



Pollution profiles, health risk of VOCs and biohazards emitted from municipal solid waste transfer station and elimination by an integrated biological-photocatalytic flow system: A pilot-scale investigation

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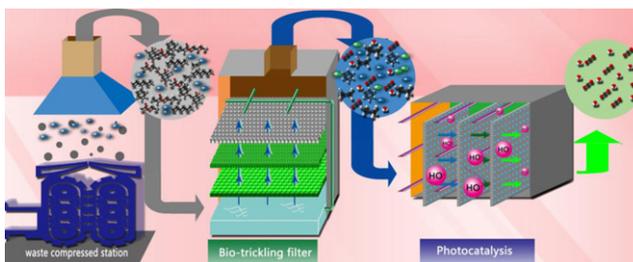
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HIGHLIGHTS

- ▶ VOCs and biohazards emitted during garbage compressing process were monitored.
- ▶ BTF-PC integrated reactor was employed for VOCs and biohazards removal.
- ▶ Health risk of target VOCs and biohazards were assessed before and after treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Volatile organic compounds (VOCs) and biohazards air pollution in municipal solid waste transfer station were investigated. As compressor working, the concentrations of almost all quantified 14 VOCs ($0.32\text{--}306.03\ \mu\text{g m}^{-3}$) were much higher than those as compressor off ($0\text{--}13.31\ \mu\text{g m}^{-3}$). Comparatively, only 3 VOCs with extremely low concentrations could be detected at control area. Total microorganism was $7567\ \text{CFU m}^{-3}$ as compressor working, which was 1.14 and 6.22 times higher than that of compressor off and control area, respectively. Bacteria were the most abundant microorganism at all three sampling places. At pilot-scale, during whole 60-day treatment, for VOCs, the average removal efficiencies were over 92% after biotrickling filter-photocatalytic (BTF-PC) treatment. Although non-cancer and cancer risks of some VOCs were over the concern level before treatment, almost all VOCs were removed substantially and both potential risks were below the concern after BTF-PC treatment. Additionally, biohazard concentrations decreased dramatically and air quality was purified from polluted to cleanness after PC treatment. All results demonstrated that the integrated technology possessed high removal capacity and long stability for the removal of VOCs and biohazards at a pilot scale.

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1. Introduction

There is an ever-increasing production of municipal solid wastes (MSW) worldwide with the rapid development of world economics. For instance, MSW production has increased

from 150 to 250 million tons from 1980 to 2010 in America (<http://www.epa.gov/osw/nonhaz/municipal/>). China also produced more than 150 million tons of MSW each year, and it increased annually with a rate of 8–10% [1]. Generally, MSW without being recycled are either landfilled or burned to eliminate or minimize adverse impact on surrounding environment. However, such massive MSW need to be compressed to high density compaction within city areas before transfer to further dispose site. Although this can reduce handling and shipment cost as well as

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facilitate long-distance transportation, volatile organic compounds (VOCs) and biohazards are produced inevitably during the MSW compressing process at transfer stations [2,3]. As well known, chronic health effects such as non-cancer or cancer of VOCs could be resulted from the inhalation and long-time exposure of polluted air [2,3]. Furthermore, inhalation of airborne biological pollutants is also particularly threatening due to the continuously increasing resistance to microorganisms against antibiotics [4]. In addition, as most of transfer stations were built within communities, an increasing concern of adverse impact of odorous VOCs emissions on human health have voiced in many communities.

Consequently, to reduce pollutant concentration and minimize odors to acceptable level, proper treatment technology is highly desirable at transfer stations, especially in communities and cities with high density population. Therefore, various techniques were employed for this purpose [5,6]. However, some conventional physico-chemical techniques, such as masking, incineration, absorption and adsorption are often unsatisfactory because these hazards may still not be fully destroyed [6]. Comparatively, biological treatment has been validated as a promising technology for odoriferous VOCs removal from gas due to its relatively low investment and operating costs, small energy requirements as well as efficient conversion of biodegradable contaminants to harmless end-products [7–9]. A number of VOCs were found to be biologically degraded using different bioreactors, for example synthetic H₂S and VOCs mixture (butanone, toluene and α -pinene) by a biofilter and an air diffusion bioreactor [10], trichloroethylene and toluene mixture by a hollow fiber membrane reactor [11], single, binary and ternary mixture gas of ethanethiol, dimethyl disulfide and thioanisole by a biotrickling filter (BTF) [12,13]. Few substances are still unable to be biologically degraded, although this technology is relatively cheap and reliable process. On the other hand, photocatalytic (PC) technology can generate powerful but not selective oxidant species, such as holes and active oxygen species, which can not only readily oxidize a wide spectrum of organic gas [14–16], but also inactivate the pathogens effectively [17–19]. Nevertheless, there are several scenarios that make them economically disadvantageous. Therefore, a better solution would be to carefully combine the biological with PC technologies to achieve a synergistic effect within reasonable economical limits.

Integration of biological with PC processes (post or pre-treatment) has gained more interest recently for waste air treatment. For instance, the degradation efficiencies of gaseous ethylbenzene [20] and styrene [21] were enhanced in the PC-biofiltration hybrid system. The enhancement of PC pre-treatment is maybe due to the reduction of pollutant concentrations and the production of more oxidized compounds, which are in most cases more easily biodegradable than the former ones and then relieve the inhibitory effect of microorganisms for degradation of toxic compounds. However, if original waste gas contains a considerable amount of biodegradable compounds, the pre-oxidation step obviously will not lead to a significant improvement of biodegradability; that is, it will only cause unnecessary consumption of chemicals [22]. Also, if PC pre-treatment can increase the biodegradability of the recalcitrant compounds, some strains isolated and used for the degradation of specific substrates might not do the degradation job because of the difference of substrates.

In addition, people may also worry about the risk of microbes used for organics degradation as well as emitted ones during MSW compression process. In such cases, a biological pre-treatment followed by a PC process may be more useful for these biohazards inactivation. However, despite the well-known potential of the integrated biological-PC technology for waste gas treatment, there is very limited information concerning the treatment of real waste gas polluted with both VOCs and biohazards by the integrated biological-PC technology, even not to say at pilot scale.

Hence, in this work, the components and concentrations of VOCs and biohazards emitted from transfer station during the compressor working and off were firstly analyzed, and then a flow-through integrated BTF-PC reactor was developed to treat this real waste gas containing VOCs and biohazards at a pilot scale. The removal efficiencies (REs) of individual VOCs were characterized and the potential risk of VOCs exposure by inhalation to people working in the transfer station was evaluated before and after by both single and combined BTF-PC technologies during whole 60-day operation. Furthermore, photocatalytic disinfection of airborne biohazards was also investigated.

2. Materials and method

2.1. Materials, microorganisms and culture medium

The commercial mixed microorganisms, B350 and B110 were purchased from Bio-System Co. USA; effective microorganism (EM) was obtained from Guangzhou yiooo Biological Technology Co., Ltd. *Lysinibacillus sphaericus* RG-1, capable of degradation of ethanethiol as well as other S-containing organics was isolated from activated sludge in our laboratory [23]. All other reagents were of analytical grade and obtained from Guangzhou Chemical Reagent Co., Inc. China. The nutrient medium for different microorganism cultivation was supplied in Supporting Information.

2.2. Experimental set-up

All experiments were performed in a large-scale custom-made stainless steel waste gas treatment system [24]. In brief, the system consisted of two zones: a BTF combined with a bioscrubber and a PC reactor. The bioscrubber and the BTF were actually combined together with the same liquid phase nutrient solution at the base of the bioreactor, and thus the removal efficiencies of the waste gas by BTF referred to the combined removal efficiencies of both bioreactors. The BTF was packed to a total height of 1500 mm with each 1/3 height of large ceramic pall rings, small ceramic raschig rings, mixture of multi-faceted hollow plastic balls and ceramic particles (Transing Chemical Packing CO., LTD, Jiangxi, China) from bottom to up. Their characteristics were listed in Table S1. For PC reactor, eight pieces of microporous nickel foam (Guangzhou Nonferrous Metal Research Institute, China) were coated with TiO₂ (Degussa P25) and installed vertically at the same distance used as catalyst (the detailed procedure to coat TiO₂ onto the nickel foam was provided in Supporting Information). Eight UV-lamp arrays (each array consisted of 8 UV lamps (ZY30S19W, Guangdong Cnlight CO., Ltd., China)) were installed parallelly and alternately between nickel foam used as the illumination source. The BTF and PC reactor were connected with stainless steel tubes.

2.3. Operating conditions

All experiments were conducted at a MSW compression transfer station, Tianhe district, Guangzhou, China, from November 2010 to March 2011. With an area of 1200 m², the station is equipped with 4 compressors working 24 h d⁻¹ to extrude an amount of 110–130 tons of wastes each day, which mainly comes from household waste, and consist of everyday items human use and then throw away, such as food scraps, waste papers, plastics, glasses, as well as construction and demolition debris, and so on. Three sampling periods, day 1, 30, and 60 were designed. For each period, triplicates were collected at the inlet and outlet of BTF, PC as well as the combined BTF-PC reactor and analyzed. A residential area in Wushan, Tianhe District was chosen as control area (CA).

Waste gas emitted from compressor waste feed inlet was continuously pumped to the reactor by an air-pump (Guangdong

Risheng Group. CO., Ltd, China) in an order of the biological reactor (up-flow counter-current mode) and then PC reactor (down-flow mode). The flow rate of the waste gas was controlled with a flow meter at about $3000 \text{ m}^3 \text{ h}^{-1}$, corresponding to a residence time of 7.2 and 10.8 s in the BTF and PC reactor, respectively.

For the BTF start-up, the microorganisms including B350, B110 and RG-1 were cultured (grown at 30°C for 24 h by constant agitation (120 rpm) under aerobic conditions) first and then seeded on the packing materials together with EM. The nutrient medium was introduced from the top of BTF with a rate of $2.6 \text{ m}^3 \text{ h}^{-1}$ for 20 min each time, six times a day. To shorten the start-up phase, waste gas ($3000 \text{ m}^3 \text{ h}^{-1}$) was continuously fed into BTF and the cultured mixture microorganisms (2 L d^{-1}) were added into the reservoir of the nutrient solution for BTF.

The PC degradation of waste gas was carried out after BTF treatment. Once the waste gas flowed through the PC reactor, it was irradiated with the UV light, signaling the start of PC degradation.

The VOCs and biohazards were collected before and after treatment to evaluate the removal efficiencies. For VOCs, samples were collected using 2.7-L stainless steel canisters (ENTECH Instruments Inc, Silonite™) which were pre-cleaned five times using high-purity nitrogen and pre-evacuated by a canister cleaner before sampling. The biohazards were collected using six-stage culturable microorganism FA-1 cascade sampler (Applied Technical Institute of Liaoyang, China) with a flow rate of 28.3 L min^{-1} (detailed information showed in Table S2). For each sampling, the FA-1 sampler was loaded with petri dishes (9.0 cm) containing different nutrient agars (Tables S3–S5) to culture bacteria, molds and actinomycetes, respectively. The sampling duration was 10 min for each sample. Exposed culture dishes were incubated at 37°C for 48 h, at 28°C for 72 h, and at 28°C for 120 h for bacteria, molds and actinomycetes, respectively.

2.4. Analysis

The qualitative and quantitative analysis of VOCs were performed by a 7890A gas chromatography coupled with a 5975C mass spectrometer detector (GC-MSD, Agilent Technologies, USA) with an Entech 7100 Preconcentrator. A HP-5MS capillary column ($60 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$, Agilent Technology, USA) was used with helium as carrier gas at a rate of 1.2 mL min^{-1} . The temperature of the injector and detector were 200 and 230°C , respectively. The GC oven temperature was programmed initially 35°C holding for 5 min, and increasing to 150°C at a rate of 5°C min^{-1} , then to 250°C at $15^\circ\text{C min}^{-1}$ and holding for 2 min. The MSD was run in full scan mode with $m/z = 45\text{--}260$, and the injection volume is 150 mL . 65 VOCs standards in a mixture gas of 1.0 ppm were purchased for the determination of VOCs from Linde Spectra Environmental Gases (Alpha, NJ). Target compounds were identified according to their retention times and mass spectra, and quantified by multi-point external calibration method (see the Supporting Information). All calibrating reference standard points were run in duplicate at a minimum. All VOCs calibration had good dose–response correlation ($R^2 > 0.9914$) within the concentration range investigated.

For the evaluation of PC inactivation efficiencies of biohazards, colony forming units (CFU) on each plate were counted, and concentrations of sampler were expressed as CFU per cubic meter of air (CFU m^{-3}). CFU m^{-3} was calculated by Eq. (1) and PC inactivation efficiency of biohazards was calculated by Eq. (2).

$$P = N \times \frac{1000}{QT} \quad (1)$$

$$\text{inactivation efficiency} = \frac{P_0 - P_e}{P_0} \times 100 \quad (2)$$

where P is the airborne bacterial concentration (CFU m^{-3}); N is the total colonies of each stage; T is the sampling duration (10 min); Q represents the airflow rate (28.3 L min^{-1}); P_0 and P_e are the inlet and outlet biohazards concentration (CFU m^{-3}), respectively.

2.5. Risk assessment

Cancer and non-cancer risks of exposure to VOCs through inhalation were assessed according to the standard methodology from US Environmental Protection Agency (USEPA). The non-cancer risk was calculated by dividing each compound's daily concentration (C_i , expressed in $\mu\text{g m}^{-3}$) by its reference concentration (RfC_i , in $\mu\text{g m}^{-3}$), regarded as hazard ratio (HR), as shown in Eq. (3). The reference concentrations for each VOC were taken from the reference [25]. Lifetime cancer risk (LCR) was calculated by multiplying each compound's unit risk (UR) values, as shown in Eq. (4), the unit risk data were obtained from USEPA.

$$\text{HR}_i = \frac{C_i}{RfC_i} \quad (3)$$

$$\text{LCR} = \sum C_i \times \text{UR}_i \quad (4)$$

3. Results and discussion

3.1. Pollution profiles of VOCs and biohazards in transfer station

VOCs can emit as intermediates or final products of decomposition of organic matter and organic chemicals present in MSW. In this paper, 14 dominant VOCs were selected as the main pollution species as well as the treated targets in the analyzed samples in MSW although many other VOCs can be also detected during the treatment of this kind waste [26]. The compositions and concentrations of VOCs in transfer station during compressor working and off are listed in Table 1. The concentrations of almost all VOCs were detected and 14 VOCs were found much higher than others and then quantified during the compressor working than those during compressor off, which were ranged from 0 (dichloroethane and tetrachloroethylene) to $13.31 \mu\text{g m}^{-3}$ (ethyl acetate). Comparatively, the concentrations of corresponding VOCs at CA were extremely low, and only benzene ($0.01 \mu\text{g m}^{-3}$), toluene ($0.01 \mu\text{g m}^{-3}$), and trichloromethane ($0.10 \mu\text{g m}^{-3}$) could be detected. During compressor working, ethyl acetate was found as the most abundant species ($306.03 \mu\text{g m}^{-3}$, accounting for 53.86% of the total VOCs), followed by the aromatics ($204.23 \mu\text{g m}^{-3}$, accounting for 35.94%), including benzene, toluene, xylene, ethylbenzene, trimethylbenzene, and 4-ethyltoluene (Fig. S1a). The other two components, chlorinated compounds and alkanes, were minor and altogether constituted about 10% of total VOCs released. As compressor off time, the predominance VOCs was aromatics with adding up to $20.82 \mu\text{g m}^{-3}$ (accounted for 52.34% of total VOCs), and followed with ethyl acetate ($13.31 \mu\text{g m}^{-3}$, accounting for 33.46%) (Fig. S1b). Like compressor working time, the concentrations of both chlorinated compounds and alkanes were also very low during compressor off time. The predominance of ethyl acetate was common, since the esters were normally observed during the initial decomposition of food waste [27]. The source of aromatic compounds included solvents, paints, and food additives in MSWs [28] and petroleum combustion [29] by compressors as well as the motor vehicles near transfer station. Additionally, similar with this work, a large portion of aromatics was also detected in a vicinity of a municipal waste organic fraction treatment plant in Spain [2] and at solid waste disposal sites in Japan [30], though chlorinated compound concentrations were very low [30]. The different portions of various VOC species between compressor working and off might be the difference of treatment process. As reported, some VOCs are

Table 1
VOCs profile at the MSW compression transfer station during compressor working and off as well as at control area.

Compounds		Concentration ($\mu\text{g m}^{-3}$)		
		Compressor off	Compressor working	Control area
Aromatics	Benzene	1.67	2.25	0.01
	Toluene	5.89	122.39	0.01
	m,p-Xylene	2.70	26.74	0
	o-Xylene	1.74	10.07	0
	Ethylbenzene	3.58	30.37	0
	Trimethylbenzene	3.40	4.29	0
	4-Ethyltoluene	1.84	8.12	0
Chlorinated	Dichloromethane	1.17	6.18	0
	Trichloromethane	0.66	0.32	0.10
	Dichloroethane	0	26.35	0
	Dichloropropane	0.95	1.88	0
	Tetrachloroethylene	0	0.37	0
Alkanes	Hexane	2.87	22.83	0
Ester	Ethyl acetate	13.31	306.03	0

present in waste gas as it is dropped off from the trucks. Shredding of waste increases the surface area of waste and exposes more surfaces to atmosphere, allowing these compounds to volatilize rapidly. Therefore, the newly shredded material has some of highest average concentrations of VOCs as compared to other sample types [31].

In addition, airborne microorganism concentrations on different particle sized fractions were illustrated in Fig. S2. It is well known that most of airborne microorganisms are absorbed onto particulate matter, and deposition behavior of inhaled particulate matter in human respiratory tract strongly depends on particle size [32]. Deposited and long-term retention study of ultrafine particles in human lung has been demonstrated previously [33]. From the figure, it can be seen that with the decrease of particle size, total microorganism distributions displayed differently for three samples. That is, microorganism concentrations decrease gradually during compressor working, while they increase firstly and then decrease for samples during compressor off and at CA though their values and specific trend were different. It is worth noting that for the finest particle (0.65–1.1 μm), total microorganism concentration during compressor working was lower than that of compressor off, indicating that biological contaminants still posed significant health risk to neighborhood even at compressor off time.

The mean total concentrations of airborne microorganisms on different particle sized fractions during compressor working and off as well as at control area are shown in Fig. 1. During compressor

working, total microorganism concentration was 7567 CFU m^{-3} , approximately 1.14 and 6.22 times higher than that of compressor off and CA, respectively. The culturable bacteria accounted for the vast majority of microorganisms for all three samples (Fig. S3). According to the Air Quality Standards of China [34], bacterial concentrations during both compressor working and off were grouped as level IV (polluted), but it was safe at CA. Actinomycetes (a group of Gram-positive bacteria) which can cause disease in humans, were also detected separately, and the pollution level during compressor working was about 11.5 and 34.6 times heavier than that of compressor off and CA, respectively. For mold, its concentration did not exceed standard for all three samples, but its pollution was indeed much heavier during compressor working than that of compressor off and CA.

3.2. Removal efficiency assessment of VOCs and biohazards

3.2.1. Removal of VOCs by single photocatalytic technology

During the start-up stage of BTF (biofilm formation), VOCs removal was only performed in PC reactor during compressor working and off time (Fig. S4). PC REs of VOCs were much higher during compressor working (ranging from 26.6% (benzene) to 91.8% (toluene), average 72.3%) than those during compressor off (ranging from 0% (dichloroethane and tetrachloroethylene) to 100% (hexane), average 48.4%) with several exceptions, because the inlet concentrations of most VOCs were much lower during compressor off. This result is consistent with reference finding that PC oxidation rate of methyl tertiary-butyl ether increases linearly at very low concentrations [35]. This is due to that before the pollutants were photocatalytically degraded, they need to be adsorbed firstly onto photocatalyst surface sites [14] and the efficient adsorption of toxic substances onto TiO_2 is an important factor determining its degradation ability at very low concentrations [14,36]. In addition, the PC REs of dichloroethane and tetrachloroethylene were not demonstrated since they could not be detected at the inlet during compressor off. The reason why RE of hexane was higher during the compressor off (100%) than that of compressor working (61.9%) was probably due to its extremely high inlet concentration during compressor working. Low RE of benzene was probably due to that benzene was produced as an intermediate from other large molecular weight aromatics, like toluene during PC treatment [37–39].

3.2.2. Removal of VOCs by BTF-PC technology

After 30-day of start-up of biological reactor [8], REs of VOCs were measured by combination BTF-PC as well as single BTF reactor on day 30 and 60 (Fig. 2). On day 30, average REs of VOCs

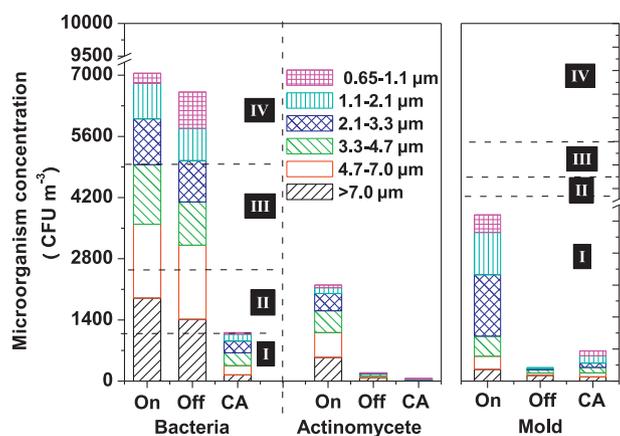


Fig. 1. The airborne microorganism concentrations at MSW compression transfer station during compressor working and off as well as at control area (CA). (I): Cleanliness; (II) lightly cleanliness; (III): lightly polluted; (IV): polluted.

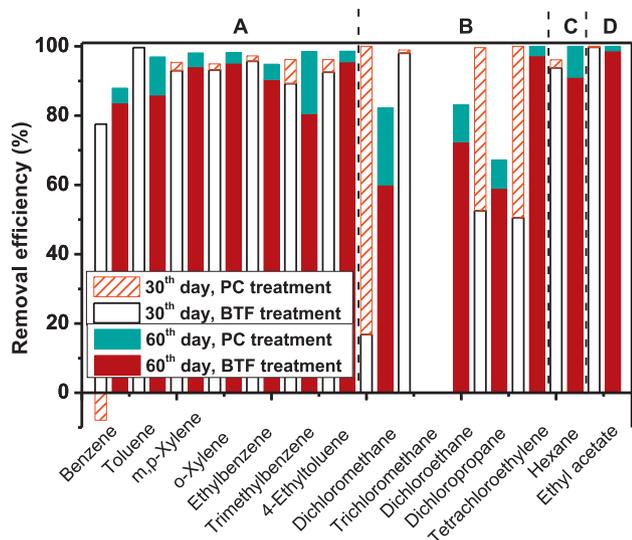


Fig. 2. Degradation of VOCs emitted from MSW compression transfer station during compressor working by BTF-PC. (A): Aromatics; (B): chlorinated; (C): alkanes; (D) ester.

were 80.9% and 95.7% after BTF and BTF-PC treatment, respectively. It seems that biological treatment played majority role in this process after the start-up of bioreactor. This is due to that abundant microbes and enough residence time for volatile organic compounds to undergo complete biodegradation before VOCs passing PC reactor at this flow rate. However, if microbes had limited ability to remove some special organics, such as dichloromethane (RE: 16.8%), dichloropropane (RE: 52.5%) and tetrachloroethylene (RE: 50.5%), PC technology would make up the disadvantage of biological treatment of them, and average RE of all organics in waste gas increased from 80.9% by single BTF to 95.7% by integrated technology. Comparatively, on day 60, average RE of 14 VOCs increased slightly to 84.9% by BTF, and still could maintain 92.7% after BTF-PC treatment. The possible reasons for this phenomena are as follows: firstly, with increase of operation time of this combination reactor, much higher ability bacterial community was re-established in BTF at stable state after another 30-day acclimatization [8]. Secondly, the different concentrations VOCs were feed at different day to day since MSW components were not same everyday. For instance, dichloroethane and trichloromethane could not be detected at the inlet on day 30 and 60, respectively. In addition, RE of benzene by BTF was also even higher than that of BTF-PC on day 30. The possible reason is the same as above mentioned that benzene could be produced as an intermediate from some large aromatics during PC treatment.

3.2.3. Removal of biohazards by photocatalytic technology

Besides the removal of VOCs emitted from transfer station, the removal of biohazards including bacteria, actinomycetes and molds, was also considered with single PC as well as BTF-PC technology at the pilot-scale (Fig. 3). It can be seen that three kinds of biohazards were greatly reduced on the whole 60-day period. On day 1 (during BTF start-up period), PC inactivation efficiencies were 93.21%, 97.86% and 80.28% for bacteria, actinomycetes and molds, respectively. After the completion of 30-day of start-up process, to remove biohazards both from MSW compression and BTF, PC inactivation was also conducted after the waste gas firstly passing through the BTF. All of the biohazards were completely inactivated except the bacteria (increased to 99.73%). After another 30-day operation, the PC reactor still maintained high disinfection ability to all biohazards with only very slightly decrease of

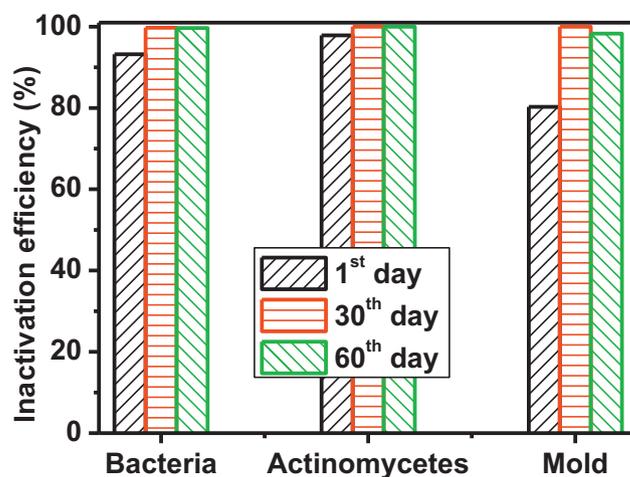


Fig. 3. Photocatalytic disinfection efficiency of biohazards emitted from MSW compression transfer station on the day 1, 30 and 60.

inactivation efficiencies of bacteria and molds. In addition, it must be noted that, usually, molds were more difficult to be inactivated than bacteria with equal concentrations by PC treatment because molds are eucaryotic organisms surrounded by a rigid cell wall, and mold cell is much larger than that of bacteria [40,41]. Nevertheless, PC inactivation efficiency of molds was slightly higher than that of bacteria on day 30 in this work. This possible reason should be that bacteria concentration was more than 10 times higher than that of molds at the inlet.

3.3. Risk assessment of VOCs and biohazards before and after treatment

Because of the ubiquitous presence of VOCs in atmosphere at transfer station, the potential chronic health effects (non-cancer and cancer risk) of exposure to VOCs by means of inhalation by people working at the station as well as the neighborhood residents were assessed. In this study, for all detected and quantified 14 VOCs, only 11 and 6 VOCs were selected to assess the non-cancer and cancer risk, respectively, due to the lack of reference concentrations of 4-ethyltoluene, dichloromethane and ethyl acetate, and unit risk values of toluene, xylene, trimethylbenzene, 4-ethyltoluene, dichloromethane, hexane, and ethyl acetate.

The non-cancer and cancer risk assessment of emitted VOCs at the transfer station during compressor working and off are shown in Fig. S5. For non-cancer risk (Fig. S5a), the HRs of all calculated 11 VOCs during compressor working were much and far higher than those during compressor off and at CA, respectively. Moreover, the HRs were by far less than 1 for all studied VOCs, indicating that their concentrations were usually below the level of concern [25]. Nevertheless, HRs of few VOCs were over 0.1 (potential concern) [42], like trimethylbenzene with the highest HR (0.715 (compressor working) and 0.567 (compressor off)), followed with benzene (0.234 (compressor working) and 0.174 (compressor off)), and m,p-xylene (0.123 (compressor working)).

Fig. S5b also shows individual LCRs for 6 quantified VOCs in the samples. According to the reference [43], compounds with an attributable cancer risk of $>10^{-4}$ were labeled as “definite risk”, between 10^{-5} and 10^{-4} as “probable risk” and between 10^{-5} and 10^{-6} as “possible risk”. In this study, the LCRs of most compounds were below than 10^{-6} , suggesting the safety of them at the current concentration levels. However, the LCRs values of benzene (1.35×10^{-5}), ethylbenzene (7.59×10^{-5}), and

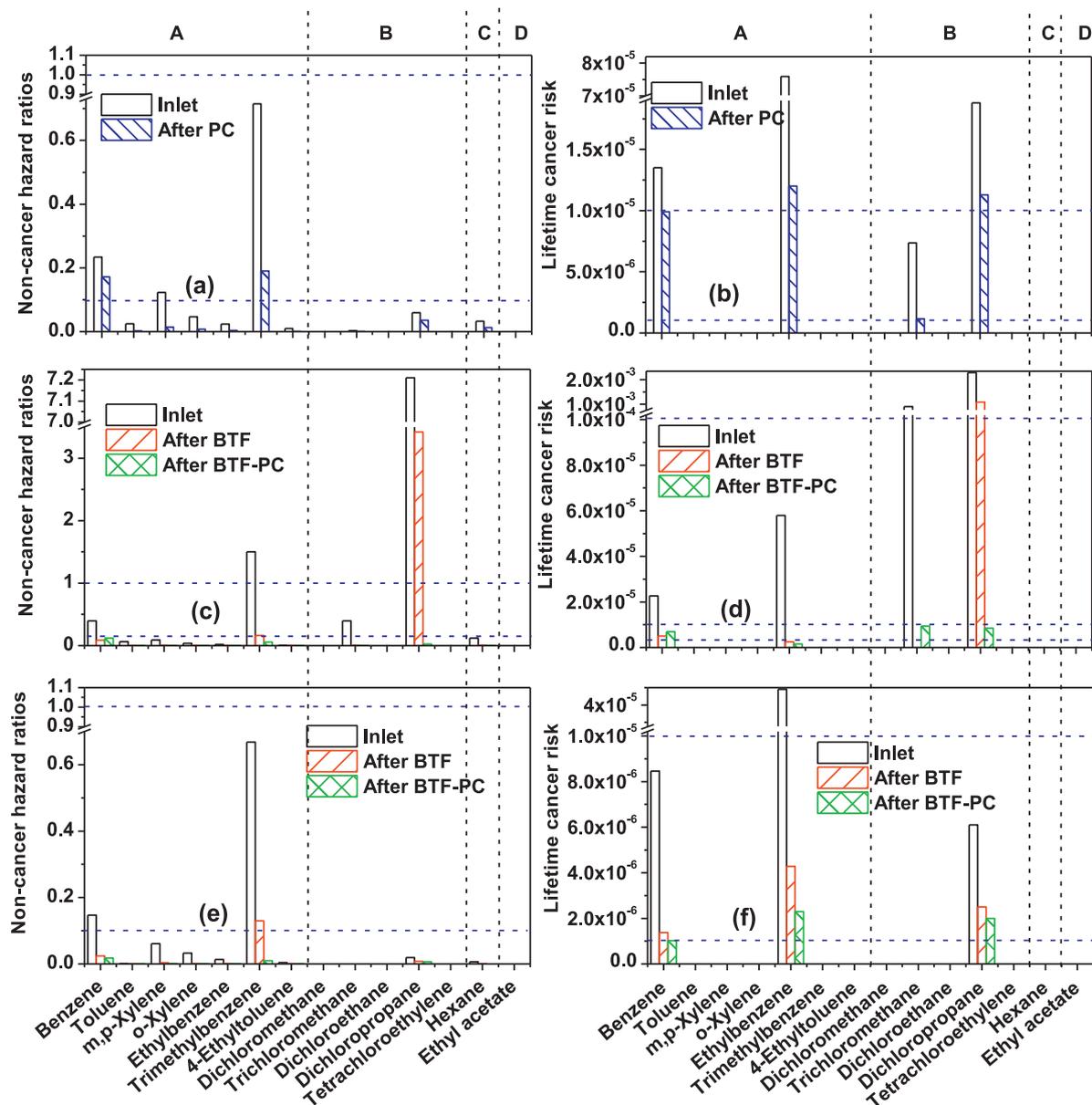


Fig. 4. Risk assessment of VOCs emitted from MSW compression transfer station during compressor working by BTF-PC treatment. (a) Non-cancer and (b) cancer hazard risk on day 1; (c) non-cancer and (d) cancer hazard risk on day 30; (e) non-cancer and (f) cancer hazard risk on day 60; (A): aromatics; (B): chlorinated; (C): alkanes; (D): ester.

dichloropropane (1.88×10^{-5}) during compressor working as well as trichloromethane (1.52×10^{-5}) during compressor off were between 10^{-5} and 10^{-4} , indicating that they were all probable risk. In addition, the LCRs values of benzene (1.00×10^{-5}), ethylbenzene (8.95×10^{-6}), and dichloropropane (9.50×10^{-6}) during compressor off as well as trichloromethane (7.36×10^{-6}) during compressor working were all between 10^{-5} and 10^{-6} , implying that they can also lead to possible risk at these current levels. Therefore, the non-cancer and cancer risk attributed to these VOCs exposure were not negligible and should be seriously taken in the future treatment into account.

Hence, it is very necessary to consider the non-cancer and cancer risk of these VOCs after both single PC and combination BTF-PC treatment (Fig. 4). On day 1, only after PC degradation during compressor working, the non-cancer (11 VOCs) (Fig. 4a) and cancer risk (6 VOCs) (Fig. 4b) of quantified VOCs decreased greatly, and especial for m,p-xylene (from 0.123 to 0.020) and trimethylbenzene

(from 0.715 to 0.190) for non-cancer risk and ethylbenzene (from 7.59×10^{-6} to 1.20×10^{-6}), trichloromethane (from 7.36×10^{-6} to 1.15×10^{-6}) and dichloropropane (from 1.88×10^{-5} to 1.13×10^{-5}) for cancer risk. Most of HRs were below than 0.1 except that benzene and trimethylbenzene were around 0.2 after PC treatment. However, after the completion of biofilm growth process (day 30), the HRs of trimethylbenzene and especial dichloropropane were higher than 1 before treatment, since their concentrations were extremely high. But after BTF treatment, the HRs of most VOCs were lower than 0.1 except for dichloropropane (3.42). What is more, after further subsequent PC treatment, all HRs were below than 0.1, indicating high removal capability of the integrated BTF-PC technology. For cancer risk, LCRs of some compounds, like dichloropropane and trichloromethane, were $>10^{-4}$ before treatment, suggesting very high cancer risk. It is worth noting that the LCR of dichloropropane (1.09×10^{-3}) was still over 10^{-4} even after BTF treatment on day 30, while it decreased swiftly to less than

10^{-5} after the subsequent PC treatment. Similar, on day 60, the non-cancer and cancer risk of the detected VOCs were reduced dramatically, most HRs and LCRs of the components were below the concern of both risks after the integrated BTF–PC treatment, although VOC constituents were different day to day since MSW components were not same every day. Of course, the risks from the combined effects of individual VOCs to human health before and after treatment deserve to further study although the non-cancer and cancer risk assessment results were considered as safe in this work.

Additionally, after PC treatment, air quality about airborne microorganisms was also evaluated as compared with the Air Quality Standards of China [34]. As shown in Fig. S6, after PC inactivation, the bacteria and mold concentrations were reduced greatly. For bacteria, the highest and lowest total concentrations on different particle sized fractions reduced from 7047 and 4859 CFU m^{-3} before treatment to 479 and 16 CFU m^{-3} , on day 1 and 60, respectively. That is, the concentrations after PC treatment were 2.3 and 67.4 times lower than that at CA (lightly cleanness). Air quality of bacterial pollution was purified from level IV (polluted) to I (cleanness) after PC inactivation. In case of molds, although it did not exceed the standard (<800 CFU m^{-3}) before treatment, its concentrations also dropped dramatically after PC inactivation, and the highest and lowest concentrations were 79 and 0 CFU m^{-3} on day 1 and 30, respectively.

4. Conclusions

The pollution profiles, health risk of VOCs and biohazards emitted from transfer station were investigated during compressor working and off time. During compressor working, ethyl acetate was the most abundant species (306.03 $\mu g m^{-3}$), followed by the aromatics at 204.23 $\mu g m^{-3}$. The other two components were minor and altogether constituted about 10% of total VOCs released. Comparatively, the concentrations of 14 quantified VOCs during compressor off were much lower and the predominance composition was aromatics followed by ethyl acetate. Bacterial concentrations during both compressor working and off were level IV (polluted), while mold concentration was not exceeded the standard for all three sampled sites. At pilot scale, over 92.7% of average REs of VOCs and 80.3% of inactivation efficiencies of biohazards were achieved during whole 60-day BTF–PC, respectively, demonstrating that the integrated technology possessed high removal capacity and long stability at pilot scale. In addition, risk assessment showed that, non-cancer risk of some individual VOCs were over the level of concern, and cancer risk of some individual VOCs could even lead to “definite risk” before treatment. But after BTF–PC treatment, both risks were reduced dramatically, and most HRs as well as LCRs of components were below the concern. Additionally, PC technology is also very powerful to inactivate all kinds of biohazards, and air pollution associated with airborne microorganisms was also safe after PC treatment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.01.059>.

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