Journal of Basic and Applied Engineering Research
p-ISSN: 2350-0077; e-ISSN: 2350-0255; Volume 4, Issue 7; October-December, 2017, pp. 640-644

http://www.krishisanskriti.org/Publication.html

Distribution of Emitted Organic Pollutants at Municipal Solid Waste Landfill Site in NCR: Temporal Variation, OFP, Mitigation Strategies and Policy Interventions

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Abstract—*The present study comprises the measurement of total volatile organic compounds (TVOC) and individual VOC (benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) in ambient atmosphere of Ghazipur landfill site located in NCR of India. Real-time monitoring was done for TVOC using a data-logging photo-ionization detector. In addition to this, the National Institute for Occupational Safety and Health (NIOSH)-1501 standard method was used for individual VOC measurements by Gas Chromatograph. The mean levels of TVOC exhibited concentration of 363.8 μg/m³ for Ghazipur solid waste landfill site. On the other hand, ΣBTEX showed the values of 99.1 μg/m³ during the whole observation period. It is noticed that the levels of TVOC were found to be higher during the morning, lower in mid-day and again increased during evening hours. Among the individual VOC, toluene and benzene had significant concentration as compared to the other studied VOCs. Winter was found to have higher concentration of VOCs as compared to summer. OFP were observed to be higher during winter as compared to summer at landfill site. The contribution of m/p-xylene and benzene exhibited the highest and lowest to the OFP. Distribution of emission sources in and around the solid waste landfill site and the prevailing meteorological conditions could be the reason for the seasonal and diurnal variability. After performing correlation analysis, strong positive correlation has been noticed among BTEX during winter as compared summer which suggested similar sources of VOCs. To manage the increasing menace of the solid waste, there is need for short and long term strategies, proper implementation of acts, rules and regulations made by the government bodies from time to time, along with it there is need to take step to make public aware and change their attitude towards the environment.*

Keywords: *Solid waste, Landfill site, TVOC, BTEX, OFP, Correlation analysis.*

1. INTRODUCTION

Municipal solid waste (MSW) landfill sites are the sources of various organic and inorganic materials such as liquid, solid and semi-solid forms. Solid waste mainly comprise packing materials, food containers, biodegradable wastes, oils, cleaning products, acids, pesticides, solvents, acids etc. [1]. MSW landfills of urban areas exhibit acidic anaerobic fermentation which releases various gases namely methane, carbon dioxide and non-methane volatile organic compounds (VOCs). The released VOCs from dumping sites include aromatic, oxygenated, chlorinated and sulfur containing hydrocarbons [2, 3]. It leads to diffusion of VOCs into the atmosphere resulting in odorous nuisances and toxic organics which has growing concern among the scientific community for the last few decades.

Diverse kinds of VOCs have an important role in ground level ozone (O_3) and secondary organic aerosol (SOA) formation. Apart from this, emitted VOCs from landfills are also known for various environmental impacts (unpleasant odors, poor air quality, health problems). The number of VOCs released from MSW landfill sites may vary between 38 and 60 from winter to summer [4]. The contribution of emitted VOCs from landfill sites is usually below 1 % (by volume) of the total landfill gas emissions but their adverse impacts on the environment are not negligible. Number of chlorofluorocarbon compounds from landfill sites also have crucial role in stratospheric ozone depletion and greenhouse effect. It exhibits long range of toxicological effects in terms of short-term and long-term exposure [5]. Health problems include airway irritation, nausea, chronic bronchitis and gastrointestinal problems [6, 7]. Some of the emitted VOCs are known to be potentially mutagenic or carcinogenic to waste collectors and nearby living habitants. Continuous exposure for longtime to these VOCs odors could lead to undesirable mental and physiological reactions [8].

The generation of MSW in major cities of India varies in the range of 0.2 to 0.6 kg/capita/day [9]. The major portion approximately 94 % of the total MSW is used for landfill while rest is processed. Due to negligence and

mismanagement of MSW at the landfill sites have threat to health of human beings in one way or the other. Numbers of studies which include the comprehensive story for emissions of VOCs from landfill sites and collection, disposal and management of MSW have been carried out [8, 9, 10]. In Indian context, very limited studies have been conducted on distribution of VOCs from MSW landfill sites. Therefore, the present study is the first attempt to find the emission sources of total volatile organic compounds (TVOC) and individual VOCs at the Ghazipur MSW landfill site located in National Capital Region of India. Apart of VOCs estimation, seasonal variability of their concentration levels, their relationships with meteorological parameters and Ozone Forming Potential have also been evaluated.

2. MATERIALS AND METHODS

2.1 Sampling site

The sampling was performed at landfill site located in National Capital Region (NCR) of India which is situated at 28.61°N and 77.23°E. It is spread over an area of 1483 km^2 (51.90 and 48.48 km dimensions). It is situated at an altitude of ~293 m above the sea level. NCR has a sub-tropical climate consisting of well-defined four seasons i.e., summer, monsoon, autumn and winter. The summer season experiences windy conditions and temperature as high as 48˚C whereas winter season is characterized by calm conditions and temperature as low as 3 to 4˚C. Delhi receives most of its rain (average annual rainfall 714 mm) during July to September from the south-westerly monsoonal winds and some rain during winters from north-westerly cold winds. For the sampling campaign, Ghazipur MSW landfill site was selected. Ghazipur landfill site is located in the east of Delhi and known as one of the largest dumping site. It has grown much in past few years and extended up to 4 km^2. Figure 1 shows the map of Delhi having location of the Ghazipur MSW landfill site.

Fig. 1: Map of location of the selected Ghazipur municipal solid waste landfill site in Delhi.

2.2 Sample collection

Sample collection for TVOC and individual VOC (benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) has been carried out during two seasons namely summer and winter at Ghazipur landfill site in the year 2013-14. These two seasons represent extreme weather conditions in terms of meteorological parameters in Delhi, India. Samples were collected for 8 hours during 9.00 to 17:00 hrs for four days at the landfill site. Simultaneously, meteorological parameters were also monitored in order to find the relationship of VOC dependence on temperature and relative humidity.

2.3 TVOC measurement

The real-time TVOC measurements were done using a portable, data-logging Pho-Check 5000 photo-ionization detector (PID) having 10.6-eV ultraviolet lamp technology (Ion Science Ltd, Cambridge, England). Here, TVOC comprise a large range of gases to characterize the pollutant load in terms of VOCs and a basis on which quality of air is assessed [11]. The instrument works on the principal that uses the ultraviolet (UV) light source to break down VOCs in the air into positive and negative ions. Then, the PID detects or measures the charge of the ionized gas, with the charge being a function of the concentration of VOCs in the air.

2.4 BTEX measurement

The National Institute for Occupational Safety and Health (NIOSH)-1501 method was used for the sampling and analysis for BTEX measurement. A portable sampler was used to collect air samples. The air was drawn through Orbo™-32 tubes (7 cm in length × 6 mm o.d., provided by Supelco) having activated charcoal. The sampling period for BTEX was kept the same as that of TVOC for 8 hours with the flow rate of 100 ml/min. After collection of sample, further the prepared samples were analyzed using Gas Chromatograph (GC-450, Bruker) equipped with a capillary column Equity-1 (60 m, 0.25 mm ID and 1.0 µm film thickness) and a flame ionization detector (FID). Targeted VOCs were identified by their retention time of calibration VOC standards (HC BTEX/MTBE Mix, 2000 µg/ml each in methanol, procured from Supelco) under a specified chromatographic condition. Aliquots of 1 µl of these standard solutions were injected into the GC and run at a specified chromatographic condition. In all cases, a good linear fit was observed with $R^2 > 0.99$. The compounds were quantified using their peak areas in the external calibration method.

3. RESULTS AND DISCUSSIONS

3.1 Seasonal variability of TVOC

Figure 2 clearly explains the levels of TVOC variations in the ambient air of selected Ghazipur landfill site during the two seasons. The plot shows the mean values along with standard

deviation of observed TVOC levels for two seasons. TVOC showed the higher values during winter as compared to summer. The mean values of TVOC are found to be 340.1 µg/m³ (ranged from 272.9 to 402.3 µg/m³) during summer. On the other hand, winter experienced the TVOC concentration of 387.5 µg/m³ (ranged from 323.1 to 511.5 µg/m³) for Ghazipur landfill site. Distribution of emission sources around the sampling site and the prevailing meteorological conditions could be on account of factors for seasonal variability. In other words, emission source variation, meteorological conditions and seasonal variability of OH radicals play a significant role in the variation of VOCs in the troposphere. Low planetary boundary layer, low temperature with calm conditions, low wind speed could be attributed to higher levels of TVOC during winter. In contrast, more dispersion, rise in mixing depth and degradation of VOCs due to OH radicals may be the reason for lower levels of VOCs during summer. Higher loss of VOCs by photochemical degradation due higher temperature and solar intensity during summer is also reported by [12].

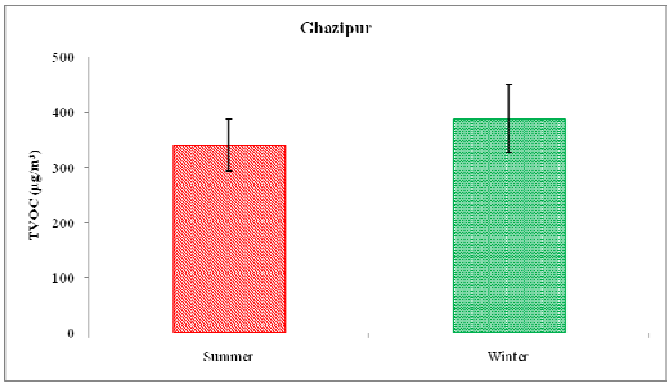

Fig. 2: Seasonal variability of TVOC at the Ghazipur MSW landfill site.

3.2 Diurnal variability of TVOC

Figure 3 shows the trend of seasonal TVOC in the ambient air of Ghazipur MSW landfill site. It is noted that the more or less similar trend of TVOC during two seasons with different magnitudes. The levels of TVOC showed increasing trend in the morning and attained peak values during 10-11 AM, then starts decreasing and again increased in the evening. Increasing degradation with the increasing solar intensity along with meteorological conditions throughout the studied period might be considered as the variability of TVOC. Due to presence of calm conditions leads to the accumulation of air pollutants in the morning. On the other hand, dispersion, dilution of air pollutants and photochemical destruction lowers the levels of TVOC during 11:00 to 15:00 hours [13, 14]. The highest and lowest concentration of OH radicals exhibited during morning/evening and daytime were the major sinks of VOCs because of its reactions with OH radical. Subsequently, the levels of VOCs generally showed maximum values in morning/evening and minimum during daytime.

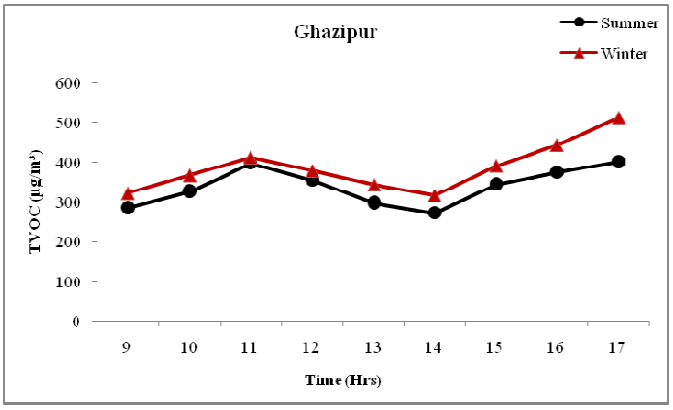

Fig. 3: Diurnal variability of TVOC at Ghazipur MSW landfill site.

3.3 BTEX concentrations

At Ghazipur landfill site, the mean values of sum of BTEX (∑BTEX) were observed to be 82.8 µg/m^3 and 115.4 µg/m^3 during summer and winter, respectively. Figure 4 illustrates the levels of individual VOC (benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) at the Ghazipur landfill site. The mean concentrations of most of the VOCs were found to be higher during winter as compared to summer at both the selected sites. During summer, toluene experienced highest mean concentration of 35.2 µg/m^3 followed by benzene (15.3 µg/m^3), m/p-xylene (14.6 µg/m^3), o-xylene (9.4 µg/m^3) and ethylbenzene (8.3 µg/m^3) at Ghazipur landfill site. In contrast, following trend has been occurred during winter as toluene (42.2 µg/m^3) > benzene (21.8 µg/m^3) > m/p-xylene (21.6 µg/m^3) > ethylbenzene (17.2 µg/m^3) > o-xylene (12.7 µg/m^3).

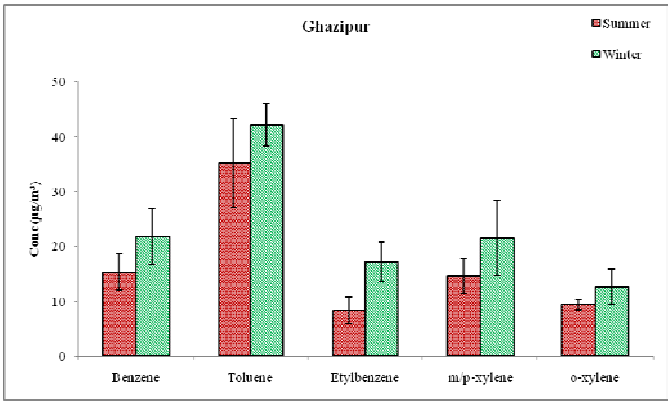

Fig. 4: Seasonal variability of BTEX at Ghazipur MSW landfill site.

3.4 Correlation analysis

Correlation analysis is widely used across the world in order to examine the distribution pattern and source origin of the pollutants [15, 16]. Therefore, pearson correlation method ($p < 0.05$, two tailed) was applied to the whole dataset of BTEX at the Ghazipur landfill site in the present study. Pearson correlation coefficients (r) among the concentrations of BTEX are presented in Table 1.

Table 1: Pearson correlation analysis of studied VOCs during two seasons (winter and summer).

Winter	Benzene	Toluene	Ethylbenzene	m/p-xylene	o-xylene
Benzene	1				
Toluene	0.81**	1			
Ethylbenzene	0.71*	0.61*	1		
m/p-xylene	0.78*	0.57*	0.51*	1	
o-xylene	0.53*	0.42	0.57*	0.81**	1
Summer					
Benzene	1				
Toluene	0.61**	1			
Ethylbenzene	0.59*	0.45	1		
m/p-xylene	0.68*	0.51*	0.36	1	
o-xylene	0.31	0.39	0.52*	0.63*	1

**** p < 0.05.***
***** p < 0.01 (correlation coefficient and significance test).***

In general, significant positive correlations are observed among BTEX during the whole sampling duration indicating that the primary source origin of VOCs is similar. It is clearly observed that the association among the BTEX during winter exhibited strong during winter as compared to summer. Benzene showed strong positive correlation with toluene (r = 0.81), ethylbenzene (r = 0.71), m/p-xylene (r = 0.78) during winter. On the other hand, benzene exhibited moderately strong correlation with (r = 0.61), ethylbenzene (r = 0.59), m/p-xylene (r = 0.68). The differences in correlation among BTEX could be due to variability in the composition of emission sources and meteorological conditions. Further, the differential decay rates of the BTEX compounds with oxidants such as OH and NO_3 also have a role in difference of correlation variability.

3.5 Ozone Formation Potential

VOCs are known to be important precursors in ozone formation in the troposphere [14, 17]. In this regard, estimation of contribution to ozone formation has been carried out using Maximum Incremental Reactivity (MIR) method [18]. Ozone Formation Potential (OFP) for individual VOC (i) using MIR method proposed by [19] is defined by the following equation:

$$OFP\ (i) = conc\ (i) \times MIR_{coeff}\ (i)$$

Here, OFP (i) designates the OFP of individual VOC (i) and MIR_{coeff} (i) (dimensionless, gram of O_3 per gram of VOC) stands for maximum incremental reactivity of compound i. MIR is used for comparing the OFP of individual VOC. Figure 5 explain the OFP of individual VOC at Ghazipur MSW landfill site. It is clearly observed that the OFP were observed to be higher during winter in contrast to summer at both sites. The contribution of m/p-xylene and benzene exhibited the highest and lowest among studied VOCs at the selected sites.

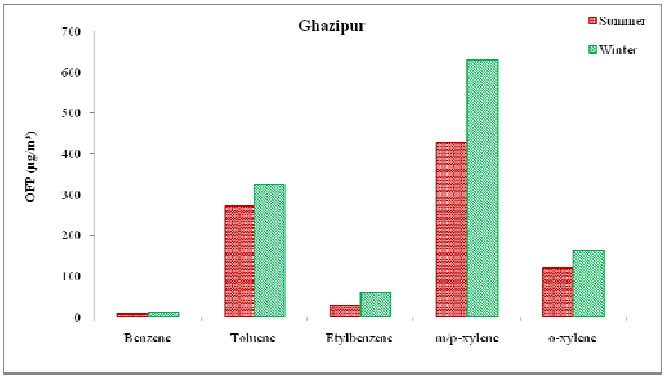

Fig. 5: Ozone formation potential (OFP) of BTEX at Ghazipur MSW landfill site.

3.6 Mitigation strategies, action plans and policy interventions for Solid Waste Management:

A long term and comprehensive strategy is needed to deal with the increasing generation of municipal solid waste due to increasing consumerism, urbanisation and industrialisation, The following points are needed to be done for the better future and sustainable development:-

- First and the most important thing is to change the attitude of human being towards the environment. Human beings should think that the whole world is his home. We have to keep our environment clean like we do for own home.

- Proper implementation of provisions of Solid waste management rules, 2016, Manual on Municipal solid waste management, 2000, Municipal solid waste processing technologies, 2002, guidelines for selection of site for landfilling, 2003.

- Proper separation of solid waste at the source and sink and recycling.

- Landfill sites should be away from the human habitat area to prevent any disease outbreak.

- There is need for invention of alternate degradable materials for plastics.

- To promote short and long term strategy to achieve sustainable development.

So to deal with increasing solid waste pollution in Indian cities, we require short term and long term integrated approach.

4. CONCLUSIONS

The present study attempts to find out the temporal variability of TVOC and individual VOC (benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) at Ghazipur landfill site of National Capital Territory, Delhi. Along with spatio-temporal analysis, the study also tries to find correlation among the studied VOCs in two different seasons. In addition to this, how the meteorological variables influences the concentration of TVOC and individual VOCs were also examined and their Ozone formation potential. Results showed that the level of TVOC and individual VOCs were observed to be higher in winter as compared to summer due to higher atmospheric stability. The levels of TVOC was found to be increasing from the morning hours and attained peak around 10 to 11 A.M. and again decreased in the daytime and again increased during evening hours. Toluene was found to be most dominant contaminant among studied VOCs. Next to toluene, benzene had also found in significant concentration. After performing correlation analysis, strong positive correlation among studied VOCs has been noticed during winter as compared to summer. On the analysis of MIR, the OFP were observed to be higher during winter in contrast to summer at both sites. The contribution of m/p-xylene and benzene exhibited the highest and lowest among studied VOCs at the selected sites. Due to high emissions of TVOC and individual VOC, some necessary steps and proper management of solid waste at the city and landfill site is needed by the local and state governments to cope of the hazardousness of VOCs in NCR, Delhi.

Conflict of Interest: All the authors hereby declare that there in no conflict of interest.

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