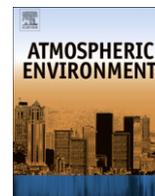


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Distribution profile, health risk and elimination of model atmospheric SVOCs associated with a typical municipal garbage compressing station in Guangzhou, South China

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H I G H L I G H T S

- ▶ TSP and model SVOCs emitted during garbage compressing process were monitored.
- ▶ Model was used to describe gas-particle partitioning of target SVOCs.
- ▶ BTF-PC integrated reactor was employed for SVOCs pollution control.
- ▶ Health risk of target SVOCs were assessed before and after treatment.

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Semi-volatile organic compounds (SVOCs) air pollution caused by municipal garbage compressing process was investigated at a garbage compressing station (GCS). The most abundant contaminants were phthalate esters (PAEs), followed by polycyclic aromatic hydrocarbons (PAHs) and organic chlorinated pesticides (OCPs). \sum_{16} PAHs concentrations ranged from 58.773 to 68.840 ng m⁻³ in gas and from 6.489 to 17.291 ng m⁻³ in particulate phase; \sum_{20} OCPs ranged from 4.181 to 5.550 ng m⁻³ and from 0.823 to 2.443 ng m⁻³ in gas and particulate phase, respectively; \sum_{15} PAEs ranged from 46.498 to 87.928 ng m⁻³ and from 414.765 to 763.009 ng m⁻³ in gas and particulate phase. Lung-cancer risk due to PAHs exposure was 1.13×10^{-4} . Both non-cancer and cancer risk levels due to OCPs exposure were acceptable. Non-cancer hazard index of PAEs was 4.57×10^{-3} , suggesting safety of workers as only exposure to PAEs at GCS. At pilot scale, 60.18% of PAHs, 70.89% of OCPs and 63.2% of PAEs were removed by an integrated biotrickling filter-photocatalytic reactor at their stable state, and health risk levels were reduced about 50%, demonstrating high removal capacity of integrated reactor.

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1. Introduction

Semi-volatile organic compounds (SVOCs) refer to a group of organic substances, most of which are highly toxic, stable, long-distance migrating and bio-accumulative, thus cause global and long lasting hazards to both wildlife and human beings (Cai et al., 2008; Lohmann et al., 2007). Some SVOCs such as polycyclic aromatic hydrocarbons (PAHs), organic chlorinated pesticides (OCPs) and phthalate esters (PAEs) have been highly concerned recently for their widespread occurrence and adverse health effect. PAHs have over 200 congeners, 16 of which have been highlighted

as the priority environment pollutants by the United States Environmental Protection Agency (USEPA). PAHs are believed to be emitted mainly by incomplete combustion processes of fossil fuels, biomasses and vehicle operation (Christensen and Arora, 2007). Epidemiologic evidences showed that significant relationship existed between PAHs exposure and cancer risk in lung, skin and bladder (Boffetta et al., 1997). OCPs are the most important group of persistent organic pollutants (POPs) defined by the Stockholm Convention (UNEP, 2001). Despite the production and application of most OCPs have been banned in China since 1984, high levels of OCPs residue have been identified in various environmental samples such as soil, water, air and biotissues as a result of their persistence (Meng et al., 2009; Tao et al., 2008; Yang et al., 2008b). PAEs are used extensively as additives in plastic products such as polyvinylchloride resins, polyethylene terephthalate, cellulose

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and polyurethanes to impart flexibility (Teil et al., 2006). They are not irreversibly bound to the polymer matrix, which makes them rather possible to migrate from plastic into environment. Investigations revealed PAEs pollutants at high level in different compartments of our environment worldwide (Liu et al., 2010; Teil et al., 2006). Some PAEs and their metabolites possessed reproductive and developmental toxicities in laboratory animals (Saillenfait et al., 2008) and potential adverse effects on human health (Matsumoto et al., 2008). USEPA has defined 6 PAE congeners as priority contaminants, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), butylbenzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DnOP).

Guangzhou is a subtropical megacity in south China. With rapid development of economy in this region, large volume of garbage is produced. In Guangdong province in 2009, annual produced wastes amounted to 19,606,000 tons, more than 60% of which were disposed by landfill according to China Statistical Yearbook (National Bureau of Statistics of China, 2010). Before transported to landfill fields, garbage is first compressed into high dense blocks at garbage compression stations (GCS) to reduce handling and shipment cost as well as facilitates long-distance transportation. Considering that most GCSs are located near residential areas, it is necessary to investigate pollution levels and assess their impact on human health. However, little has been known about the contamination level of total suspended particles (TSP) and associated SVOCs emitted during garbage compression process. Moreover, effective measures should be taken to control the emitted contaminants and reduce human exposure to them especially at GCS, since many toxic SVOCs, such as PAHs, OCPs and PAEs, are adsorbed on the surface of respirable air particles, and some of components are known, or suspected, human carcinogens or endocrine disruptors.

Therefore, TSP and particle associated SVOCs possibly emitted during the garbage compress process such as PAHs, OCPs, and PAEs were investigated in this work, since the sources of garbage disposed at GCS can be very complex in composition. PAHs may come from road dust and cooking refuse, and diesel exhaust of the compressing machine (Kuusimäki et al., 2002). OCPs exist in food waste as fruits and vegetables. For example, Hellstrom et al. (2011) detected OCPs of 15 ng g⁻¹ in household waste. PAEs are rather abundant in various plastic wastes. Additionally, human exposure and health risk of selected SVOCs were assessed. For comparison, a residential area far away from the GCS was simultaneously investigated as control area (CA). Moreover, a custom-made integrated biotrickling filter (BTF)-photocatalytic (PC) reactor was employed to remove contaminants at GCS at pilot scale. Treatment effect was assessed by calculating removal efficiencies (REs) and risk levels of selected SVOCs before and after treatment.

2. Materials and method

2.1. Materials

Sixteen PAH standards specified by USEPA Methods 610 in a mixture solution of 2000 µg mL⁻¹ and 5 deuterated PAH surrogate standards in a mixture solution of 4000 µg mL⁻¹ were purchased from Supelco (Bellefonte, PA, USA). Internal standard for PAHs quantification, hexamethylbenzene (HMB) was from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Twenty OCP standards, two surrogate standards (2,4,5,6-tetrachloro-m-xylene and 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl) and one internal standard pentachloronitrobenzene were also from Supelco. Fifteen PAE standards mixture solution at 1000 µg mL⁻¹ and surrogate standards in a mixture solution of 500 µg mL⁻¹ were supplied by

AccuStandard (New Haven, USA). HMB was also used as internal standard for PAEs analysis. The detailed standard compounds involved were listed in Supplementary Materials (SM).

2.2. System setup and removal efficiency calculation

Fig. S1 demonstrates structure and parameters of the integrated BTF-PC reactor employed at pilot scale at GCS to eliminate airborne SVOCs emitted during garbage compression process. The emitted waste gas was first introduced into BTF from bottom to top, and then delivered into PC reactor. Finally, clean air was blown off through outlet into environment. The detailed information was in SM.

The RE of SVOCs was investigated by comparing concentrations of samples collected from inlet and outlet of the reactor simultaneously, and calculated according to Equation (1):

$$RE = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \times 100\% \quad (1)$$

where C_{inlet} and C_{outlet} represent inlet and outlet concentrations of SVOCs. REs of PAHs, OCPs and PAEs were studied respectively to evaluate SVOCs elimination capacity of integrated reactor.

2.3. Study site and sample collection

The study was conducted at a GCS in Tianhe district, Guangzhou from November 2010 to January 2011. With an area of 1200 m², the station is equipped with 4 compressing machines working 24 h a day to compress daily amount of 110–130 tons of garbage. The wastes mainly consist of household garbage. Considering that it takes time for BTF to grow biofilm and achieve its steady state, three sampling periods, day 15, 45, and 75, named 1st, 2nd and 3rd were designed. For each period, triplicates were collected at the inlet and outlet of the BTF-PC reactor and analyzed, respectively. A residential area in Wushan, Tianhe District was chosen as CA.

Two intelligent high volume air samplers (KC-1000, Qingdao Laoshan electronic instrument factory Co. Ltd., China) were placed at inlet and outlet of the integrated reactor to collect air samples before and after treatment. TSP (particles with aerodynamic diameters less than 100 µm) was blocked by glass fiber filters (GFF) and gas phase samples were absorbed by polyurethane foam (PUF) plugs. A total air volume of approximate 250 m³ was drawn for 8 h. After sampling, loaded GFFs were wrapped by pre-baked aluminum foil and PUFs were placed in solvent rinsed glass jars with aluminum foil lined lids. Both GFF and PUF samples were transport to laboratory and stored at -20 °C until extraction. TSP masses were determined by weighing equilibrated filters before and after sampling.

2.4. Sample extraction, cleanup and analysis

PUF plugs and GFFs were spiked with surrogate standards of OCPs, PAHs and PAEs, and Soxhlet extracted with 200 mL dichloromethane for 72 h. Activated copper pieces were added to the solvent before extraction to remove sulfur. The extract was rotary evaporated to approximate 2 mL and solvent was exchanged to hexane. The concentrated extract was cleaned and fractionated on a silica gel-aluminum oxide column according to reference (Zeng et al., 2008) and the detailed procedure was described in SM.

All samples were analyzed using an Agilent Technologies 7890A gas chromatography coupled with a 5975C mass spectrometer detector (GC-MSD) following documented methods (An et al., 2011b; Qiao et al., 2010; Zeng et al., 2008) with slight modification. A HP-5MS silica fused capillary column (30 m × 250 µm × 0.25 µm) was applied for three groups of analytes in this study. Detailed parameters were shown in SM.

2.5. Quality control

Procedure and spiked blank experiments were conducted triplicately for both GFF and PUF samples. PAHs recoveries ranged from 63.3 to 101% for GFF and from 54.9 to 102.3% for PUF, OCPs ranged from 62.6 to 133.8% and from 58.6 to 118.8% for GFF and PUF, respectively, and PAEs ranged from 57.1 to 127.8% for GFF and from 69.4 to 112.7% for PUF. Surrogate standards were added to all samples to monitor procedural recoveries. Quantification was performed using internal standard method based on a five-point calibration curve for individual component, and correlated coefficient for every target analyte is greater than 0.99. When sampling volume was set at 230 m³, the detection limits of individual PAHs, OCPs and PAEs fell into the range 0.001–0.006, 0.001–0.016 and 0.002–0.031 ng m⁻³, respectively.

3. Results and discussion

3.1. TSP contamination

TSP concentrations of inlet samples during different sampling periods at GCS and CA are illustrated in Fig. 1. The GCS was seriously contaminated, with TSP concentrations of 344.99 ± 205.47 , 855.84 ± 98.55 and 818.55 ± 428.41 $\mu\text{g m}^{-3}$ for 3 sampling periods. TSP concentrations during the 2nd and 3rd sampling periods were relatively higher, which are about 2 times of the 3rd grade value of Chinese ambient air quality control criteria (GB3095-1996). TSP concentration during the 1st period is slight lower, but still higher than the 2nd grade value. This is because the 1st sampling period fell on the 16th Asian Games held in Guangzhou. Great efforts had been made to improve environmental quality of the city. Additionally, the proportion of garbage compressed during night increased to reduce possible garbage rot, which also resulted in less waste compressed during day (samples collected). Comparatively, TSP concentration at CA was rather low, with a value of 119.99 ± 41.2 $\mu\text{g m}^{-3}$, which was almost equal to the 1st grade value of the criteria.

3.2. Concentrations and congener profiles of SVOCs

Gaseous and particle associated SVOCs concentrations at GCS and CA were shown in Fig. 2. $\sum_{16}\text{PAHs}$ concentrations ranged from

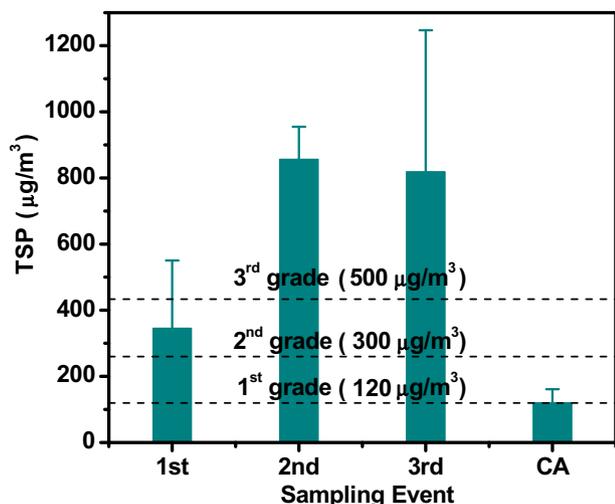


Fig. 1. Comparison of TSP concentrations between samples collected from GCS and CA (1st, 2nd and 3rd represent the 3 sampling periods and the 3 dashed lines mean the 3 grades of TSP concentration defined by Chinese ambient air quality control criteria GB3095-1996.).

58.773 to 68.84 ng m⁻³ in gas phase and from 6.489 to 17.291 ng m⁻³ in particulate phase for GCS air samples, vs. 15.101 and 7.659 ng m⁻³ in gas and particulate phase, respectively, for CA samples. Gaseous and particle-related $\sum_{16}\text{PAHs}$ concentrations at GCS were approximately 4 and 2 times higher than those at CA, indicating considerable PAHs pollution caused by waste compression.

$\sum_{20}\text{OCPs}$ concentrations at GCS were rather low (Fig. 3a), ranged from 4.181 to 5.550 ng m⁻³ for gas phase, and from 0.823 to 2.443 ng m⁻³ for particulate phase, yet much higher than those at CA which were 0.353 and 0.289 ng m⁻³ for gas and particle, respectively. The concentrations were much higher than those at an urban site in Guangzhou, which were 0.771 and 0.0462 ng m⁻³ in gas and particles (Yang et al., 2008a), but only slightly higher than those at another urban site in Guangzhou, which were 5.083 and 0.153 ng m⁻³ in gas and particulate phase (Li et al., 2007). Therefore, the waste compressing process can result in slight contamination to on-site air by OCPs.

$\sum_{15}\text{PAEs}$ concentrations ranged from 46.498 to 87.928 ng m⁻³ in gas phase and from 414.765 to 763.009 ng m⁻³ in particulate phase in GCS. GCS suffers severe PAEs contamination since $\sum_{15}\text{PAEs}$ concentrations at GCS were nearly 10 times above those at CA. Furthermore, PAEs concentrations at GCS in this work were apparently much higher than others. For instance, total atmospheric concentrations of 6 priority PAEs were 80 and 17 ng m⁻³ in gas and particles in Nanjing urban center (Wang et al., 2008), and 55.3 and 8.2 ng m⁻³ in gas and particulate phase at Paris, respectively (Teil et al., 2006). Though 15 congeners were investigated here, the 6 priority PAEs were predominant in most cases. This will be further discussed in the following parts.

Fig. 3 shows congener profiles of 3 groups of contaminants. For PAHs (Fig. 3b), compositions of gas and particle samples were rather different. More volatile PAHs with <4 aromatic rings such as naphthalene (Nap), fluorene (Flu), phenanthrene (Phe) and anthracene (Ant) were detected almost exclusively in gas phase, and less volatile ones with ≥ 4 rings such as benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IncdP) and benzo[g,h,i]perylene (BghiP) were primarily associated with particulate phase. Flu and pyrene (Pyr) were detected both in gas and particulate phases. And no significant differences in congener composition were observed between GCS and CA.

For OCPs (Fig. 3a), similar congener profiles existed between GCS and CA both in gas and particulate phases. Main OCPs species in gas were γ -HCH, δ -HCH, heptachlor, endosulfans and endrin aldehyde, whereas endosulfans, endrins and DDT dominated in particulate phase. Greater portions of β -HCH and dieldrin were found in gas phase at CA than GCS. Dieldrin, endosulfan II and endrin aldehyde accounted for most part of particulate phase at CA, which was different from the case at GCS. This may be caused by new input of some pesticides for agricultural purpose and termite control (Qiao et al., 2010), which assembled to GCS in forms of kitchen waste such as fruits, vegetables or discarded home decoration materials and finally emitted during compression process.

Fig. 3c illustrates PAEs congener composition in all samples. It is obvious that the priority PAEs were predominant both in gas and particulate phases. DMP and DEP were mainly found in gas phase whereas DnBP and diisobutyl phthalate (DiBP) were in both phases. Contrarily, most DEHP were associated with particles, with less than 10% of total gaseous PAEs at GCS. In fact, DiBP, DnBP and DEHP accounted for more than 97% of $\sum_{15}\text{PAEs}$ bound to particles. $\sum_{5}\text{PAEs}$ mentioned above contributed more than 98% of $\sum_{15}\text{PAEs}$ in all samples, which is consistent with a previous investigation about home dust in several cities of China (Guo and Kannan, 2011). Thus, other PAEs were neglectable.

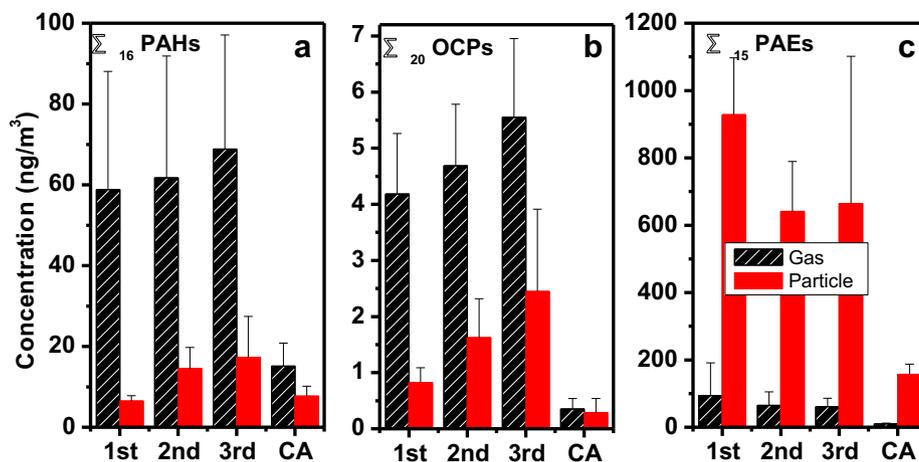


Fig. 2. Concentrations of target organic contaminants in air samples from GCS and CA.

3.3. Gas-particle partitioning

Gas-particle partitioning behavior plays an important role in the environmental fate of SVOCs such as their distribution, deposition, transport and transformation. Fig. S2 demonstrates partition profiles of PAHs, OCPs and PAEs between gas and particulate phases at GCS. For PAHs, more than 90% of small molecules (<4 rings) were mainly detected in gas phase, such as Nap, Ace, Flu and Ant, while PAHs with 4 rings were more particle-related. For example, about 80% of Flu and Pyr was as gas phase which was consistent with the findings of Arey et al. (1989) who detected less than 20% of Flu and Pyr in particles, and 80% of BaA and Chry were in particulate phase. Much larger molecules (>4 rings) such as BbF, BkF, BaP, IncdP, dibenzo[a,h]anthracene (DiB) and BghiP were primarily in particulate phase, with only less than 1% existed as vapor phase. Conclusively, light molecular PAHs preferred to exist in gas phase, while heavy ones were more likely to be particle associated. This is consistent with the fact that larger molecular PAHs were more lipophilic and tend to be adsorbed by organic matters (Ma et al., 2011).

Similar trends were found for OCPs. That is, most low molecular weight OCPs, such as HCHs, chlordanes, heptachlor and aldrin tended to distribute to vapor phase except heptachlor epoxide, which was only detected in particles. Dieldrin, DDE, endrin and endosulfan II were almost equally distributed between gas and particulate phases. When molecular weight further increased, OCPs species such as p,p'-DDD, endosulfur sulfate and p,p'-DDT were more likely to distribute to particles.

PAEs were mainly distributed to particulate phase with several exceptions. More than 85% of DMP, 50% of DEP and 100% bis(2-ethoxyethyl) phthalate (BEEP) and di-hexyl phthalate (DHP) were present as gas phase. The findings were rather different from other researches (Teil et al., 2006; Wang et al., 2008) indicating that PAEs were more abundant in vapor phase. This is because, during garbage compression, plenty of PAEs abundant particles were emitted by crush of various plastic, and immediately sampled by high-volume sampler before equilibrium of gas-particle partition can be reached. Thus high proportion of PAEs in particulate phase was reasonable.

The $\log K_p$ vs. $\log P_L^0$ model has been widely used to describe gas-particle partitioning of SVOCs (Cindoruk, 2011; Sitaras et al., 2004). K_p is partition coefficient ($\mu\text{g m}^{-3}$), defined as $(F/TSP)/A$, where F and A are particle and gas phase associated SVOCs concentrations (ng m^{-3}) respectively, and TSP is total suspended particle matter concentration ($\mu\text{g m}^{-3}$). P_L^0 is subcooled liquid vapor pressure (Pa). A linear relationship exists between $\log K_p$ and $\log P_L^0$ expressed as:

$$\log K_p = m_r \log P_L^0 + b_r \quad (2)$$

When at equilibrium, slope m_r should be close to -1 according to reference (Pankow, 1987, 1994). But it has been argued that a slope of -1 is not necessarily to describe equilibrium partitioning (Simcik et al., 1998). Differences in composition of particle matter may be responsible for the observed slopes deviating from -1 .

Fig. S3 shows plots of $\log K_p$ vs. $\log P_L^0$ for SVOCs measured in this study. Gas-particle partitioning of OCPs at CA was not shown since most of congeners were below detecting limits and K_p can not be calculated. Temperature-dependent P_L^0 values were calculated for all PAHs and most OCPs according to methods (Paasivirta et al., 1999), with temperature of 25, 15, 15 and 12 °C adopted for 1st, 2nd, 3rd and CA, respectively. Published P_L^0 of PAEs (25 °C) and several OCPs (20 °C) are adopted directly for lack of such temperature-dependent relations (Cindoruk, 2011). Some compounds were not included due to the lack of P_L^0 values. Parameters used are given in Table S1.

As shown in Fig. S3a, good linear correlations were obtained for PAHs, with R^2 values ranged from 0.7897 to 0.8958 and slope values ranged from -0.5558 to -0.5962 for different sampling periods. The deviation of m_r values from -1 may suggest disequilibrium between gas and particulate phases, which may be caused by various factors including changes of temperature in sampling duration, reactions of vapor phase PAHs in atmosphere and emissions by local sources (Sitaras et al., 2004). The presence of non-exchangeable fractions for more volatile PAHs may also be responsible for the shallower slope than -1 . Additionally, similar results at GCS and CA may indicate that garbage compressing process is probably not the major source of atmospheric PAHs.

Comparatively, relatively poor linear correlations were obtained in all samples for OCPs, with R^2 in the range 0.245–0.4558. Slope m_r ranged from -0.4467 to -0.6832 , significantly greater than -1 , which was assumed to reflect the disequilibrium state of OCPs partitioning between gas and particulate phases. As mentioned, this may be related to new input of several OCPs still in use in this region, such as lindane, heptachlor, endosulfans and dicofol for agricultural and mite control usage. New input in various patterns as vapor, droplets or dry particles may disrupt the equilibrium established between gas and particulate phases, especially when there was no enough time for the partitioning to occur when compressors were working at GCS. And $\log P_L^0$ values adopted at different temperatures from reality may influence, too.

Less PAEs target compounds were involved in the partition model due to lack of $\log P_L^0$ values. The slope factors acquired were

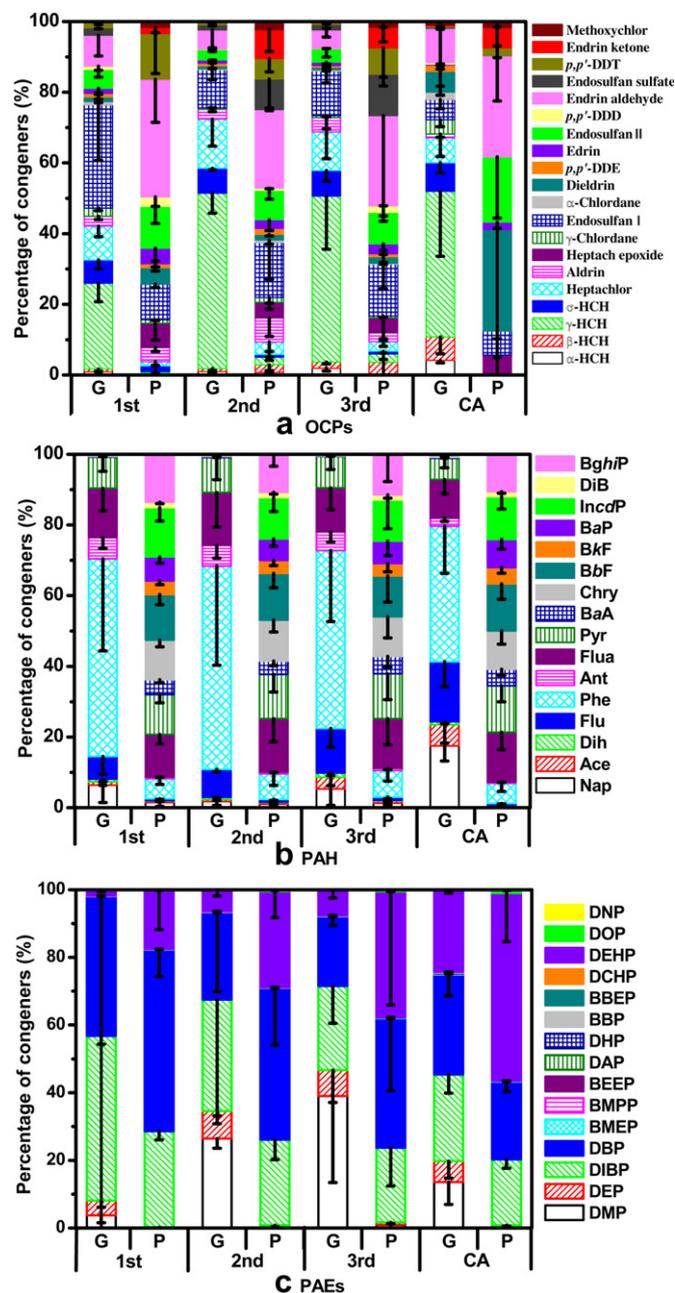


Fig. 3. Congener profiles of OCPs (a), PAHs (b), and PAEs (c) in gas (G) and particulate (P) phases.

within the range of -0.4609 to -0.6913 , with R^2 ranged 0.6919 – 0.7823 . The slope shallower than -1 may indicate that distribution between gas and particles of investigated PAEs occurred under non-equilibrium conditions. It can be attributed to the emission of local sources, especially at GCS, where large amounts of plastic waste were collected and compressed. PAEs may release into environment both as vapor and particulates.

3.4. Occupational health risk at GCS

Cancer risk for the workers at GCS due to inhalation of PAHs was assessed based on BaP Toxic equivalency factors (TEFs) method (Petry et al., 1996). BaP was the most carcinogenic PAHs and assigned the unit TEF, and carcinogenic potencies of other PAHs

were determined by TEFs relative to BaP (Table S2). BaP equivalency (BaP_{eq}) was calculated by multiplying the concentration with TEF. A unit risk of 7×10^{-2} per $\mu\text{g m}^{-3}$ BaP_{eq} for 25-year occupational exposure was used to evaluate health risk due to PAHs exposure (Petry et al., 1996).

Non-cancer risk from OCPs inhalation was assessed based on average daily intake (ADI, $\text{ng kg}^{-1} \text{d}^{-1}$) and reference dose (RfD, $\text{mg kg}^{-1} \text{d}^{-1}$) recommended by USEPA, and cancer risk was calculated via inhalation unit risk (IUR, per $\mu\text{g m}^{-3}$) from USEPA (An et al., 2011a; Qiao et al., 2010):

$$ADI = C \times \frac{T}{24} \times \frac{IR}{BW} \quad (3)$$

$$\text{Non-cancer risk} = \sum (ADI/RfD) \quad (4)$$

$$\text{Cancer risk} = \sum (C \times IUR) \quad (5)$$

where C is average concentrations of contaminants (ng m^{-3}); T is the time spent at target region every day (h), and 24 h was used to consider people at GCS and CA since they spend a whole day working and living in the same place; IR is the average inhalation rate, $20 \text{ m}^3 \text{d}^{-1}$ for Chinese adults adopted (An et al., 2011a); BW represents body weight, where an average of 70 kg was used. RfD and IUR of OCPs were listed in Table S3. Some data were obtained from other agencies such as Agency for Toxic Substances and Disease Registry (ATSDR) and California Environmental Protection Agency (Cal/EPA) for unavailability at USEPA. For OCPs 19 and 12 congeners were assessed for non-cancer and cancer risk, respectively, and α and γ isomers of chlordane were processed as chlordane with the same specie, and so did of endosulfan. For PAEs, only DEHP was recognized as probable carcinogen by USEPA, so only non-cancer risk was evaluated for PAEs following the same procedure as OCPs. But for PAEs, 7 species in total were included to consider the risk assessment.

Significant differences existed between the profiles of PAHs concentrations and corresponding BaP_{eq} values (Table S4). $\sum_{16}\text{PAHs}$ concentration in gas was 63.679 ng m^{-3} with total (gas plus particle) value of 76.906 ng m^{-3} , while the gaseous concentration of 7 carcinogenic congeners ($\sum_{7\text{Car}}\text{PAHs}$) was only 0.472 ng m^{-3} against total of 7.280 ng m^{-3} . When concentrations were converted to BaP_{eq} , the proportion of particle-associated $\sum_{16}\text{PAHs}$ elevated drastically, with total BaP_{eq} of 1.4913 ng m^{-3} in particle and 1.6128 ng m^{-3} in total. This is because carcinogenic PAHs are generally high molecular weight particle-bound congeners with much larger TEFs than non-carcinogenic PAHs. The lifetime lung cancer risks at GCS and CA were 1.13×10^{-4} and 7.22×10^{-5} , respectively. They were much lower than the significant risk level (10^{-3} , means acceptable) (Rodricks et al., 1987). However, atmospheric PAHs measured might underestimate at least by a factor of 2 using conventional sampler, compared with sampler equipped with a denuder tube for ozone trap upstream from the filter (Goriaux et al., 2006). Additionally, high ozone concentration was produced and partial atmospheric PAHs were degraded by photocatalysis at GCS. Thus, the risk of PAHs exposure should not be overlooked at GCS.

Non-cancer and cancer risks of OCPs in gas and particulate phases at GCS were all higher than those at CA (Fig. 4). Gas phase possessed larger parts in both cancer and non-cancer risks than particulate phase at GCS, and vice versa at CA, which is due to the differences in congener profiles. For non-cancer risk, γ -HCH, aldrin and heptachlor epoxide dominated at GCS, whereas heptachlor epoxide and dieldrin were major congeners at CA. Aldrin accounted for much larger proportion in gas at GCS than CA.

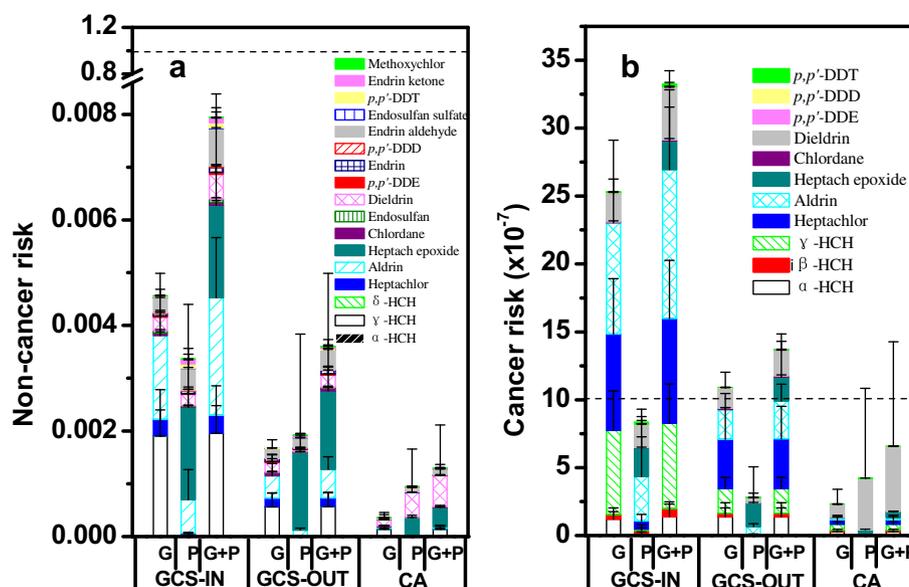


Fig. 4. Comparison of non-carcinogenic and carcinogenic risks of OCPs congeners at GCS and CA.

Additionally, RfD for aldrin was relatively lower than other congeners for its severe developmental, endocrine and neurological toxicity, which resulted in higher risk of aldrin at GCS. For cancer risk, main OCPs congeners were γ -HCH, heptachlor, aldrin and dieldrin at GCS, while was dieldrin at CA. Aldrin again, is responsible for different risk distribution patterns in gas and particle between GCS and CA. Non-cancer and cancer risks due to OCPs exposure at GCS were approximately 6 and 5 times higher than those at CA, respectively. However, non-cancer risks were far below unit hazard, meaning rather low chronic hazard risk in both sites due to OCPs exposure; Carcinogenic risks were near one per million which is a relatively low risk level recommended by USEPA, indicating that cancer risk caused by OCPs exposure was acceptable (less than 10^{-3}).

For PAEs, non-cancer risk level at GCS was 4.58×10^{-3} , nearly 3 times higher than that at CA (Table 1). Most of the risk was posed by particulate rather than gas phase, with DiBP, DnBP and DEHP as the dominant congeners, which is consistent with PAE congener profiles. Relatively lower risk of PAEs may be due to relatively higher RfD of PAEs than other toxicants. The RfD of PAEs were derived long time ago by the USEPA before there was much consideration of endocrine disruption effects of phthalates, so it is probable that the risk was underestimated. Additionally, the combined toxic effects of investigated SVOCs were not considered

Table 1
Calculation of non-cancer risk of available PAEs congeners.

	RfD ^a (mg kg ⁻¹ d ⁻¹)	Non-cancer risk								
		GCS-untreated			GCS-treated			CA		
		G	P	T	G	P	T	G	P	T
DMP	0.8 ^b	5.62E-06	1.07E-06	6.69E-06	1.55E-06	9.45E-08	1.64E-06	4.68E-07	1.42E-07	6.10E-07
DEP	0.8	1.67E-6	1.38E-6	3.04E-6	8.63E-7	4.85E-8	9.12E-7	2.13E-7	3.04E-7	5.17E-7
DiBP	0.1 ^b	7.48E-5	5.32E-4	6.07E-4	2.84E-4	9.48E-5	3.78E-4	7.06E-6	8.74E-5	9.45E-5
DnBP	0.1	6.21E-5	9.65E-4	1.03E-3	1.56E-4	7.82E-5	2.34E-4	8.18E-6	1.03E-4	1.11E-4
BBP	0.2	1.46E-7	7.44E-7	8.90E-7	2.22E-7	5.02E-7	7.24E-7	2.17E-8	1.49E-7	1.71E-7
DEHP	0.02	5.09E-5	2.88E-3	2.93E-3	7.46E-5	1.15E-3	1.22E-3	3.33E-5	1.24E-3	1.28E-3
DOP	0.4 ^c	6.36E-09	1.36E-06	1.37E-06	1.14E-08	9.85E-07	9.96E-07	3.07E-09	1.02E-06	1.02E-06
Σ 7PAEs		1.95E-04	4.38E-03	4.58E-03	5.16E-04	1.32E-03	1.84E-03	4.93E-05	1.44E-03	1.49E-03

Notes: G-gas phase, P-particulate phase, T-total = G + P, Car-carcinogenic.

^a Data obtained from USEPA's Integrated Risk Information System (IRIS).

^b Data of DEP adopted for structural analogy: data of DnBP was adopted.

^c Data obtained from Agency for Toxic Substances and Disease Registry (ATSDR).

in this study. Thus, true hazard risk may be more severe than presented above.

3.5. Removal efficiency and occupational health risk of SVOCs after treatment

As mentioned, an integrated BTF-PC reactor was employed to eliminate airborne SVOCs emitted during garbage compression process. The inlet and outlet total concentrations of each category of SVOCs were graphed in Fig. S4. Outlet concentrations decreased with increased operation time of reactor, except Σ_{15} PAEs (caused by extremely high DEHP level). This may be caused by possible contamination during sampling. When DEHP was excluded, similar trend was obtained as other SVOCs. REs were relatively low on day 15 (10.65–22.59%) (Table 2), which was due to low removal capacity of BTF since biofilm was still in the forming stage (An et al., 2010). On day 45, REs were improved to about 2 times of day 15, because bacteria had been acclimating to the waste gas and biofilm was further developed. On day 75, the biofilm had been developed successfully (Wan et al., 2011), even higher REs were achieved. Noting that 71.51% of total OCPs were eliminated on day 45 and RE was not further elevated on day 75. It was likely that OCPs were more bioavailable for microorganisms employed than other group SVOCs. High level DEHP in outlet samples on day 45 decreased

Table 2
Removal efficiencies of total contaminants by bio-photocatalytic coupled facility.

Contaminants	Removal efficiency		
	1st	2nd	3rd
16 PAHs	21.50%	40.45%	60.18%
20 OCPs	22.59%	71.51%	70.89%
15 PAEs	10.65%	–	63.20%
14 PAEs (without DEHP)	12.57%	25.60%	57.96%

overall PAEs RE drastically (not shown), and RE of the rest 14 PAEs was up to 25.60%. Thus the conclusion may be drawn that PC reactor alone showed relatively poor treatment capability to target SVOCs, but when combined with BTF, RE was greatly improved, which may be due to the synergy effect of them.

Health risk after treatment was also evaluated. For PAHs (Table S4), the outlet $\sum_{16}\text{PAHs}$ concentration was reduced to 34.295 ng m^{-3} on day 75, which is about half of the average inlet concentration of all the 3 periods. And $\sum_{7\text{Car.}}\text{PAHs}$ concentration was reduced to 4.022 ng m^{-3} , which is even lower than that at CA. BaP_{eq} value decreased to 0.7558 ng m^{-3} for $\sum_{16}\text{PAHs}$ and to 0.7172 ng m^{-3} for $\sum_{7\text{Car.}}\text{PAHs}$, both of which were lower than those of CA. The cancer risk after treatment for $\sum_{16}\text{PAHs}$ and $\sum_{7\text{Car.}}\text{PAHs}$ were approximately half of the levels before treatment.

For OCPs (Fig. 4), both non-cancer and cancer risks were also significantly reduced after treatment. Non-cancer and cancer risks were 3.6×10^{-3} and 1.4×10^{-6} , respectively, which were lower than or near benchmark risk levels. Thus, OCPs in the treated air samples posed less hazardous to people's health. Similar as inlet samples, cancer risk was mainly due to inhalation of gaseous-related HCH, heptachlor and aldrin, while non-cancer risk was more related to particle ingestion, with heptachlor epoxide as the dominant congener.

Total risk due to PAEs inhalation (Table 1) decreased to 1.84×10^{-3} after treatment, with almost 60% removed. Main PAEs species such as DiBP, DnBP and DEHP were all greatly eliminated by the integrated reactor, and their hazard quotients were approaching the levels at CA, suggesting that PAEs pollution at GCS was effectively eliminated and detoxified.

4. Conclusions

The possible SVOCs air pollution caused by garbage compressing process was investigated at GCS. The most abundant contaminants were PAEs, followed by PAHs and OCPs. DMP, DEP, DiBP, DnBP and DEHP were dominant congeners of PAEs fractions. Low molecular weight PAHs with higher vapor pressure were mainly found in gas phase. γ -HCH, endosulfans and endrins were primary OCPs species. Partitioning of SVOCs between the gas and particulate phases was modeled using $\log K_p - \log P_L^0$ model, and good correlations were acquired. Non-equilibrium state existed for the partitioning. Cancer risk posed by PAHs inhalation was acceptable, but it may be minimized from the real level. Cancer and non-cancer risks due to OCPs exposure were also acceptable. PAEs exposure risk may be underestimated due to relatively higher RfD. All investigated airborne SVOCs could be greatly eliminated and detoxified by the integrated BTF-PC reactor at pilot scale.

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.atmosenv.2012.06.027>.

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