.e. 1060 pg m^{-3} (11.95 pg I-TEQ m^{-3}) (Grochowalski et al., 1995). The explanations provided included the usage of leaded petrol at that time and the general higher atmospheric PCDD/F levels in Cracow (59.5 pg m^{-3}) due to domestic waste incineration and coal heat facilities (Grochowalski et al., 1995). Deng et al. (2011) reported lower atmospheric PCDD/Fs in a tunnel in Guangzhou in spring and summer of 2006 than our values at GJ and HY, while their winter results were slightly higher than those of HY (Table 1). Various vehicle types and higher flow rate (>2000 h^{-1}, Deng et al., 2011) might contribute to recent differences between parks and the tunnel in Guangzhou. Comparatively, our results (1.60–22.2 pg m^{-3}) were higher than data of most similar studies (0.48–20.2 pg m^{-3}, Table 1). Furthermore, dioxin TEQ values at HY significantly exceeded the upper limit for ambient air in Japan, i.e. 0.6 pg TEQ m^{-3}. Therefore, possible dioxin pollution in these enclosed/semi-enclosed parking lots should be considered during their design and construction, especially in areas of increasing congestion.

3.2. Congener/homologue profiles of PCDD/Fs

Fig. 2 illustrates the congener/homologue profiles of atmospheric PCDD/Fs (gaseous combined particulate) of the three parks. OCDD/Fs and 1,2,3,4,6,7,8-HpCDD/Fs were the dominant 2,3,7,8-substituted congeners, which also have been reported in vehicle exhausts and air from high traffic areas (e.g. Geueke et al., 1999; Ryan and Gullett, 2000; Gullett and Ryan, 2002; Kim et al., 2003; Chang et al., 2004; Lee et al., 2004). The published data showed that, even though engine type, start condition (cold or hot), operation mode, engine age/condition, vehicle load and fuel characteristics all impacted the emission factors of PCDD/Fs from diesel- or gasoline-fleet, no significant differences were found between their 2,3,7,8-PCDD/F isomer profiles (Kim et al., 2003; Chuang et al., 2010). This profile repeatability was also confirmed by Gullett and Ryan (2002) via multivariate analysis comparisons between 16 run types and tunnel data. In our study, principle component analysis was performed to extract the main factors for the 2,3,7,8-PCDD/F congener profiles of the three parks. For each individual park or the total three parks, only one component was extracted, which explained 94.8–97.4% of the total variance and was heavily weighted in OCDD, OCDF and 1,2,3,4,6,7,8-HpCDF (Supporting information, Table S3). Factor extraction was also conducted between our data and other tailpipe results (USEPA, 2001; Chuang et al., 2010). One only component, responsible for 92.2% of the total variance and similar to that extracted from the parks, was obtained (Table S3). All these results indicated that congener patterns of 2,3,7,8-PCDD/Fs emitted from diesel-trucks, LPG-buses and unleaded gasoline-cars were no different.

As for 2,3,7,8-substituted homologues, high-chlorinated (hexa- through octa-) 2,3,7,8-PCDD/Fs were dominant, and the patterns for the three parks showed a consistent trend characterized by increasing concentrations of more chlorinated homologues except for OCDF. By comparison, homologue profiles of total PCDD/Fs demonstrated more variety between the three parks (Fig. 2), and are obviously different from those of tail-pipe data (USEPA, 2001; Gullett and Ryan, 2002). Intercorrelations between PCDD/F homologue profiles of on-vehicle and tunnel samples were also found to be poor by Gullett and Ryan (2002). This was partly attributed to engine-specific distinctions and the mixture of vehicle types in the tunnel. In addition, exchange with outdoor air due to park ventilation systems was also speculated as a possible contributor. Park SY showed a pattern similar to that of TH in summer (Yu, 2007).

3.3. Gas–particle distribution of PCDD/Fs

In our study, average percentages of gaseous 2,3,7,8-PCDD/Fs and PCDD/Fs relative to total concentrations (gaseous + particulate) were 6.9% and 30% for SY, 3.0% and 19% for GJ, and 3.0% and 16% for HY, respectively. Gas–particle partitioning of PCDD/Fs is a function of their degree of chlorination and the air temperature, i.e. higher chlorinated homologues and lower temperatures exhibit greater tendencies to associate with particulates (Lohmann and Jones, 1998). Mean sampling temperatures (range) were 35.4 °C (34.5–37.7 °C), 32.8 °C (32.1–34.0 °C) and 27.4 °C (22.7–30.6 °C) for SY, GJ and HY, respectively (Supporting information, Table S1). Therefore, gaseous PCDD/Fs at SY, especially low-chlorinated homologues, showed higher percentages than at GJ and HY.

As shown in Fig. 2, congener/homologue patterns of gaseous and particle-bound PCDD/Fs showed significant differences. Low-chlorinated PCDD/Fs dominated in the gas phase and high-chlorinated ones (hexa- through octa-) dominated in the particle phase, similar to a tunnel study by Deng et al. (2011). But this trend is quite different from the results for automobile exhaust via direct tailpipe sampling (Chuang et al., 2010), in which congeners in gaseous and particulate phases showed almost the same pattern. Gas–particle re-distribution with decreasing environmental temperature and admixture with ambient air, which occurs as the exhaust being emitted out, was suspected as the most possible reason.

Gas–particle partition coefficients K_p (m^3 μg^{-1}) of PCDD/F can be calculated with Eq. (1). The relationship between K_p and the

Table 1
A summarization of concentrations (pg m^{-3}) and TEQs (pg TEQ m^{-3}) of atmospheric 2,3,7,8-PCDD/Fs in high traffic areas.

Sampling sites	Description	Sampling year	Concentration	TEQ	References
Antwerp, Belgium	The Craey-beckx Tunnel	1991		0.0803 ± 0.0451	Wevers et al., 1992
Cracow, Poland	Heavy traffic crossroad	1995	1060	11.95	Grochowalski et al., 1995
Los Angeles, USA	Major freeway interchange	1990		0.08	Jones, 1995
Taipei, Taiwan	Highway tunnel	2001–2002	0.43–1.66 (1.03)	0.026–0.071 (0.052)	Chang et al., 2004
Kaohsiung, Taiwan	Traffic area		1.2	0.073	Lee et al., 2004
Rome, Italy*	Medium-traffic road site	2000–2001	1.70	0.060	Turrio-Baldassarri et al., 2005
		2001–2002	1.22	0.050	
Guangzhou, China*	Central bus station	2005	5.18	0.252	Yu, 2007
Hong Kong	Roadside site	2004		0.012–0.126	Choi et al., 2008
Guangzhou, China	The Pearl River tunnel	2006**	3.74–4.69 (4.19)	0.207–0.39 (0.297)	Deng et al., 2011
		2006***	18.6–20.4 (19.5)	1.27–1.39 (1.33)	
Guangzhou, China	Vehicle parks	SY, 2006	1.60–7.77 (3.99)	0.066–0.301 (0.166)	This study
		GJ, 2006	3.07–11.4 (7.51)	0.167–0.656 (0.370)	

* Only particle-bound concentrations.
** Values for summer and spring of 2006.
*** Values for December, 2006.

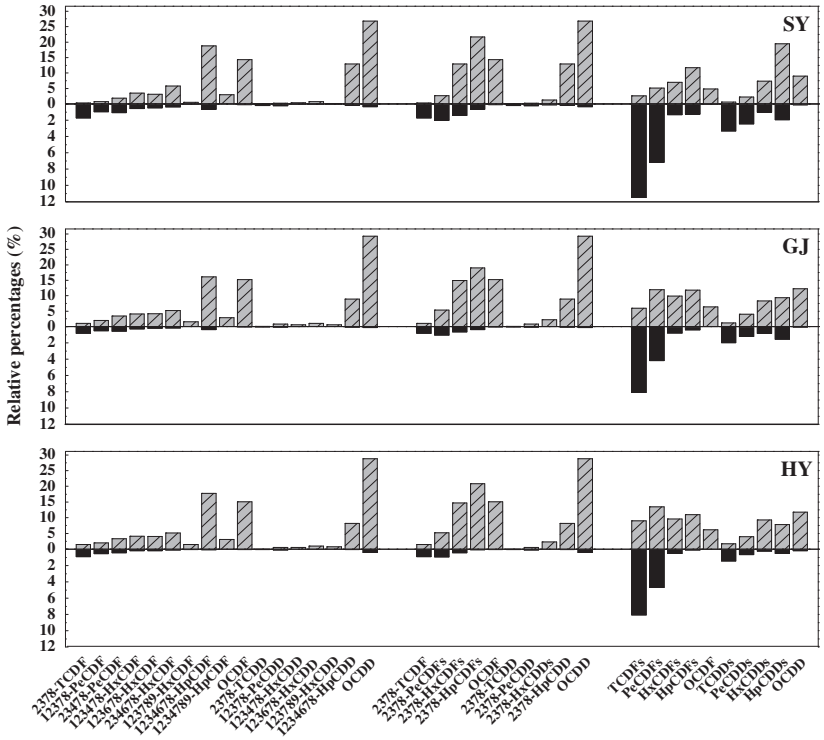

Fig. 2. Relative percentages of PCDD/F congeners and homologues in ambient air around SY, GJ and HY parking areas (Data were normalized to total (gaseous + particulate) concentrations; light gray column represents particle phase and dark column signifies gas phase).

temperature-corrected sub-cooled liquid vapor pressure $\boldsymbol{p_L}$ is depicted in Eq. (2) with $\boldsymbol{m_r}$ and $\boldsymbol{b_r}$ being constants (Lohmann and Jones, 1998; Li et al., 2008). Log $\boldsymbol{K_p}$s of the three parks were linearly correlated with the corresponding log$\boldsymbol{p_L}$s ($R = 0.824–0.971$; $p < 0.0001$) (Supporting Information, Fig. S1). The linear-fitted $\boldsymbol{m_r}$s ranged from −0.663 to −0.968 and $\boldsymbol{b_r}$s ranged from −4.94 to −6.61, in accordance with several previous field researchers (Lohmann and Jones, 1998; Li et al., 2008). However, log$\boldsymbol{K_p}$–log$\boldsymbol{p_L}$ plots of HpCDDs (log$\boldsymbol{p_L}$: −5.65–−6.29) are the most divergent points within the five PCDD homologues, which weakens their linear correlation coefficients. The reasons for this are unclear.

$$K_P = \frac{C_{GFF}/TSP}{C_{PUF}} \quad (1)$$

$$\log K_P = m_r \cdot \log p_L + b_r \quad (2)$$

3.4. Inhalation risk assessment

In our study, two common measures are adopted to approximate PCDD/F inhalation risk. One is calculating daily inhalation dose (DID) and comparing it with the total daily intake (TDI) limit. Another is combining inhalation exposure data with cancer potency factors to quantify associated cancer risks (Aries et al., 2008). The inhalation absorption factor is assumed to be 1.

3.4.1. DID of PCDD/Fs

DIDs of PCDD/Fs were calculated with an equation provided in Exposure Factors Handbook (USEPA, 1997). The park-related occupations (e.g. security, toll-collection) are defined as 8-h light activities with an average daily inhalation rate of 1.3 $m^3\ h^{-1}$ (USEPA, 1997). In the remaining 16 h, the workers are exposed to general urban air, of which PCDD/F concentrations are assumed the same between day and night, indoor and outdoor. The formula is:

$$DID = (C_{on\text{-}duty} \times 8\ h\ d^{-1} + C_{off\text{-}duty} \times 16\ h\ d^{-1}) \times 1.3\ m^3\ h^{-1}/BW \quad (3)$$

In which average body weights (BWs) of 67.7 and 59.6 kg are used for men and women, respectively (Chinese National Physique Monitoring data in 2000). The annual average atmospheric PCDD/F concentration in TH (0.240 pg I-TEQ m^{-3}), a representative urban area of Guangzhou (Yu, 2007), was adopted as $C_{off\text{-}duty}$. The average DIDs calculated were 0.113–0.227 and 0.099–0.199 pg I-TEQ kg^{-1} - d^{-1} for female and male park-workers, respectively (Table 2), higher than those of residents in Shanghai, China (Li et al., 2008).

Dietary intake has been reported to be a major dioxin exposure pathway for humans (Zhang et al., 2008). However, there are still no dietary exposure data for Guangzhou residents. Zhang et al. (2008) estimated the monthly dioxin intake of a study population from Shenzhen, China as 40.9 pg TEQ kg^{-1} (=1.36 pg TEQ $kg^{-1}\ d^{-1}$) based on food intake profiles. Due to the very close distance (<150 km) and similar dietary habits between Shenzhen and Guangzhou, we assume their residents share similar dietary dioxin intake doses and calculated the park-workers' TDIs accordingly. The results were 1.44–1.66 pg TEQ $kg^{-1}\ d^{-1}$, which are within the WHO TDI limit range (1–4 pg TEQ $kg^{-1}\ d^{-1}$, including dioxin-like polychlorinated biphenyls, PCBs) but close to the TDI limit (2 pg TEQ $kg^{-1}\ d^{-1}$) recommended by the UK Committee on the Toxicity of Chemicals in Food, Consumer Products and the Environment. Considering that PCBs and other important exposure pathways, e.g. indoor dust and dermal intake, are not included, our values may underestimate the park-workers' overall TEQ exposure risk.

3.4.2. Cancer risk of park-workers to PCDD/Fs

The cancer risk potency is calculated based on whole life inhalation doses, multiplied by the cancer potency factors, which is 1.3×10^5 $(mg\ kg^{-1}\ d)^{-1}$ for 2,3,7,8-TCDD (Aries et al., 2008). In our study, occupational exposure duration is 40 years, working

Table 2
The estimated daily intake doses and cancer risk potencies of PCDD/Fs via inhalation for workers in the three specific vehicle parks (SY, GJ and HY).

Daily PCDD/Fs intake doses of park-workers					
Park	TEQ (pg TEQ m^{-3}) mean (min–max)	Daily inhalation dose (pg TEQ d^{-1}) mean (min–max)		Mean TDI (pg TEQ d^{-1})	
		Woman	Man	Woman	Man
SY	0.166 (0.100–0.301)	0.113 (0.095–0.136)	0.099 (0.084–0.120)	1.47	1.46
GJ	0.370 (0.167–0.656)	0.148 (0.113–0.198)	0.131 (0.099–0.174)	1.51	1.49
HY	0.818 (0.290–1.26)	0.227 (0.134–0.303)	0.199 (0.118–0.267)	1.59	1.56
General	0.240	0.126	0.111	1.49	1.47

Park-workers' cancer risk potency of PCDD/Fs via inhalation									
Park	TEQ (pg I-TEQ m^{-3})			Cancer risk potency			Cancer risk per million		
	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
SY	0.301	0.100	0.166	1.28×10^{-5}	1.16×10^{-5}	1.08×10^{-5}	13	12	11
GJ	0.656	0.167	0.370	1.57×10^{-5}	1.33×10^{-5}	1.16×10^{-5}	16	13	12
HY	1.26	0.290	0.818	2.07×10^{-5}	1.71×10^{-5}	1.27×10^{-5}	21	17	13
General		0.240			1.22×10^{-5}			12	

time is 250 d $year^{-1}$ and 8 h d^{-1}; averaging time period is 70 years (365 d $year^{-1}$); and the average BW of women and men is 63.4 kg. The formula is:

$$\begin{aligned}\text{Cancer Risk Potency} = \big[&C_{\text{on-duty}} \times 1.3\,m^3\,h^{-1} \times 8\,h\,d^{-1} \\ &\times 250\,d\,year^{-1} \times 40\,years/(BW \times 70\,year \\ &\times 365\,d\,year^{-1}) + C_{\text{off-duty}} \times 1.3\,m^3\,h^{-1} \times 16\,h\,d^{-1} \\ &\times 365\,d\,year^{-1} \times 70\,years/(BW \times 70\,year \times 365\,d\,year^{-1})\big] \times 1.3 \times 10^5\end{aligned} \quad (4)$$

As shown in Table 2, results of park-workers significantly exceeded those for the general population (*t*-test, $p = 0.000$–$0.027 < 0.05$), except those in SY. Cancer risks per million were 12 to 21 people. However, all values (1.08×10^{-5}–2.07×10^{-5}) were in the range of 1.0×10^{-4}–1.0×10^{-6}, which is indicated as acceptable by U.S. EPA (Aries et al., 2008).

4. Conclusion

Compared with LPG-buses and gasoline-cars, operation of HDDVs resulted in statistically higher atmospheric PCDD/F levels in their associated parking area, which might affect the park-workers' health. Advanced emission control technologies (Pakbin et al., 2009), improved engine design (Laroo et al., 2011) and cleaner alternative fuels (Lin et al., 2011), which have been reported capable of reducing PCDD/F emissions, should be encouraged; together with more better engineered vehicle-park construction. As most PCDD/Fs are particle-bound (>70% TEQ), use of personal protective equipment would also lower the park-workers' cancer risks greatly.

Acknowledgements

We would like to thank Professor Robert C Hale for his generous help with the English grammar and wordings. The research was financially supported by National Natural Science Foundations of China (Nos. 41130752, 41073083, 40903043), and the Earmarked Fund of the State Key Laboratory of Organic Geochemistry (No. SKLOG2011A01). This is a contribution No. IS-1723 from GIGCAS.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.09.061.

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