ORIGINAL ARTICLE

Assessing Emissions of Volatile Organic Componds from Landfills Gas

Fahime Khademi[1],
Mohammad Reza Samaei[1],
Kourosh Azizi[2],
Abbas Shahsavani[3,4],
Hassan Hashemi[1],
Aida Iraji[5],
Abdolkhalegh Miri[1]

[1]Department of Environmental Health Engineering, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran;
[2]Department of Entomology, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran;
[3]Environmental and Occupational Hazards Control Research Center, ShahidBeheshti University of Medical Science, Tehran, Iran;
[4]Department of Environmental Health Engineering, School of Public Health, ShahidBeheshti University of Medical Science, Tehran, Iran;
[5]Central Research Laboratory, Shiraz University of Medical Sciences, Shiraz, Iran

Correspondence:
Mohammad Reza Samaei, PhD;
Department of Environmental Health Engineering,
School of Health,
Shiraz University of Medical Sciences,
Shiraz, Iran
Tel: +98-917-7320737
Fax: +98-71-37260225
Email: mrsamaei@sums.ac.ir
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Abstract

Background: Biogas is obtained by anaerobic decomposition of organic wastes buried materials used to produce electricity, heat and biofuels. Biogas is at the second place for power generation after hydropower and in 2000 about 6% of the world power generation was allocated to biogas. Biogas is composed of 40–45 vol% CO_2, 55–65 vol% CH_4, and about 1% non-methaneVOCs, and non-methane volatile organic compounds. Emission rates are used to evaluate the compliance with landfill gas emission regulations by the United States Environmental Protection Agency (USEPA). BTEX comounds affect the air quality and may be harmful to human health. Benzene, toluene, ethylbenzene and xylene isomers that are generally called BTEX compounds are the most abundant VOCs in biogas.

Methods: Sampling of VOCs in biogas vents was operated passively or with Tedlar bags. 20 samples were collected from 40 wells of old and new biogas sites of Shiraz' landfill. Immediately after sampling, the samples were transferred to the laboratory. Analysis of the samples was performed with GC-MS.

Results: The results showed that in the collection of the old and new biogas sites, the highest concentration of VOCs was observed in toluene (0.85ppm) followed by benzene (0.81ppm), ethylbenzene (0.13ppm) and xylene (0.08ppm).

Conclusion: The results of the study showed that in all samples, most available compounds in biogas vents were aromatic hydrocarbon compounds.These compounds' constituents originate from household hazardous waste materials deposited in the landfill or from biological/chemical decomposition processes within the landfill.

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Introduction

Reduction in greenhouse gas emissions, limited fossil fuel resources and global energy needs have led to increased attention to the expansion of renewable fuels such as biogas. Biogas is the result of anaerobic decomposition of organic buried waste to produce electricity, heat and biofuels for vehicles.[1-3] Since the two past decades, biogas has been used all over the world, especially in North America and Europe for energy production.[4] Energy from biogas is in the first place in the world as renewable energy.[5] Biogas is at the second place for power generation after hydropower and in 2000 about 6% of the world power generation was allocated to biogas. In the biogas landfill, the biogas is collected and sent to the extraction system through extraction wells in the landfill. Composition of constituent gases of biogas in both temporal and spatial dimensions is very different. Generally, biogas is a flammable mixture, containing 45-40% volume by of carbon dioxide, methane, 65-55% by volume and an amount of organic compounds such as alcohols, aromatic hydrocarbons, halogenated compounds, sulfur compounds and siloxane compound.[1,6,7] Although the concentration of VOC_s is very low in comparison with methane concentration, the same concentration affects global warming, an increase in the troposphere ozone, stratospheric ozone depletion, and loss of regional air quality.[3,8,9] Also some of the VOC_s cause serious damage to the engines and energy utilizations if biogas is used as an energy source.[4] Many volatile organic compounds in biogas have a high impact on the environment and human health due to the very low solubility.[10] Especially at the funeral of industrial waste materials, a high concentration of these compounds has been identified.[2] Many VOC_s present in the biogas are produced by microbial decomposition of waste, household materials including cleaning products, pesticides, pharmaceuticals, plastics and artificial textiles.[11-13] For the production of energy from biogas, various technologies such as internal combustion engines, gas turbines and fuel cells are used.[2] The biogas produced in the site can be used or transferred through a gas vent.[2] Even low concentrations of VOC_s in biogas cause serious damages to the production and energy utilization facilities. So far, various VOC_s have been detected in biogas landfill. VOC_s in biogas can be used in a range of 0.05 up to 1000 mg/m^3. Benzene, toluene, ethylbenzene and xylene isomers, generally called BTEX, are the most abundant VOC_s in biogas.[1] The BTEX ingredients of volatile aromatic hydrocarbons have toxic properties.[14,15] Benzene is a compound with high carcinogenic potential and toluene, ethylbenzene and xylene are highly toxic and mutagenic.[16,17] Allen and colleagues (1997) collected VOC_s from biogas collection vents of seven landfills in UK. More than 140 VOC_s were identified and 90 compounds were common in the landfills. Brookes and Young and colleagues (1983) examined the VOC_s of biogas vents and obtained concentration of benzene (5), Toluene (15), Ethylbenzene (14) and xylene (34) in ppm. Eklund and colleagues (1998) studied VOC_s of biogas vents in New York and obtained the concentration of benzene (2.9), Toluene (54.9), Ethylbenzene (20.5) and xylene (53.4). The purpose of this study was to determine the type and concentration of VOC_s in various biogas sites (old and new site) due to the need for purification of biogas before use in power generation applications.

Description of the Study Area

The wastes produced in the city are disposed in a site with a total area of 2197 hectares, located in the southeast of Shiraz (latitude 29° 25′, longitude 52° 42′, 1590m above sea level), in an area called *Barmshoor* (Figure 1). The Shiraz Landfill has accepted the MSW since 1998. During this time, the characteristics of MSW collected in Shiraz gradually changed. Due to absence of another site for disposal of other wastes, such as industrial and hospital ones, these wastes have been disposed along with solid urban wastes. Biogas plant of Shiraz was established in 2007 (Figure 2 view of the city landfill is shown) in an area of 1 acre landfill. This plant with natural consumption gas of 740 m^3/hr is the largest power plant in the Middle East. The amount of electricity generation in the power plant is 7188 megawatt hours per year. The landfill gas management system is composed of extended sectors of biogas collection, natural gas transmission network to the consumer, equipment available in the collection area and gas transmission network, gas preparation system (main and blower condensate trap) and consumer gas system (Feller or power generator) (see Figure 1). Biogas collection from 40 wells (old and new biogas sites) was conducted in two ways: active and passive. The plant consists of two units of biogas generator engine with a capacity of 500 kv/h that is connected through a main network to 20 kV power distribution network in Shiraz. The biogas new site has been launched about 1 year but old biogas was launched several years ago.

Figure 1: Shiraz biogas power plant with gas collection wells

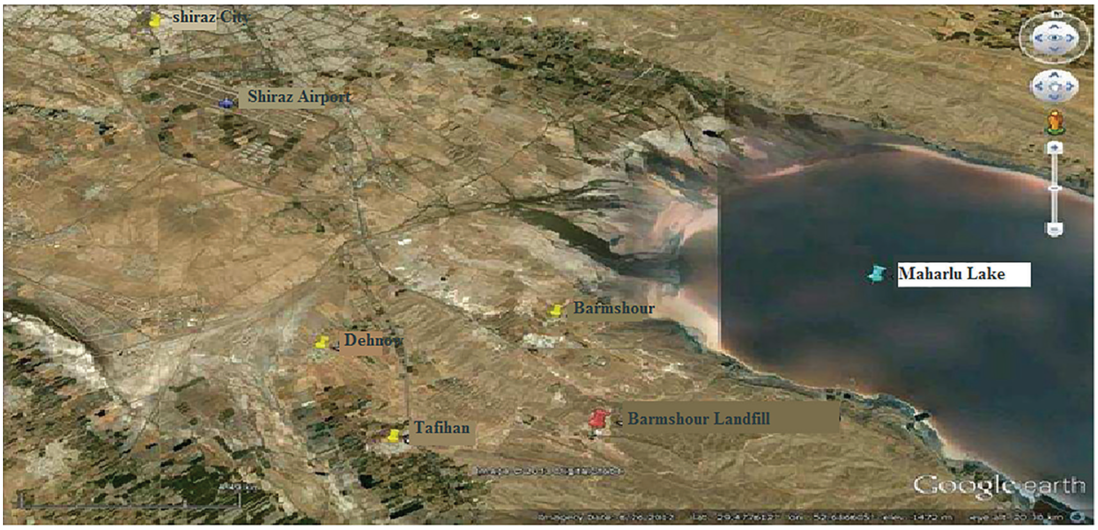

Figure 2: Location of Shiraz Urban Waste Disposal Site and the Areas Surrounding it

Materials and Methods

Sampling and Data Analysis Method

Sampling and analysis of VOC_s in biogas vents is performed by different methods (sampling bags, metal canisters or sorbent tubes). There isn't any standard method for this sampling and data analysis. In this study, sampling of biogas vents was conducted passively. Biogas directly entered the Tedlar bags (1L) from the vents. Tedlar bags, which are widely used to collect air samples, especially VOCs and odorous atmospheres, can allow humidity to diffuse when relative humidity levels differ between the inside and outside. Samples were directly collected from 20 wells (depth of 20 m) from old and new biogas sites. Major advantages of passive sampling compared to active sampling was its simplicity, no need to pump, maintenance, no need to charge and electricity, and no need to thermal desorption. The benefits of these bags were lack of absorption of organic pollutants, good chemical resistance and resistance to weathering. Sampling bags were used to collect gases and vapors for analysis. Before sampling, the sampling bags were filled and emptied with clean air for three times. After sampling, the bags were kept away from sunlight and at a temperature of 0 °C. Since the membrane of these bags is semi-permeable, water may penetrate into the membranes. To ensure the absence of leaks, the bags were immersed in the water for one minute. According to a similar investigation, 20 samples (From 23 August to 24 September, 2014) were collected from old and new vents. In order to have equal sampling conditions, all samples were collected at 10-12 am. In order to minimize the effects of the walls of the air, the bags were filled up to 80% capacity. Immediately after sampling (kept at 4 °C), the samples were taken to laboratory and analyzed. To determine the concentration of VOC_s in Tedlar bag of 1000 µl syringe, Hemiton was immersed into the bags through septum sealed syringe and 500 µl of the sample injected into the GC-MS device. Chromatograph was used for sample analysis model Varian Saturn 3 model with MS detector and a capillary column of DB 624 with a length of 30 m, internal diameter of 0.32 mm for column, and film thickness of 1.8 µl was used. Helium gas was used as the carrier.

Standardization Method in Tedlar Bags

In order to prepare the calibration curve, certain concentrations of each BTEX compound in methanol with purity above 98% were prepared. The stock solution with concentration of 6 (0.5,1,10,50,100,150) ppm in the sample bags with 3 repetitions was prepared to determine the concentration of BTEX compounds in biogas vents. The prepared concentration was injected into the Tedlar bags, and after 30 minutes a certain concentration of the sample was injected. The area under the curve level was determined for each concentration. Methanol was used as an internal standard. In this study, the samples were chosen based on the objectives. At each sampling station, three samples were taken. The values shown in the figures represent the average of their data. In the present study, descriptive statistics such as mean, standard deviation, percentage, etc. were used.

Results

The average concentration of each BTEX compound in total old and new biogas vents is shown in Figure 3. As it can be seen in the Figure, the highest concentration of total VOC_s in both old and new biogas sites is related to toluene (0.85) followed by benzene (0.81), ethylbenzene (0.13) and xylene (0.08) ppm.

The findings of comparing the results of VOC_s in biogas of old and new sites are shown in Figure 4. As shown, the concentration of VOC_s in new biogas vents is more than old ones.

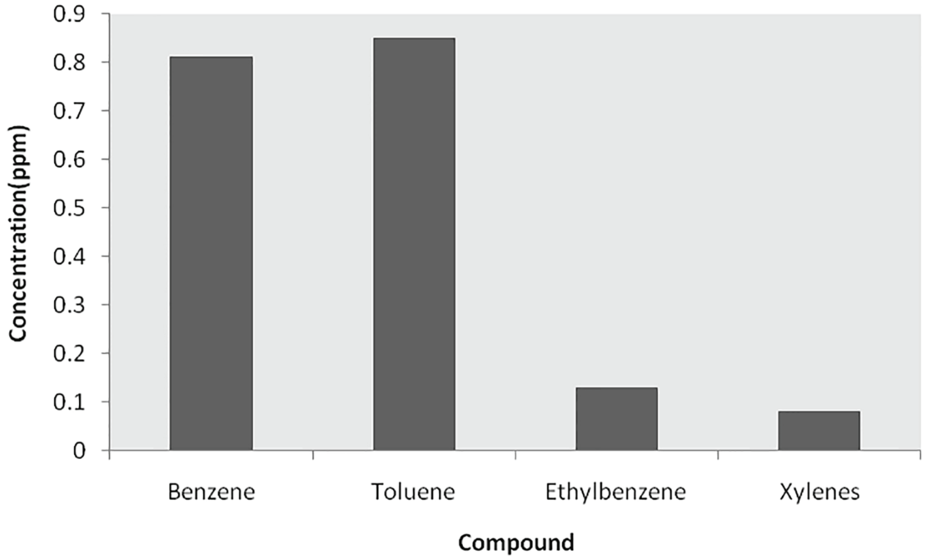

Figure 3: Total concentrations of each compound of VOC_s in both old and new biogas sites.

Discussion and Conclusion

In this research, we assessed the gases emitted from landfills of Shiraz for BTEX. To the best of our knowledge, this is the first time that measurement of the concentration of VOC_s in biogas vents using sampling Tedlar bags is reported.

In new and old sites, most available compounds in biogas vents were aromatic hydrocarbon compounds. These compounds' constituents originate from household hazardous waste materials deposited in the landfill or from biological/chemical decomposition processes within the landfill. According to obtained results, the highest concentration of total VOC_s in the collection of old and new biogas vents is related to toluene and benzene, followed by ethylbenzeneand xylene, respectively. The quantity and quality of the waste used in biogas production have a significant influence on the concentration and type of different VOC_s. In ideal conditions, according to Raoult's law, the concentration of VOC_s in the saturated gas is affected by gas pressure, gas composition, molar weight of the compound and temperature. According to this law, we can calculate the maximum concentration of each compound in the gas phase, but in practice the actual concentration is always less than the maximum concentration level. As shown in Figure 4, there was a significant difference between the concentrations of volatile organic compounds found in old and new biogas sites. Due to the difference in volatility and degradation rate, some materials were available in the produced biogas for several years; for example, benzene and toluene can be absorbed by solid organic carbon without being completely removed from landfill gases while some compounds such as Freon can be present for two years in landfill gases. In old biogas, the highest concentration was related to toluene, (0.5) followed by benzene (0.06), Ethylbenzene (0.02), and xylene (0.01) ppm. In new biogas sites, the highest concentration was related to toluene (1.2ppm) followed by benzene (0.75ppm), ethylbenzene (0.25ppm) and xylene (0.15ppm). Kim and colleagues (2008) collected the gas samples in

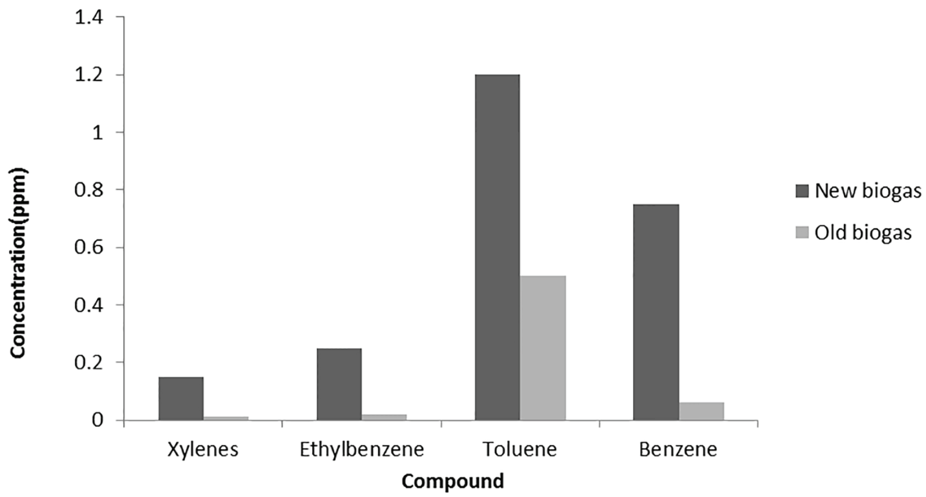

Figure 3: Total concentrations of each compound of VOC_s in both old and new biogas sites.

biogas. The mean concentrations of benzene, toluene, ethylbenzene, and xylenes were found to be 0.4–8.7, 1.5–953.5, 6.3–99.0, and 1.1–21.1ppm, respectively. Abderrahim and colleagues (2014) sampled the biogas vents in Canada and obtained the concentration of benzene (BLD), toluene (15ppm), ethylbenzene (5.5ppm) and xylene (17ppm). Rettenberger and Stegman (1996) studied VOC_s of the biogas vents and obtained the concentration of benzene (0.03–15.0), toluene (0.2–615.0), ethylbenzene (0.5–236.0), and xylene (0.2–383.0). Toluene is a compound widely used in industry as a solvent, cosmetic, rubber, and paint thinners. Ethylbenzene is used in pesticides, and paints. The concentration of VOCs at two sites of the biogas can vary in both temporal and spatial dimensions. There was very minor changes in the type of VOCs from sample to sample; also, there was a lot of changes in concentration of the compounds in each sampling. Type and concentration of VOCs in the biogas vents of both old and new sites are dependent on the type and composition of waste decomposition, mechanisms, stage reached in the decomposition process, landfill age, the amount of produced gas, weather conditions, landfill conditions, and changes in process conditions (temperature, humidity). Buried wastes in old landfills are very heterogeneous. Even if the separation of recyclable materials is performed at the source place, again biodegradable organic materials will be available in the buried wastes. Landfills that receive industrial waste will release a large amount of VOCs. The health risk associated with VOCs in the biogas is related to the release of these compounds in the atmosphere, and the degree of dilution of the composition with atmosphere. Therefore, protective equipment for workers and operators should be considered. Monitoring the health of workers should be considered periodically.

The present results demonstrate different problems related to the presence of VOCs in the biogas. Obviously, the economic use of biogas cannot be achieved without a proper abatement technique. Since several VOCs were measured, the results of this study can be of help when there is a need to assess the cause of total VOCs (TVOC), especially in complex plants, like landfills, where various sources are present.

Conflict of Interest: None declared.

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