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Estimation of emissions of nonmethane organic compounds from a closed landfill site using a landfill gas emission model

A. N. Nwachukwu[1], A. W. Diya[2]

[1] Williamson Research Centre for Molecular Environmental Sciences, School of Earth, Atmospheric and Environmental Science, University of Manchester M13 9PL, UK.
[2] Health Sciences Research Group, School of Medicine, University of Manchester M13 9PL, UK.

Abstract
Nonmethane organic compounds (NMOC) emissions from landfills often constitute significant risks both to human health and the general environment. To date very little work has been done on tracking the emissions of NMOC from landfills. To this end, a concerted effort was made to investigate the total annual mass emission rate of NMOC from a closed landfill site in South Manchester, United Kingdom. This was done by using field estimates of NMOC concentration and the landfill parameters into the Landfill Gas Emission Model embedded in ACTS and RISK software. Two results were obtained: (i) a deterministic outcome of 1.7218 x 10^{-7} kg/year, which was calculated from mean values of the field estimates of NMOC concentration and the landfill parameters, and (ii) a probabilistic outcome of 1.66 x 10^{-7} - 1.78 x 10^{-7} kg/year, which is a range of value obtained after Monte Carlo simulation of the uncertain parameters of the landfill including NMOC concentration. A comparison between these two results suggests that the probabilistic outcome is a more representative and reliable estimate of the total annual mass emission of NMOC especially given the variability of the parameters of the model. Moreover, a comparison of the model result and the safety standard of 5.0 x 10^{-5} kg/year indicate that the mass emission of NMOC from the studied landfill is significantly less than previously thought. However, given that this can accumulate to a dangerous level over a long period of time (such as the age of this landfill site); it may have started affecting the health of the people living within the vicinity of the landfill. A case is therefore made for more studies to be carried out on the emissions of other gases such as CH_4 and CO_2 from the studied landfill site, as this would help to understand the synergistic effect of the various gases being emitted from the landfill

Keywords: ACTS & RISK software; Biodegradation; Emission model; Health risk calculations; Landfill gas (LFG); Monte Carlo analysis, Random numbers; Stochastic behaviour.

1. Introduction
Gases released from municipal waste landfills have the potential to cause odours in neighbourhoods surrounding the landfill. This set of gases is referred to as "landfill gas" (LFG). They are produced under anaerobic conditions by microbial decomposition of the organic fraction in waste disposed off in landfills [1-5]. This process produces hazardous and odorous gases; the amount of which depends upon a variety of factors such as the nature and moisture content of the waste, amount of oxygen present, and temperature inside the landfill [2, 4]. Less odorous gases can also be generated at landfills due to

chemical reactions and due to evaporation of chemicals put into the landfill. Any gases generated tend to rise through the landfill and reach the air above [6], although the rate at which this occurs is affected by landfill content and by weather [2, 4], and therefore varies from site to site and throughout the year.

Once emitted into the air, landfill gases are carried on surface level winds. While this dilutes the gases with fresh air [6], it can also move them into the neighbouring communities. Naturally, wind speed and direction determine whether local residents will notice landfill odour so the degree of the problem varies greatly from day to day. At locations near the landfill, the worst time of the day may be early morning when winds tend to be most gentle, providing the least dilution of the gases. Additionally, this early morning effect is usually greatest in fall and spring.

Methane and carbon dioxide are the major gases produced by biodegradation of landfill wastes [2-4, 7]. According to Scheutz et al. [2], the biodegradable organic material in waste includes paper, animal and vegetable matter, and garden waste. Other gases produced by landfill microbial degradation are reduced sulphur gases or sulfides (example, hydrogen sulfide, dimethyl sulfide, mercaptans). These odorous gases give the landfill gas mixture its characteristic “rotting” smell.

Other chemicals can also be present in landfill gases, although they are typically in trace amounts compared to the levels of methane, carbon dioxide, and sulfides [7-9]. These hydrocarbon trace components of landfill gases are classified as nonmethane organic compounds (NMOCs) or nonmethane hydrocarbons (NMHCs) [3]. Volatile organic compounds (VOCs) are important component of NMOC which have been found in landfill gases with the amount varying from landfill to landfill depending upon whether the landfill received wastes containing these chemicals. Also, the amount of VOCs in landfills depend upon whether chemical reactions are occurring which either remove or create them.

Methane is highly explosive at concentrations of 5–15% in air [10] and can accumulate to dangerous levels virtually undetected [11]. Carbon dioxide on the other hand is an asphyxiant [12]. Both methane and carbon dioxide are two major greenhouse gases [2, 13]. Even though VOCs are usually found in trace concentrations in landfill sites [14], they still constitute risks since they can accumulate to a dangerous level over time [15]. For example, VOCs such as benzene and formaldehyde have been recognised by International Agency for Research on Cancer as human carcinogens even in low concentrations [16]. Given the significant environmental and human health effects caused by landfill gases, there is, therefore, often a requirement to monitor the migration of these gases to ensure the safety of both in-situ and ex-situ structures, and to ensure the safety and protection of personnel and local populations.

The migration of methane and carbon dioxide produced by decomposition reaction through the landfill serves to carry with it nonmethane organic compounds (NMOCs) that were originally present in the municipal solid waste [5]. In the United States for example, MSW landfills were estimated to release about 9.0 x 10^5 mg/year of methane and 1.3 x 10^4 mg/year of NMOCs without any form of regulation until recently [5]. Under the Clean Air Act, any large landfill that emits more than 50 mg/year of NMOCs is required to capture and reuse or destroy these gases [17].

In order to comply with the new regulations, MSW landfill operators are required to determine the generation rate of NMOC of their landfill through modelling and/or measurements. This would help to (i) determine whether the site specific value for a given landfill varies from the regulatory default values for parameters such as the average total NMOC concentration and emission in the landfill. The higher the deviation from the default value, the greater the need for site specific measurements (ii) quantify the variability in landfill gas composition from one emission source to another across a landfill and within a given emission source. Emission sources include passive vents, soil surfaces, and gas collection systems. The expected variability will determine where samples should be collected to characterise landfill gas compositions and how many samples should be collected.

This study has attempted to provide answers to the above questions using some data collected from a closed landfill site in South Manchester, United Kingdom. The paper specifically aims to estimate total annual mass emission rate of Nonmethane organic compounds (i.e. VOCs) emitted from the studied closed landfill site using Landfill Gas Emission Model.

1.1 Landfill gas emission model

The landfill gas emission model used in this paper is one of the numerous models embedded in Analytical Contaminant Transport Analysis System (ACTS) software. This particular model is based on the USEPA model LandGEM [7, 18]. In this model, the landfill gas is assumed to be roughly half methane and half carbon dioxide, with additional, relatively low concentrations of other air pollutants.

According to Mustafa [11], the estimation method used by this model is based on a simple first order decay equation and requires limited input data such as:
(i) The design capacity of the landfill
(ii) The amount of refuse in place in the landfill
(iii) The methane generation rate
(iv) The potential methane generation capacity
(v) The concentration of total nonmethane organic compounds (NMOC) and speciated NMOC found in the landfill.
(vi) The years the landfill has been in operation
(vii) Whether the landfill has been used for disposal of hazardous waste (co-disposal).
Since the data available on the quantity, age, and composition of the refuse in the landfill are limited, using a more sophisticated calculation was not attempted in this model (USEPA, [7]). The Landfill Emissions Model estimates emission of methane, carbon dioxide, nonmethane organic compounds, and selected air pollutants [11]. For more information on the assumptions used in this model, see [1].
Depending on the amount of knowledge on the year-to-year solid waste acceptance rate, the Landfill Emissions Model is of two categories. For example, if the actual year-to-year solid waste acceptance rate is known, the following mathematical model is used to estimate gas emissions:

$$M_{NMOC} = 2\sum kL_o M_i C_{NMOC}\left(e_i^{-kt}\right)\left(3.6\times10^{-9}\right) \qquad (1)$$

However, if the actual year-to-year solid waste acceptance rate is unknown, the mathematical model used is:

$$M_{NMOC} = 2RL_o C_{NMOC}\left(e^{-kc} - e^{-kt}\right)\left(3.6\times10^{-9}\right) \qquad (2)$$

where M_{NMOC} = the total landfill NMOC emission rate (Mg/year), k = the methane generation rate constant (year^{-1}), L_o = the methane generation potential (m^3/mg of waste), M_i = the mass of solid waste in the *i*th section of the landfill (mg), t_i = the age of the *i*th section of the section of the landfill (years), t = the age of the landfill (years), R = the average annual acceptance rate (mg/year), C = the time since closure (years). Note that for active landfills, c = 0, C_{NMOC} = the concentration of NMOC (ppm by volume as hexane).
The constant is a conversion factor to render the outcome of the emission rate in (mg/year) [11]. Also, when calculating the value of M_i as can be seen in equation 1.0, the mass of non-degradable solid waste should be subtracted from the total mass of solid waste in a particular section of the landfill, however; this is contingent on the availability of a record on the nature and amount of such wastes in the studied landfill [11].
In equations 1.0 and 2.0, the methane generation rate constant, k, denotes the rate of generation of methane for each submass of refuse in the landfill. The higher the value of k, the faster methane generation rate increases and then decays over time. The value of k depends on the following factors: (i) refuse moisture content; (ii) availability of nutrients for methanogens; (iii) landfill pH; and, (iv) the prevailing temperature. The k values obtained from the field data collected range from 0.003 - 0.21 year^{-1} [11].
The value for the potential methane generation capacity of refuse, L_o, depends on the type of refuse present in the landfill. For example, the higher the cellulose contents of the refuse, the higher the value of L_o. The values of the theoretical and field data for L_o range from 6.2 - 270 m^3/mg refuse [11].
Table 1 below displays the values of the methane generation rate and methane generation capacity for typical landfill conditions [7].

1.2 Assumptions and limitations of the landfill emissions model
The model has the following assumptions and limitations:
i. the methane generation process is based on a first order decay mechanism
ii. Parameters of the model are empirical variables
iii. Some important physical conditions of a landfill which may affect the methane generation are neglected.
iv. These limitations may tend to underestimate or overestimate the methane generation at a site.

Table 1. Values for methane generation rate, k and potential methane generation capacity, L_o

Emission type	**Landfill type**	**K (year^{-1})**	**L_o (m^3/mg)**
CAA	Conventional	0.05 (Default)	170 (Default)
CAA	Arid area	0.02	170
Inventory	Conventional	0.04	100
Inventory	Arid area	0.02	100
Inventory	Wet (bioreactor)	0.7	96

Source: [11] CAA = Clean Air Act (1970)

2. Application of the model

The Landfill Emissions Model was applied to estimate the total mass emission rate of nonmethane organic compounds (NMOC) emitted from a closed landfill site in Manchester, UK. The local council describes this particular landfill as an infilled brick pit, which is known to be producing landfill gas and leachate. Records indicate that the landfill site was infilled until late 1960s with inert, household, commercial, and industrial waste materials. This landfill site is surrounded by council halls. The requirement to quantify the mass emission rate of landfill gas was prompted by the complaints received from the inhabitants of the halls concerning strange odours from the site. There is also fear of potential hazards of explosion, asphyxiation and toxicity from methane, carbon dioxide, and volatile organic compounds respectively.

The generation of methane and carbon dioxide from landfills has been well studied, and a very large body of literature exists about the factors controlling gas production and the amount of gas that is produced per category of waste material and per mass of waste, however; only few studies have reported air emission of NMOC from municipal solid waste sites [3, 5]. This coupled with the fact that volatile organic compounds (VOCs), a major group of NMOC are recognised to be highly carcinogenic even in low concentration [16]; are the main reasons nonmethane organic compound was chosen for this study.

In order to determine the potential exposure and health effects due to NMOC, the air emission of NMOC and the concentrations of NMOC need to be ascertained. Based on field studies using GFM 435 landfill gas analyser, the total concentration of nonmethane organic compounds in the landfill site is determined to be 2500 ppm. Field studies also indicate that the time since closure of the landfill is 42 years, the age of the landfill is 60 years, and the average annual waste acceptance rate is 1000 mg/year. Given that this is a conventional landfill site with inventory emission type, the methane generation rate constant, k and the methane generation potential, L_o are assumed to be 0.04 year^{-1} and 100 m^3/Mg respectively (see Table 1). With the above values, the total mass emission rate of NMOC can be calculated in the deterministic mode from the emission model.

However, the values of these parameters of the model are field estimates averages and could result in an uncertainty in the final result of the total mass emission rate of NMOC. For example, the NMOC concentration in the landfill is not known precisely but it is estimated to be in the range of (100-3000) ppm, while the average annual refuse acceptance rate also varies in the range of (500-2500) mg/year. Similarly, the age of the landfill site is estimated to be in the range of (50-70) years. This information shows that the expected total mass emission rate of NMOC from this landfill is not just a single numerical value (deterministic value) but a range of numerical values (probabilistic value), hence, the need for uncertainty analysis using Monte Carlo simulation. This simulation is built into individual models of the ACTS and RISK software including the Landfill Gas Emission Model (Mustafa [11]).

"Monte Carlo simulation or analysis is a process that utilizes random numbers to define the parameters in a model in an effort to identify the stochastic behaviour of the model with respect to the parameters of the model" [11]. In this paper, the concentration of NMOC, the average annual acceptance rate, and the age of the landfill were analyzed using Monte Carlo simulation. This is because, their actual values are not known but are estimated to be in ranges. In this simulation, the original values of the uncertain parameters used in the deterministic mode were assumed to be representative of the mean value of the parameters, with the range of values of the parameters representing their minimum and the maximum values. Also, the form of Landfill Emission Model used is that represented by equation 2.0 since the actual year-to-year solid waste acceptance rate is unknown.

3. Results

The range of values of concentration of NMOC in the studied landfill after 5000 Monte Carlo analysis terms using Landfill Emission Model is represented by Figure 1 below. The corresponding Monte Carlo statistics show the minimum and maximum concentration of nonmethane organic compounds (NMOC) to be 2499.1 ppm and 2500.8 ppm respectively. The mean, variance, and standard deviation are 2500 ppm, 0.0513, and 0.227 respectively.

Figure 2 represents range of values of the average annual acceptance rate of waste in the studied landfill after 5000 Monte Carlo analysis terms using Landfill Emission Model. The corresponding Monte Carlo statistics show the minimum and maximum annual average acceptance rates to be 999.2 mg/year and 1000.8 mg/year respectively. The mean, variance, and standard deviation are 1000 mg/year, 0.0504, and 0.225 respectively. The number of Monte Carlo terms chosen was based on the level of uncertainty believed to exist in the values of the uncertain parameters.

In Figure 3, the range of values of the age of the studied landfill after 5000 number of Monte Carlo analysis terms using Landfill Emission Model is presented. The corresponding Monte Carlo statistics show the minimum and maximum age of the landfill to be 60.85 years and 59.08 years respectively. The mean, variance, and standard deviation are 60 years, 0.0496, and 0.223 respectively.

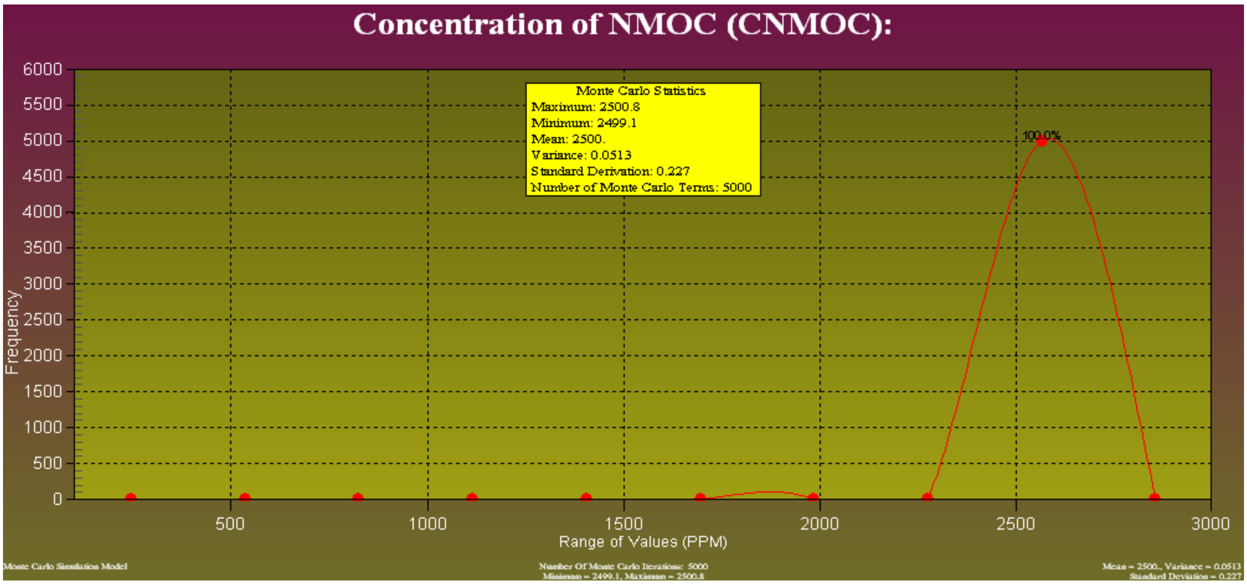

Figure 1. Graph of the frequency against the range of values of CNMOC

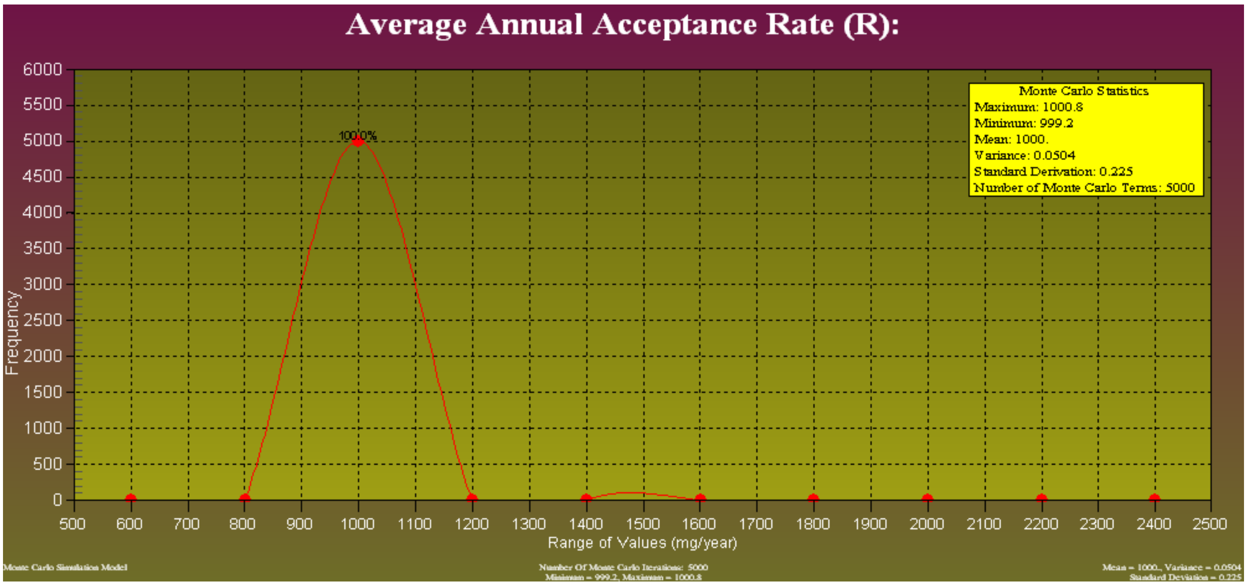

Figure 2. Graph of frequency against range of values of average annual acceptance rate ®

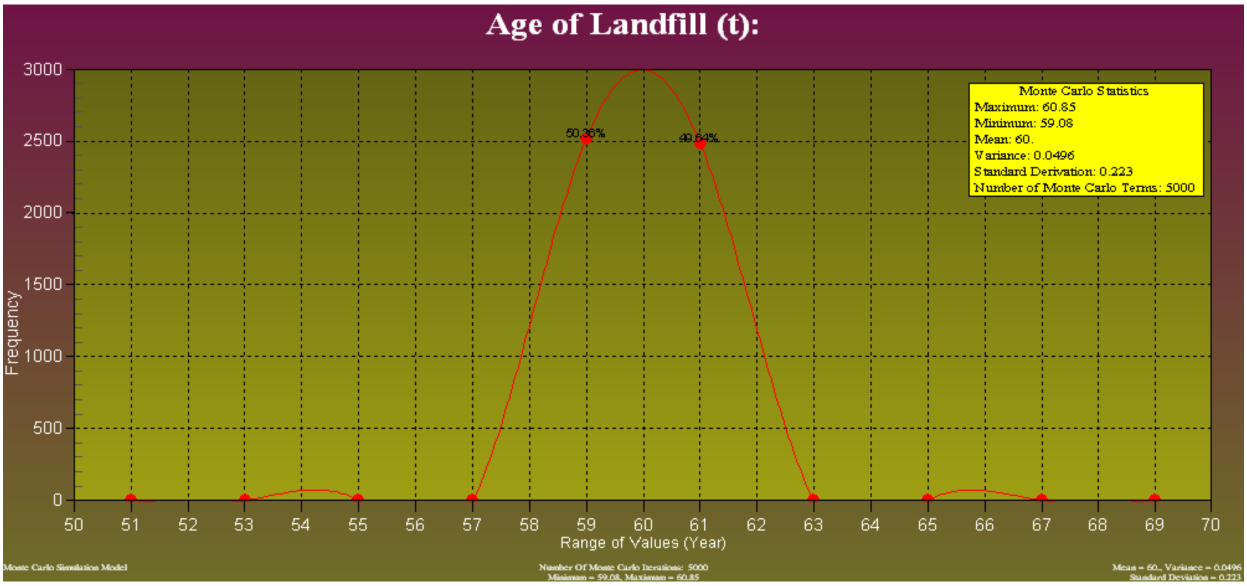

Figure 3. Graph of frequency against range of values of age of landfill (t)

Figure 4 represents range of values of the total annual mass emission rate of nonmethane organic compounds (NMOC) in the studied landfill after 5000 Monte Carlo analysis terms using Landfill Emission Model. This is the probabilistic result gotten after the incorporation of Monte Carlo statistics of the uncertain parameters (as shown in Figures 1-3) into the emission model. The corresponding Monte Carlo statistics show the minimum and maximum NMOC total annual mass emission rate to be 1.66 x 10^{-7} kg/year and 1.78 x 10^{-7} kg/year respectively. The mean, variance, and standard deviation are 1.72 x 10^{-7} kg/year, 2.12 x 10^{-18}, and 1.46 x 10^{-9} respectively.

Note that, the deterministic estimate of the total annual mass emission rate of nonmethane organic compounds is approximately 1.7218 x 10^{-7} kg/year. This is, however; gotten from the field estimates of the parameters of the model. With this, there now exist two results of the mass emission rate of NMOC.

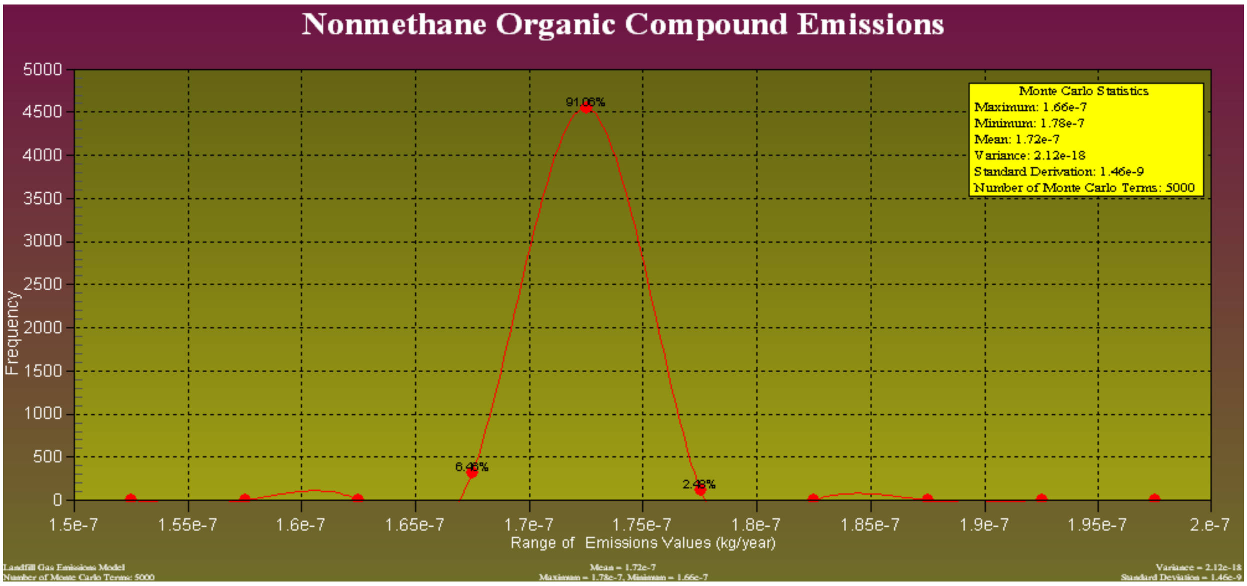

Figure 4. Graph of frequency against range of emission values of NMOC

4. Discussion

As can be seen from Figures 1-3, rather than a absolute (deterministic) outcome, as obtained from the field estimates for the concentration of nonmethane organic compounds (NMOC) (ppm), average annual refuse acceptance rate (mg/year) and age of the landfill (years) respectively; there now exists a probability density which appears to be a normal distribution for each of them, thereby reducing the uncertainties associated with the estimated data from field studies.

For example, the deterministic value for the concentration of NMOC is 2500 ppm, whereas its corresponding probabilistic outcome is in the range of 2499.1-2500.8 ppm (Figure 1). Similarly, the field studies estimate for the average annual refuse acceptance rate is 1000 mg/year, however; after Monte Carlo analysis, the outcome is now in the range of 999.2-1000.8 mg/year (Figure 2). Also, the estimated field value for the age of the landfill is 60 years, but its corresponding probability outcome is in the range of 59.08-60.85 years (Figure 3).

The total annual mass emission rate of nonmethane organic compounds after Monte Carlo analysis is in the range of 1.66 x 10^{-7} - 1.78 x 10^{-7} kg/year. This is however, not the same with the deterministic outcome which is a single value of 1.7218 x 10^{-7} kg/year. This probability distribution outcome provides information on the variability of the total annual mass emission rate of NMOC based on the variability of the concentration of NMOC, the age of the landfill and the annual refuse acceptance rate. For example, a comparison of the result of the probabilistic outcome of the total annual mass emission rate of NMOC, 1.66 x 10^{-7} - 1.78 x 10^{-7} kg/year, and the deterministic value that was obtained before, 1.7218 x 10^{-7} kg/year, indicates that the uncertainty in the concentration of NMOC, annual waste acceptance rate, and the age of the landfill have significant effect on the expected mass emission outcome of NMOC.

When considered in the context of exposure analysis, these results may imply important shifts in the overall exposure and health risk calculations; hence the reason uncertainty analysis was used to ensure a more representative and reliable exposure and health risk results.

5. Conclusions

- This study has demonstrated the utility of the Landfill Gas Emission Model for estimating the total annual mass emission of nonmethane organic compounds (NMOCs) especially when there is insufficient information (data) about the parameters of the landfill.
- The total annual mass emission of nonmethane organic compound was calculated from the model to be in the range of 1.66 x 10^{-7} - 1.78 x 10^{-7} kg/year. This probabilistic outcome is different from the deterministic value, 1.7218 x 10^{-7} kg/year, which was calculated from the field studies estimates.
- However, given that the field parameters used in the calculation of NMOC emission are highly variable, there is an accompanying realisation that the deterministic outcome which is a single value would be unrepresentative of the total annual mass emission of NMOC, which is expected to be variable. There is, therefore, a need for uncertainty analysis (i.e. Monte Carlo simulation) which results in the probability outcome – a more reliable and representative result of NMOC emissions.
- This result when compared to the standard of 50 mg/year (5.0 x 10^{-5} kg/year) implies that the mass emission of NMOC from the studied landfill is still below the acceptable level. However, given that this can accumulate to a dangerous level over time; it may have started affecting health of the people living within the vicinity of the landfill.
- It is therefore recommended that this type of study should be extended to other landfill gases such as CH_4, and CO_2.

References

[1] Bogner JE, Chanton JP, Blake D, Abichou T, and Powelson D (2010). Effectiveness of a Florida landfill biocover for reduction of CH4 and NMHC emissions. Environmental Science Technology, vol. 44, pp 1197-1203.

[2] Scheutz C, Kjeldsen P, Bogner JE, Visscher AD, Gebert J, Hilger HA, Huber-Humer M, Spokas K (2009). Microbial methane oxidation processes and technologies for mitigation of landfill gas emissions. Waste Management and Research vol. 27, pp 409-455.

[3] Scheutz C, Bogner J, Chanton JP, Blake D, Morcet M, Aran C, Kjeldsen P (2008). Atmospheric emissions and attenuation of non-methane organic compounds in cover soils at a French landfill. Waste Management, vol. 28, pp1892-1908.

[4] Streese J, and Stegmann R (2003). Microbial oxidation of methane from old landfill in biofilters. Waste Management vol. 23, pp573-580.

[5] Eklund B, Anderson EP, Walker BL, and Burrows DB (1998). Characterization of landfill gas composition at the Fresh Kills Municipal Solid-Waste Landfill. Environmental Science Technology, vol. 32, pp 2233-2237.

[6] Kjeldsen P, Dalagar A, and Broholm K (1997). Attenuation of methane and nonmethane organic compounds in landfill gas affected soils. Air and Waste management Association. 14: 1268-1275.

[7] USEPA (1991). Air emissions from Municipal Solid Waste Landfills – Background Information for Proposed Standards and Guidelines. U.S Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC.EPA-450/3-90-011a (NTISPB91-197061).
[8] Environmental Risk Limited (1995). Evaluation of air emissions at the Hartford Landfill. ERL Project No. 4100003346.
[9] Huber-Humer M (2004). International research into landfill gas emissions and mitigation strategy – IWWG working group “CLEAR”. Waste Management, vol. 24, pp 425-427.
[10] Boyle R, Witherington P (2007). Guidance on evaluation of development proposals on sites where methane and carbon dioxide are present. National House-BuildingCouncil (NHBC), Report No. 04.
[11] Mustafa MA (2010). Environmental Modelling and Health Risk Analysis (ACTS/RISK). Springer Dordrecht Heidelberg, London New York. ISBN 978-90-481-8607-5, DOI 10.1007/978-90-481-8608-2.
[12] Agency for Toxic Substances Disease Registry (ATSDR), (2001). Landfill gas primer. An overview for environmental health professionals [available online] URL: http://www.atsdr.cdc.gov/HAC/landfill/html/intro.html. Accessed 7th May, 2009.
[13] International Panel on Climate Change (IPCC), (2007). The physical science basis, Fourth Assessment Report, Working Group I. Cambridge: Cambridge University; http://www.ipcc.ch/ipccreports/ar4-wg1.htm.
[14] Katy, B., Helen, H., Lara, P., Don, B., and Cecilia, M, (2009).The VOCs Handbook: Investigation, assessing, and managing risks from inhalation of VOCs at land affected by contamination. CIRIA Report 766.
[15] West, O. R., Siegrist, R. L., Mitchell, T. J., and Jenkins, R. A., (1995). Measurement error and spatial variability effects on the characterization of volatile organic in the subsurface. Environmental Science and Technology, 1995, 29 (3), 647-656.
[16] IARC, (2004). International Agency for Research on Cancer (IARC). Overall evaluation of carcinogenicity to humans, IARC monographs vol. 1-88.
[17] Standards of performance for new stationary sources and guidelines for control of existing sources: Municipal solid waste landfills. Code of Federal Regulations, 61: 9905, March 12, 1996.
[18] USEPA (1998). Municipal Solid Waste landfills, volume 1: Summary of the requirements for the new source performance standards and emission guidelines for municipal solid waste landfills. U.S Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA-453/R-96-004.

Nwachukwu, Arthur Nwachukwu is a doctoral research student in the University of Manchester, Manchester, United Kingdom. He is also a graduate teaching assistant (GTA) in the School of Earth, Atmospheric and Environmental Sciences of the same University. He received his B.Sc. degree in Industrial Physics from Ebonyi State University, Abakaliki, Nigeria (2005) and M.Sc. degree in Environmental Physics from University of Agriculture, Makurdi, Nigeria (2009). His doctoral research in the University of Manchester focuses on how to derive a methodology for improved prediction of risk due to hazardous ground-gases. He is a member of different professional bodies such as Nigeria Institute of Physics (NIP), Nigeria Environmental Society (NES), British Organic Geochemists (student member), and Yorkshire Contaminated Land Forum (YCLF) United Kingdom.
E-mail address: arthurdeconvenantchild@yahoo.com

Diya, William Abigail received her M.Sc. in Medical Microbiology from the University of Agriculture, Makurdi, Nigeria (2009) and B.Sc. (Microbiology) from University of Jos, Jos Nigeria (2005). She is presently doing PhD in Medicine at the University of Manchester, Manchester, UK.
E-mail address: diya.abigail@yahoo.com