

Municipal Solid Waste in Delhi: Ambient VOCs, Health Risks, GIS Modeling, Management, Policy Intervention, Climate Change and a Manmade Disaster in Waiting

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Abstract The increasing population pressure in today's world has led to the increase in the different types of waste on the earth and one of them being the solid waste. Solid wastes are constituted of different type of inorganic and organic material which releases different types of pollutants. In present study, total volatile organic compounds (TVOC) and individual VOC (benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) in ambient atmosphere of Okhla solid waste landfill site of National Capital Region of India have been measured. The study has been carried out during two seasons i.e., winter and summer. The measurement of TVOC was done by using Real-time monitoring was done for TVOC using a data-logging photo-ionization detector. In addition to this, NIOSH-1501 standard method was used for individual VOC measurement using Gas Chromatograph. The mean levels of TVOC exhibited the concentration of 526.7 $\mu\text{g}/\text{m}^3$ while ΣBTEX showed the concentration of 148.1 $\mu\text{g}/\text{m}^3$ Okhla landfill site during the studied period. It is clearly noticed that the levels of TVOC were found to be higher in the morning, lower in the mid-day and increased during evening hours. Seasonal and diurnal variability of TVOC and ΣBTEX might be due to the emission sources and prevailing meteorological conditions. Toluene and benzene had significant concentrations among the studied VOCs. The strong positive correlation has been found among BTEX during winter as compared summer which suggested similar sources of VOCs. On analysis of theoretical health risk assessment, it is found that the benzene has contributed the largest in non-cancer hazard as compared to others VOCs. It is also found that the observed Lifetime Cancer Risk (LCR) has exceeded the standard guideline value (1.0 E-06) established by WHO. Due to the release of greenhouse gases (nitrous oxide, methane and carbon dioxide), solid wastes have potential to contribute to global warming and climate change in short term and long term period. The proper management also requires the proper use of information system in the form of GIS. For the sustainable environment, there is need for change in attitude of peoples towards the consumerism, proper management through separation of solid waste at source and sink, recycling it to reusable product like compost, generation and capture of methane, invention of easily degradable plastic are the need of the day so as to avoid a manmade disaster.

Keywords: VOCs, solid waste, health risk assessment, policy intervention, climate change, manmade disaster

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1. Introduction

Increasing levels of urbanization and industrialization in and around the Delhi has led to the increased generation of solid waste. With the economic growth and increase in population leads to increase in solid waste and this requires proper disposal and efficient management of solid waste [1,2] (McCarthy, 1994; Magrinho et al., 2006). In India, 31% of the total population generates 1,43,449 metric tonnes per day of solid waste [3]. As per the Planning commission report, 2014, the per capita waste generation is increasing at the rate of 5% and it varies

between 200-300, 300-400 and 400-600 gms/person for small towns, medium cities and larger cities respectively. The urban solid wastes are sources of various organic and inorganic materials as liquid, solid and semi-solid forms. They mainly comprise packing materials, food containers, biodegradable wastes, oils, cleaning products, acids, pesticides, solvents, acids etc. [4]. The presence of moisture and soluble organic compounds results in undesirable microorganisms turn into degradation to more toxic substances [5,6]. Due to the acidic anaerobic fermentation at the landfill sites, different types of gases are released in the atmosphere like methane, carbon dioxide and non-methane volatile organic compounds (NMVOCs) [7,8]. The released VOCs from dumping sites

include aromatic, oxygenated, chlorinated and sulfur containing hydrocarbons. Depending on the type of wastes and degradation conditions, the total number of VOCs released varies between 38 and 60 from winter to summer [9]. These gases due to their harmful effects on the human health have led to the growing research during the last decades. VOCs varying characteristics play an important role in formation of surface ozone (O_3) and secondary organic aerosol (SOA) and have various environmental impacts (such as unpleasant odors, poor air quality, health problems).

Out of the total released gases from the landfill sites, the concentration of VOCs constitutes usually below 1% (by volume) but their adverse impacts on the environment are not negligible. The different types of VOCs like chlorofluorocarbon compounds released from landfill sites have also play crucial role in greenhouse effect and stratospheric ozone depletion. The short-term and long-term exposure leads to toxicological effects, undesirable mental and physiological reactions [10,11,12,13] and different types of health problems like airway irritation, nausea, chronic bronchitis and gastrointestinal problems [14,15,16]. Some of the emitted VOCs are known to be potentially mutagenic or carcinogenic to waste collectors working at the landfill sites and people living nearby. In majority of cities of India, the solid waste generation varies in the range of 0.2 to 0.6 kg/capita/day [17]. Approximately, 94 % of the total MSW goes to the landfill site for disposal while rest is separated and processed.

Many studies have been carried out which include the comprehensive work related to emissions of VOCs from landfill sites and collection, disposal and management of MSW have been carried out [4,9,10,13]. In Indian context, very limited studies have been conducted on release of VOCs from MSW landfill sites [17]. Therefore, the present study is relates to emissions of total volatile organic compounds (TVOC) and individual VOCs at the Okhla landfill sites of National Capital Region of India. Apart of VOCs estimation, seasonal variability of their levels and relationships with meteorological parameters and their associated health risk also has been carried out.

2. Materials and Methods

2.1. Sampling Site Description

The sampling was performed in National Capital Region (NCR), India which is situated at 28.61°N and 77.23°E. It is spread over an area of 1483 km² (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 southwesterly monsoonal winds and some rain during winters from north-westerly cold winds. For the sampling campaign,

Okhla landfill site was selected. The Okhla landfill site is located in south Delhi on Aravalli range near Tughlaqabad fort, near the bank of the Yamuna River. Figure 1 shows the map of Delhi having location of the Okhla landfill sites and Figure 2 (Plate 1, Plate 2, Plate 3 and Plate 4) shows the actual site mound and solid waste constituents at the landfill site. Okhla landfill site is the main landfill site for the South Delhi municipal corporation. The site was started in the year 1994 and is spread over 56 acres. The total waste at the site is around 7 million tonnes. Whole of the south Delhi generates around 3,500 tonnes everyday and around 1,200 tonnes of garbage are dumped at Okhla landfill site [18]. The total height of the Okhla landfill site is around 55 meters which is almost thrice the permissible limit. According to Municipal Solid Waste Manual, the permissible height of the landfill sites should not be more than 30 meters. The site has already been declared saturated in 2010. The South Delhi Municipal corporation has established waste-to-energy generation at the Okhla landfill site which processes around 1500 tonnes everyday where there is separation of solid waste and converted to compost which is sold to the horticulture department [19].

2.2. Sample Collection

The Total VOC and individual VOC (benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) sample collection has been done for two seasons namely summer and winter at Okhla landfill site during the year 2013-14. Summer and winter season of the Delhi are the two extreme weather conditions in terms of meteorological parameters.

These two seasons represent extreme weather conditions in terms of meteorological parameters in Delhi, India. At each site, samples were collected for 8 hours during 9.00 to 17:00 hrs for four days during each season at each site. Simultaneously, temperature and humidity was also measured to see whether there is any dependence of VOC concentration on these parameters.

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 [20]. The instrument works on the principle 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. The concentration is displayed in the monitor digital display. Over 220 ml/min of air was drawn through the Pho-Check's internal pump into the instrument and a 1-s measurement interval was set for the PID data logger. Calibration was performed by 100 ppm isobutylene and zero air according to the manufacturer's instructions. The details of technical specifications of Ion Science PhoCheck 5000 TVOC monitor are listed in Table 1.



Figure 1. (a) Map of location of the selected Okhla solid waste landfill site (Source: Map of India) and (b) Areal view of the studied site (Source: Google Earth)



Figure 2. Plates 1 and 2 shows the actual site mound of the Okhla solid waste landfill site (Source of map: Google earth) and Plates 3 and 4 shows the different constituents of solid waste at the landfill site

Table 1. Technical specifications of Ion Science PhoCheck 5000 TVOC monitor

Technical specifications	
Detector	10.6eV Krypton PID lamp
Detection range	1 ppb-10000 ppm
Accuracy	± 5% displayed reading ± one digit
Linearity	± 5%
Temperature	Operating: -20 to 60°C, - 4 to 140°F
Humidity	Operating: 0-99% RH (non-condensing)

2.4. BTEX Measurement

The National Institute for Occupational Safety and Health-1501 method [21] was used for the sampling and analysis for BTEX measurement. A portable sampler (Satyam Scientific Instruments Company, New Delhi) 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 TVOC for 8 hours with the flow rate of 100 ml/min. After collection of sample, each Orbo™-32 tubes was wrapped with aluminium foil and sealed with a Teflon bag. Then, Orbo™-32 tubes were taken back to the laboratory and stored in refrigerator before further analysis using gas chromatography. The charcoal of the Orbo™-32 was transferred into amber-coloured glass vial (2ml). Afterward, 1 ml of low benzene CS₂ (99% purity with less than 0.001% benzene, purchased from Supelco) was added and put on a shaker for 30 min. Further, prepared samples were analysed using a 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). The initial oven temperature was kept at 35°C for 4 min and then increased by 8°C/min to 240°C and kept for 6 min. 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. Five levels of standard solutions in methanol were used to obtain a calibration curve. Aliquots of 1µl 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 R²>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 3 clearly explains the levels of TVOC variations in the ambient air of Okhla landfill site during the two seasons. The plot shows the mean values along with standard deviation of observed TVOC levels. TVOC showed the higher values at both sites during winter as compared to summer. The mean values of TVOC are found to be 481.3µg/m³ (ranged from 365.2 to 686.8µg/m³) during summer.

On the other hand, winter experienced the TVOC as 572.1µg/m³ (ranged from 442.3 to 731.7µg/m³) for Okhla landfill site. Distribution of emission sources

around the sampling site and the prevailing meteorological conditions could be an 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 seasonal variation of VOCs in the troposphere. Low planetary boundary layer, low temperature with calm conditions, low wind speed could be attributed as higher levels of TVOC during winter. In contrast, more dispersion, raise in mixing depth and degradation of VOCs due to OH radicals cause the lower levels during summer. High loss of VOCs by photochemical degradation due higher temperature and solar intensity during summer is also reported by [22].

3.2. Diurnal Variability of TVOC

Figure 4 showed the trend of seasonal TVOC in the ambient air of selected Okhla landfill site. It is noted that the more or less similar trend of TVOC with different magnitudes during the two seasons. 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. Traffic flow and its volume along with meteorological conditions throughout the studied period might be considered as the variability of TVOC. Due to presence of calm conditions explains 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 [23,24]. The highest and lowest concentration of OH radicals exhibited during morning/evening and day time where major sinks of VOCs are its reactions with OH radical. Subsequently, the levels of VOCs generally showed maximum values in morning/evening and minimum in daytime.

3.3. BTEX Concentrations

ΣBTEX experienced 117.6µg/m³ and 178.5µg/m³ at Okhla during summer and winter, respectively. Figure 5 illustrates the levels of individual VOC (benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) at the Okhla landfill site. Toluene was found to be highest as 47.5µg/m³ followed benzene (28.1µg/m³), m/p-xylene (17.4µg/m³), o-xylene (13.3µg/m³) and ethylbenzene (11.3µg/m³) during summer. On the other hand, following trend were noticed with different magnitudes as toluene (66.3µg/m³) > benzene (36.7µg/m³) > m/p-xylene (35.5µg/m³) > ethylbenzene (21.6µg/m³) > o-xylene (18.4 µg/m³).

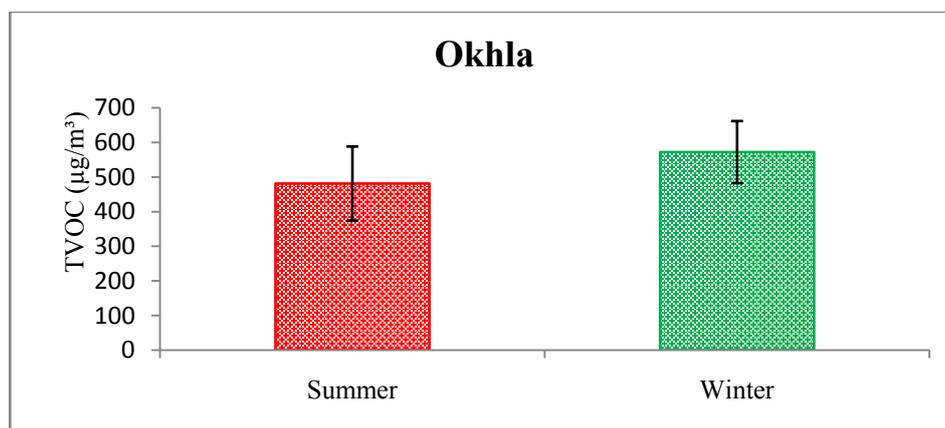


Figure 3. Seasonal variability of TVOC at the Okhla solid waste landfill site

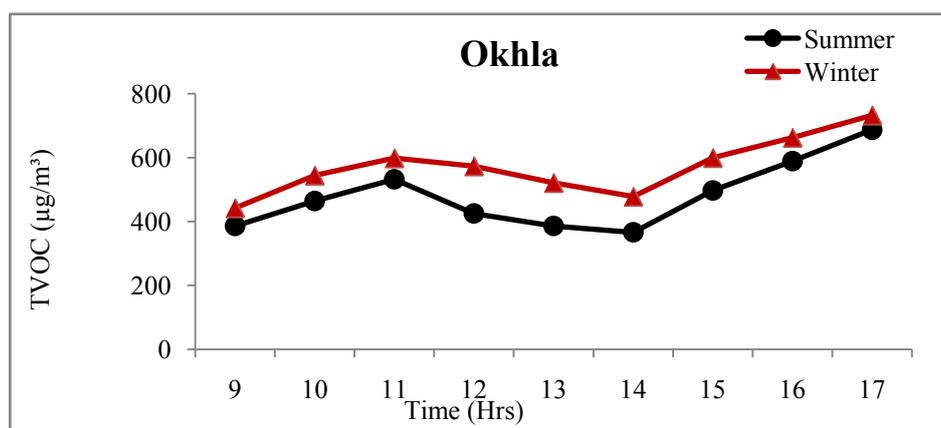


Figure 4. Diurnal and seasonal variability of TVOC at Okhla solid waste landfill site

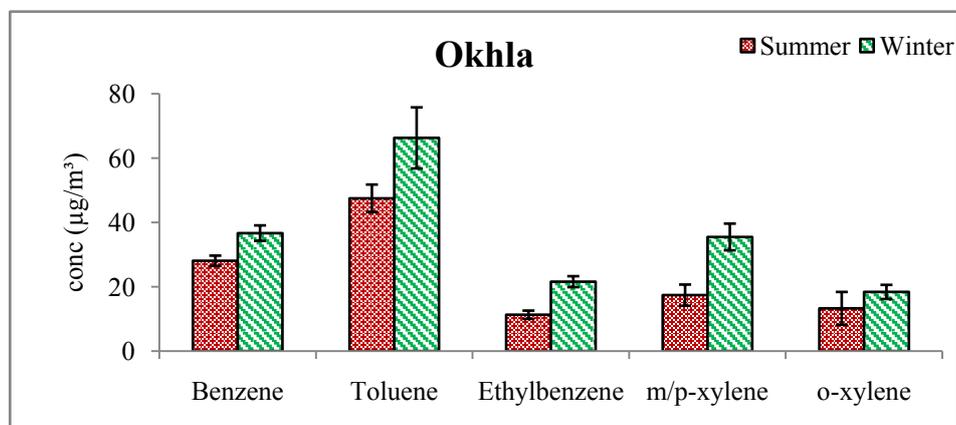


Figure 5. Seasonal variability of BTEX at Okhla landfill site

Table 2. Pearson correlation analysis of studied VOCs during two seasons (summer and winter)

Winter					
Benzene	1				
Toluene	0.75*	1			
Ethylbenzene	0.67*	0.63*	1		
m/p-xylene	0.58*	0.71*	0.69*	1	
o-xylene	0.50*	0.34	0.75*	0.79**	1
Summer					
Benzene	1				
Toluene	0.55**	1			
Ethylbenzene	0.52*	0.22	1		
m/p-xylene	0.62*	0.51*	0.17	1	
o-xylene	0.23	0.18	0.67*	0.72*	1

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 [25,26]. Therefore, Pearson correlation method ($p < 0.05$, two tailed) was applied to the whole dataset of BTEX at the selected two landfill in the present study. Pearson correlation coefficients (r) among the concentrations of BTEX are presented in Table 2.

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 positive correlation with toluene ($r = 0.75$), ethylbenzene ($r = 0.67$), m/p-xylene ($r = 0.58$) during winter. On the other hand, benzene exhibited moderately strong correlation with toluene ($r = 0.55$), ethylbenzene ($r = 0.52$), m/p-xylene ($r = 0.62$). 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 NO₃ also have a role in difference of correlation variability.

3.5. Health Risk Assessment

The health risk assessment was carried out using USEPA methodology given in 1997 [27] (USEPA), the potential outdoor health risks (non-cancer and cancer risks) assessment has been estimated in the present section. The estimated health risk in the current study is based on the assumption of lifetime exposure to the ambient VOCs. The values of the risk assessment are not the actual risk, but are generally regarded for the screening purposes and preliminary assessment.

The estimation of non-cancer risk was done by comparing the ambient concentration (daily) to their respective chronic non-cancer inhalation level. The single VOC is expected to have no adverse effects. These levels are called as reference concentrations (RfCs) and taken from USEPA Integrated Risk Information System (IRIS) [28]. The hazard ratio (HR) of each volatile organic compound (i) represented as the ratio of daily ambient concentration, (C_i in $\mu\text{g}/\text{m}^3$) to corresponding reference concentrations (RfC_i in $\mu\text{g}/\text{m}^3$).

$$\text{Hazard Ratio} = \text{VOC} (i) / RfC_i \quad (1)$$

Life time cancer risk is calculated by multiplying the average daily VOC concentration with Unit Risk (UR) of each compound (i). UR values were taken from WHO [29].

$$\text{LCR} = \text{VOC}_i \times \text{UR}_i \quad (2)$$

Table 3 presents the non-cancer hazard of the studied VOCs which infers that total HR values for both seasons were greater than 1 which has potential concern. Benzene has contributed the largest in non-cancer hazard as compared to others. In addition to this, LCR for two compounds (benzene and ethylbenzene) during two seasons has been presented in Figure 6. It infers that the

observed LCR has exceeded the standard guideline value ($1.0 \text{ E-}06$) established by WHO [29].

Table 3. Non-cancer hazard ratio at Okhla solid waste landfill site during summer and winter

VOCs	Summer	Winter
Benzene	2.93	3.82
Toluene	9.50E-03	1.33E-02
Ethylbenzene	8.69E-03	1.66E-02
m/p-xylene	8.02E-02	1.64E-01
o-xylene	6.13E-02	8.48E-02

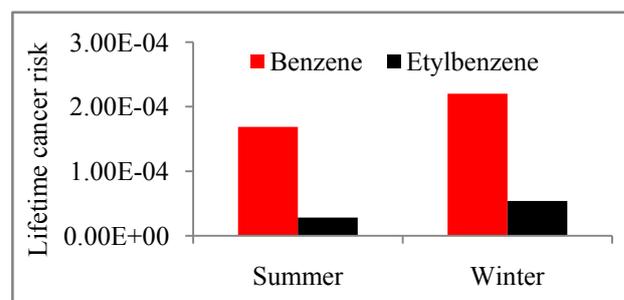


Figure 6. Lifetime cancer risk of benzene and ethylbenzene at Okhla solid waste landfill site

3.6. Ozone Formation Potential (OFP)

Ozone formation in the troposphere is dependent concentration of VOC present. VOCs are known to play important role in the atmospheric photo-chemistry and are important precursors of ozone formation. [24,30,31]. For the evaluation of VOC's photochemical reactivity with OH radicals and their contribution in formation of ozone, the propylene equivalent concentration (Prop-Equiv) and Maximum Incremental Reactivity (MIR) method were used [23,31,32,33]. The Prop-equiv concentration gives the relative VOCs contribution with respect to the rate of reaction with hydroxyl radicals. Chameides et al., [34] gave the Prop-equiv. method and defined as follows:

$$\begin{aligned} \text{Prop - Equiv} (i) \\ = \text{conc} (i) \times K_{\text{OH}} (i) / K_{\text{OH}} (\text{C}_3\text{H}_6), \end{aligned} \quad (1)$$

where, $\text{conc} (i)$ represents the VOC concentration in ppbC, $K_{\text{OH}} (i)$ and $K_{\text{OH}} (\text{C}_3\text{H}_6)$ are the rate constants for the reaction of compounds i and C_3H_6 (propylene) with OH radical, respectively. Prop-Equiv (i) can be defined as the measure of concentration of VOC (i) on an OH-reactivity based scale normalized to the reactivity of C_3H_6 [31]. Carter (1994) [35] proposed the Ozone Formation Potential (OFP) for individual VOC (i) using MIR method which is represented by the equation:

$$\text{OFP} (i) = \text{conc} (i) \times \text{MIR}_{\text{coeff}} (i), \quad (2)$$

where, OFP (i) designates the OFP of individual VOC (i) and $\text{MIR}_{\text{coeff}} (i)$ (which is a dimensionless and represented by gram of O₃ per gram of VOC) stands for maximum incremental reactivity of compound i . MIR is used for comparing the OFP of individual VOC.

The NO_x concentration, solar intensity and meteorological factors along with reactivity, also influence the photochemical formation of ozone. MIR is considered as a

good indicator for comparing the OFP of individual VOC. Figure 7 shows explain the OFP of individual VOC at Okhla MSW landfill site for the two studied season. It can be clearly interpreted that the OFP for the VOCs were found to be higher during the winter compared to summer. The contribution of m/p xylene was found to be highest towards the Prop-equiv and OFP, followed by toluene, o-xylene, ethylbenzene. While benzene was observed to be least contributing factor in Prop-equiv and OFP in both winter and summer.

Previously reported works [24,31,36,37,38,39] also found that aromatic hydrocarbons like toluene and xylene isomers were major contributors towards the formation of ozone.

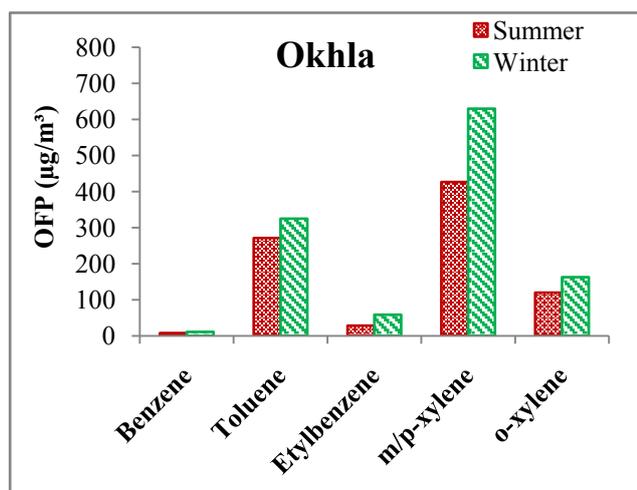


Figure 7. Ozone formation potential (OFP) of BTEX at Okhla MSW landfill site

3.7. Challenges, Management, GIS and Policy Interventions

A comprehensive strategy in terms of short and long term is needed to deal with the menace of municipal solid waste and to achieve zero waste society. The increasing consumerism, urbanisation and industrialisation have lead to this disaster in waiting. To achieve cleaner, liveable environment, and sustainable development: -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. There is need to educate school children about the solid waste management because they are more sensitive to the environment which they have shown by not using Deepawali crackers in the past years. Proper separation of solid waste at the source and sink into degradable and non degradable waste so that it can be send for recycling. There is need for invention of alternate degradable materials for plastics. There is need for suitable and proper implementation of different acts, regulations and 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. Landfill sites should be away from the human habitat area so as to prevent any type of disease outbreak. An integrated approach is needed in short and long term

where every human being and private and government agency should play their role honestly towards environment so that better future is achieved and coming generation does not feel handicapped. The management of solid waste also requires use of remote sensing and GIS for future planning and management. They can be used in the waste collection, transportation data, location of landfill sites, future locations etc.

3.8. Impact of Solid Waste on Climate Change

The solid waste generated from the urban and rural areas have both long term and short term impact on Climate. The release of different types of greenhouse gases from the burning, fires, degradation of waste at the dumping sites due to physical, chemical and biological processes are the main reason for the climate change. The main greenhouse gases that are released from the solid wastes are the carbon dioxide, nitrous oxide and methane. The methane is released from the degradation of organic waste present in the solid waste while nitrous oxide and carbon dioxide is released at all the stages from waste collection to dumping and recycling at the landfill site. The nitrous oxide and carbon dioxide is released during the transportation, recycling process during incineration process. These greenhouse gases have short to long period of half life (nitrous oxide: 5 min, methane: 10 years, carbon dioxide: 200 years) in the atmosphere and are very potential for the global warming phenomenon due to the greenhouse effect of released gases from solid waste management on the environment.

3.9. Manmade Disaster in Waiting to Happen

Once a solid waste comes into existence or in our environment then it can follow two paths i.e., degradation due to different physical, chemical and biological processes or it does not degrade at all and exist in the environment for long period of time. If human beings keep generating the solid waste at the present pace, then after sometime there will be no space left for human beings to live. Everywhere there will be solid waste which keep our environment i.e., hydrosphere, lithosphere and atmosphere contaminated and non-liveable. There will be no clean drinking water, no clean air and no clean land due to which human being will be exposed to different types of unknown problems and disease out breaks. So there will be a disaster on the earth and human existence comes to end.

4. Conclusions

The present study attempts to find out the spatio-temporal variability of TVOC and individual VOC (benzene, toluene, ethylbenzene, m/p-xylene and o-xylene) at Okhla landfill site of NCR, Delhi. The study also tries to find correlation among the studied VOCs in two different seasons. In addition to this, how the meteorological variables influence the concentration of TVOC and individual VOCs is also examined. Results showed that the level of TVOC and individual VOC are observed to be higher in winter as compared to summer due to high

atmospheric stability. The levels of TVOC found to be increasing from the morning hours and attained peak around 10 to 11 AM and again decreased in the noon time and again increased during evening hours. Toluene was found to be most dominant contaminant among studied VOCs. Nest to toluene, benzene had also significant concentrations. After performing correlation analysis, strong positive correlation among studied VOCs has been noticed during winter as compared to summer. Due to high emissions of TVOC and individual VOC, some necessary steps should take up by the local and state governments to cope of the hazardousness of VOCs in NCR, Delhi. Along with this, there is need for communication of information and education the people about the economic and environmental benefits of less use of solid waste.

Conflict of Interest Statement

All authors hereby declare that there is no conflict of interest.

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