Environmental Challenges of Landfills and their Chemistry: Critical Analysis

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Abstract: Increasing population, urbanization and industrialization has increased the generation of waste manifold as also the need to dispose of this huge amount of waste. This has led to mushrooming of landfills which has now become a common landscape feature in many Indian cities

Landfill is an engineered site where waste is dumped till it is completely biologically, chemically and physically degraded. Modern landfills also known as sanitary landfills are well designed and engineered to avail leachate collection and treatment system a methane recovery system along with the baseliner to prevent the leakages of leachate into the underground aquifers.

As per World Bank report in 2016 the world produced 2.01 billion tons of waste which is estimated to increase upto 3.4 billion tons by 2050 an increase of almost 70% over a 30 year period. Another World Bank report in 2018 pegs India's per capita waste generation is 0.5 kg/day as compared to 0.7 kg/day at the global level; the bank also underlines the connection between economic development and waste generation indicating that the fast growth in Indian economy shall further increase the generation of waste at a faster rate. Landfills especially open ones without a proper base liner where soil below is in direct contact with garbage mound above produce toxic leachates due to various chemical reactions described here and carry heavy metals along with them percolating and contaminating underground aquifers and connected water bodies and rivers , these carcinogenic and mutagenic contaminants thus enter our food cycle, besides causing soil and water contamination , landfills also release toxic gases in air like dioxins and furans along with GHG gases like CH_4, CO_2 besides others like, H_2S. Efficient landfill management and leachate collection and its safe disposal are key to achieving Swachh Bharat mission aiming to keep our cities clean and free from soil , water and air pollution for a better and healthy life.

Index terms: Landfill, MSW (Municipal solid waste), aquifer contamination, Dioxins, Furans, hydrolysis, acidogenesis, methanogenesis, aerobic, anaerobic decomposition, fermentation leachates, trichloroethylene (TCE), Volatile fatty acids (VFA), carcinogenic, mutagenic, GHGs (Greenhouse gases), WTEs (Waste to recovery boilers), Geosynthetic Clay Liner (GCL), COD (Chemical oxygen demand) BOD (Biological oxygen demand)

I. INTRODUCTION

India's capital city Delhi generates waste 8500 metric tons per day which is disposed of in three landfill sites namely Ghazipur, Bhalswa and Okhla commissioned in 1984, 1994 and 1996 respectively ,all these three landfill sites have not been designed as per schedule 3 of the MSW rules which came into force in 2000 .They have also run out of space nearly a decade ago as the permissible limit for garbage dumping is not more than 20 m in height and the sites are well beyond their permission limits with Ghazipur, Bhalswa reaching as high as the height of Qutub Minar. They also lack proper leachate management system or a gas sucking system and therefore one can find waste burning at any given time in these landfills. These sites are therefore great environmental hazard causing soil and aquifer pollution due to leakage of leachates and air pollution due to release of dioxin and furans along with GHG gases. The first scientifically engineered landfill in Delhi was commissioned in 2011 in Narela Bawana which caters to 1300 metric tons of solid waste per day and his spare capacity.

II. CHEMISTRY OF LANDFILLS

MSW (Municipal solid waste) when first deposited in a landfill undergoes an aerobic decomposition in the first stage wherein a small amount of methane is generated and after a time lapse of about 1 year when the oxygen is depleted anaerobic decomposition takes place where in methane producing bacteria start decomposing the MSW to generate methane.

Bacteria in the landfill decompose the SMW waste in four stages or phases with the gas produced composition changing in each phase due to different chemical reactions happening in them. Multiple phases of decomposition may be overlapping in landfill at the same time. The total time and phase duration differs with landfill conditions and the type of MSW waste composition mix.

The various processes involved are hydrolysis, acidogenesis and methanogenesis which produce acetic acid and butyric acid to produce Methane.

The following diagram illustrates the changes in typical Landfill gas composition after waste placement in landfill.

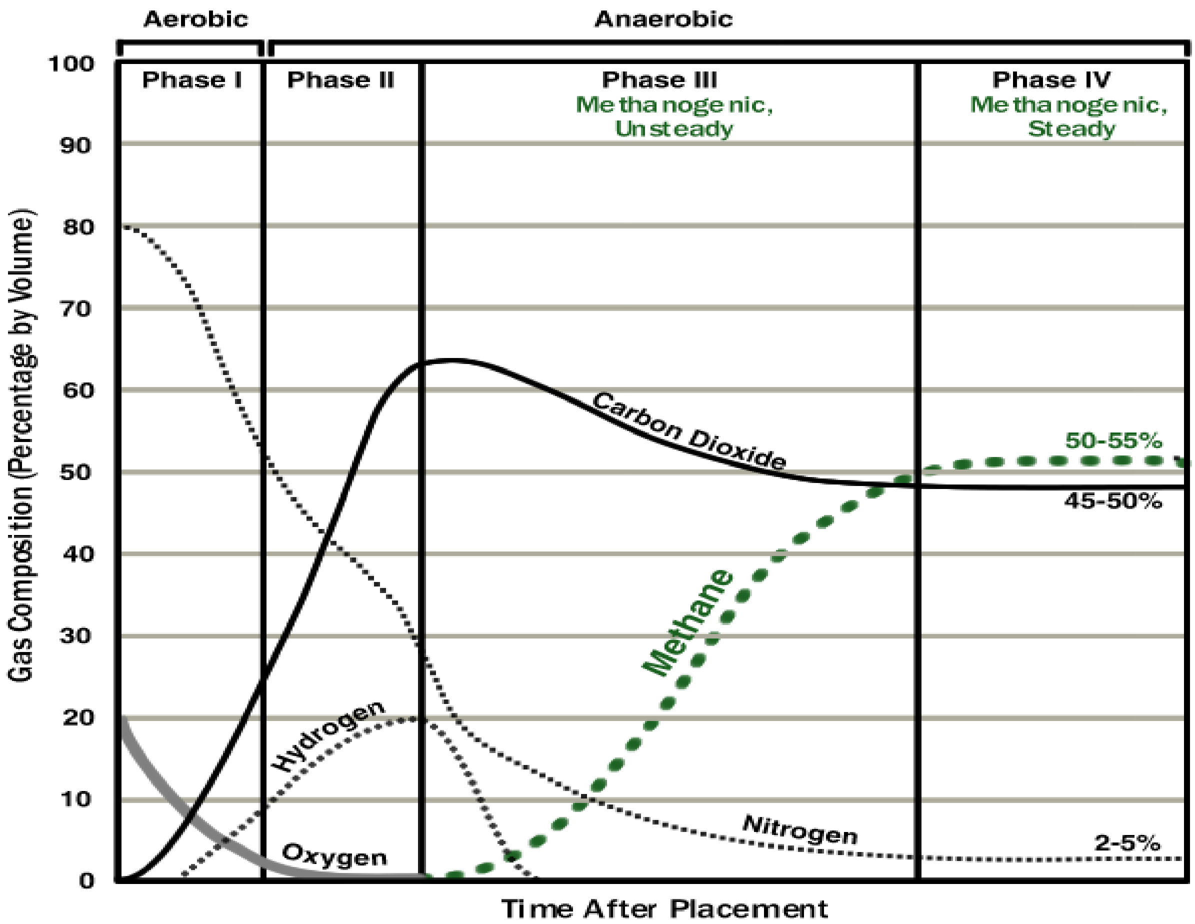


Figure adapted from ATSDR 2008. Chapter 2: Landfill Gas Basics. In Landfill Gas Primer - An Overview for Environmental Health Professionals. Figure 2-1, pp. 5-https://www.atsdr.cdc.gov/HAC/landfill/PDFs/Landfill_2001_ch2mod.pdf (PDF)(12 pp, 2MB)

The waste decomposition happens in 4 - 5 phases with the last one being the stabilization phase and the leachates are produced in each phase this phase is a described as below[1]:

Microbiological processes

Phase 1

The moisture in the municipal waste supports microbes which breakdown cellulose into soluble sugars and proteins into amino acids.

Polymers (Proteins Cellulose) → Amino acids, soluble sugars

For example

$$(C_6H_{10}O_5)_n + H_2O \xrightarrow{Hydrolysis} C_6H_{12}O_6 + (C_6H_{10}O_5)_{n-1}$$

Free soluble sugar is obtained during hydrolysis are used by bacteria to produce CO_2,H_2 and organic acid in the acidogenesis process.

Phase 2

After the oxygen is consumed the aerobic environment shifts to anaerobic one. COD (chemical oxygen demand) and VOAs (volatile organic acids) appear and can be measured in leachates at the end of this phase. Bio-degradable organic part in MSW is converted into volatile organic acids by microbes and the acid produced lowers the pH value in this phase.

Acidogenesis

The product of hydrolysis(soluble organic monomers of sugars and amino acids) undergo a fermentation process or are oxidized anaerobically by a process called acidogenesis in which is biodegradable materials like, protein, fats, amino acids and acetate undergo fermentation to form sugars, hydrogen, *and some* intermediates such as propionate, butyrate, lactate, and ethanol.

Degradation is carried out by acidogenic species of bacteria like, *Clostridium, Streptococcus, and Eubacterium limosum*, that transform sugars into intermediary fermentation products (Stronach et al., 1986) to produce alcohols and volatile fatty acids (VFAs) and acetate together with H_2 and CO_2 (Sambusiti, 2013).

Sugars and amino acids are converted to long chains of fatty acids which by *β-oxidation* are converted to VFAs (mainly acetate, propionate, butyrate), hydrogen (H_2), CO_2, and ammonia (lactate and alcohols may also be produced) via fermentative reactions like:

$C_6H_{12}O_6 \rightarrow 2C_2H_5\text{OH} + 2CO_2$

$C_6H_{12}O_6 + 2H_2 \rightarrow C_2H_5\text{COOH} + 2H_2O$

$C_6H_{12}O_6 \leftrightarrow 3CH_3\text{COOH}$

The degradation of amino and acids also liberates ammonia gas (NH_3). Bacteria like *Streptococcus, Desulfobacter*, and *Desulforomonas* convert amino acids to fatty acids, acetate, and NH_3 (Stronach et al., 1986). VFA production and composition

during and acidogenesis processes are affected by temp. and pH changes. (Temperature also affects the VFAs composition, observing a metabolic shift from acetic and propionic acids to butyric acid when the temperature increased)
The highest VFA production (4.6 gCOD/L) was obtained at 37 °C, while decreasing to 2.8 gCOD/L at 55 °C)
As a result of the acidogenesis process, volatile fatty acids, CO_2, H_2S and NH_3 are produced. The chemical equations associated with the acidogenic process are:

(Sugars) $\xrightarrow{Fermentation}$ VFA (Volatile fatty acids)

For example

$$C_6H_{12}O_6 + 2H_2O \rightarrow \underset{Butyrate}{CH_3CH_2CH_2COO^-} + 2H_2 + 2HCO_3^- + 3H^+$$

$$\underset{Butyrate}{CH_3CH_2CH_2COO^-} + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$$

$$Acetate$$

Phase 3 and 4: Methane Formation Phase

The Methane forming consortia responsible for conversion of intermediate acids into Methane and carbon dioxide in this phase. Increase in pH which causes the growth of methanogenic bacteria
Methane formation Phase

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$$

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$$

So, the chemistry chain in a landfill is summarised from above equations in various stages/phases as below:
Organic polymers like cellulose in MSW undergo $\xrightarrow{Hydrolysis}$ to form sugars & amino acids which then undergo $\xrightarrow{Fermentation}$ to form alcohols, Butyric & propionic acids which degrade $\xrightarrow{Anaerobically}$ into acetic acid and hydrogen which undergoes $\xrightarrow{Methanogenosis}$ to emit methane and carbon dioxide Greenhouse gases.

III. ENVIRONMENTAL ISSUES OF LANDFILLS

The three main issues with landfills that are causing soil, water and air pollution are:

(a) Production and leakage of leachates into the soil:

This is the biggest and most serious issue and challenge in the landfills. Since MSW contain large amount of wet organic waste, the chemical reactions in the presence of moisture and rainfall are responsible for production of leachates**.** The thick slurry of liquid garbage formed can penetrate soil and reach the underground aquifers and pollute rivers[2]. The toxic chemicals and heavy metals in these leachates ultimately enter the food chain causing damage to natural and human resources. These leachates contain heavy metals and toxic elements biodegradable organic compounds, nitrate, nitrite, calcium etc. As the leachate slurry seeps through the cross section of the landfill collecting the decomposed waste components, various chemical reactions are involved in the production of Leachates.

Toxic elements[3] and chemicals generally found in leachates include (1) Dissolved organic matter which interacts with organic and inorganic contaminants (2) heavy metals[4] like Ar, Ba, Se, Cu, Pb, Cr ,Cd , Ni, Zn, Hg coming mostly from the remnants of e-waste and dumped CFLs and with Cd , Cr and Pb coming from burning of plastics in landfills. Their concentration increases[5] during acidogenic phase when pH is low as heavy metals dissolve in low pH. (3) Inorganic elements[6] like Ca, Mg, Na, K, ammonium iron sulphate etc., their concentration depending on landfill phase for instance in methanogic phase when pH is high their concentration decreases (4) Xenobiotic organic compounds[7] like benzene, toluene, xylene, tetrachloroethylene, trichloroethylene (TCE). Trichloroethylene is used mainly as a degreaser for metal parts. TCE is carcinogenic and causes liver and kidney cancer and non-Hodgkin lymphoma.

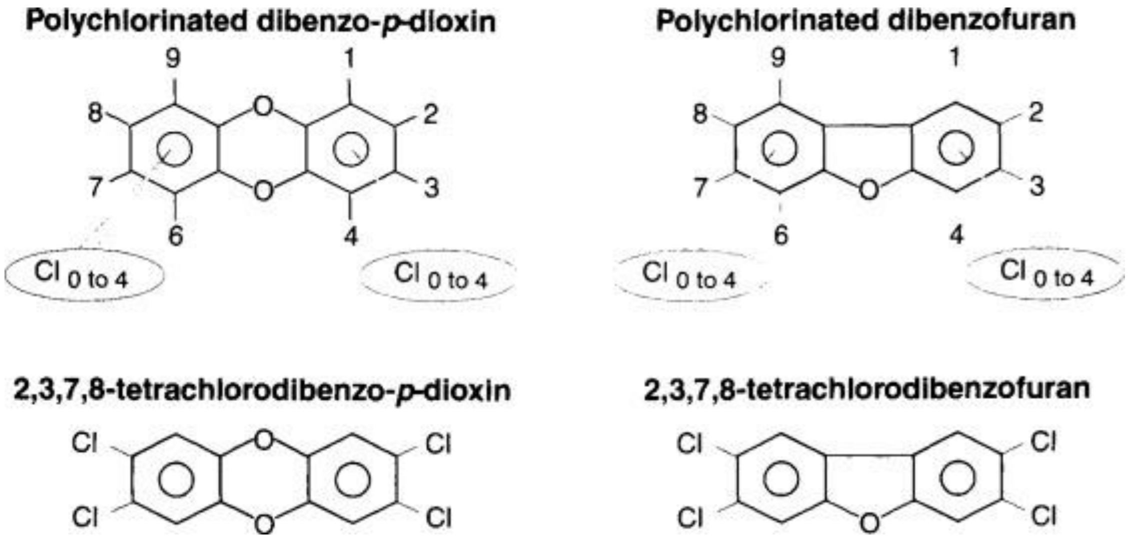
Ammonia is another important leachate that comes from decomposition of proteins in kitchen trash. The presence of above leachate ions in the soil disturbs the osmotic pressure making it harder for plants to absorb water from roots.The quantity and quality of leachate[3] depends upon the moisture content of MSW, its amount and composition, the degradation state and the landfilling technology.

(b) Emission of dioxins and furans which are highly carcinogenic and mutagenic in nature:

Dioxins and furans common name for a group of chemicals that are formed during the combustion of municipal solid waste (MSW) during spontaneous and uncontrolled fire in landfills, Plastic combustion in landfills releases toxic gases like furans and dioxins and polychlorinated biphenyls known as BCPs into the atmosphere.

The polychlorinated dibenzo-para-dioxin (PCDDs) and polychlorinated dibenzofuran (PCDFs) are two series of tri-cyclic chlorinated aromatic compounds with different levels of chlorine substitution in their parent molecules[8]

These persistent carcinogenic and mutagenic pollutants originate from combustion (Altarawneh et al., 2009) and their chemical and toxicological properties depend on the number and position of chlorine atoms bound to the two aromatic rings (Altarawneh et al., 2009). for instance the dioxin isomer with chlorine substituents in positions 2, 3, 7, and 8, or 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), is among the world's most toxic substances (Huang and Buekens, 1996; Assunção and Pesquero, 1999). Furan causes cancer.



Molecular structure and numbering system of polychlorinated dibenzo-p-dioxins and dibenzofurans.

It is important to note that dioxins do not exist in materials before they are burnt, they are formed when products which utilize chlorine and carbon in their making undergo combustion in landfills where they stay even after they are shut down since they have half lives up to 90-100 years

(c) Emission of GHGs :

Greenhouse gases carbon dioxide and methane are formed during various phases of landfill during methanogenesis and acidogenesis phases. On a 100-year timescale, methane has 28 times greater global warming potential than carbon dioxide and is 84 times more potent on a 20-year timescale.

IV. POSSIBLE SOLUTIONS

The three main environmental issues of landfills have possible solutions as below

(a) Design and engineering of landfills:

Modern sanitary landfills designs incorporate a leachate collection system and protective HDPE layers provided between the waste and the bottom ground below so that contamination of underground water aquifers by penetration of liquid leachates are minimized. In sanitary landfills with the protected bottom SMW is buried in layers and compressed to make it more solid with alternate layers of soil are provided which helps in faster decomposition and allow trapping of toxic gases released in the process. This soil is compacted to achieve 90% maximum dry density as obtained from proctor compaction test. The base of the landfill should have a gentle slope minimum 2% for draining of leachate and storm water The design and engineering of modern sanitary landfills is aimed at efficient management of leachate collection system such that there is no room for the penetration of liquids, and the collection from the landfill should be at a rate sufficient to prevent hydraulic head more than 12 inches at any point over the lining system. The bottom layer of sanitary landfill is compacted clay as clay doesn't allow water to pass through and an HDPE layer over the compacted clay layer. Geosynthetic clay liner (GCL) is used to create an impermeable barrier. GCL is actually a bentonite (calcium bentonite is commonly used in India) sandwiched between geotextiles and reinforced by HDPE liner so that leachates don't percolate into soil below. Further leachate management involves monitoring and assessment of leachate parameters like TDS, nitrate, sulphate, electrical conductivity, alkalinity, pH, BOD, COD, etc. and its treatment in biological reactors where aerobic and anaerobic processes are used to remove heavy metals before it is finally released in a safe manner. Latest leachate treatment Technologies use magnetic adsorbents and Nano materials for removing organic acids and heavy metals.

(b)***WTEs (waste to energy) incinerators*** :

These burn the trash to generate electricity, for example Ghazipur landfill in Delhi which receives 2000 TPD (Tonne/day) of trash and processes 1300 TPD to generate 433 TPD of RDF (refuse dry waste) which is fed into a WTE boiler operating at temperature above 1200-1400℃ so that Dioxins and Furans are not produced at these high temperatures. Steam produced in this boiler drives a steam turbine to generate 12 MW of power.

Of the total solid Municipal waste (SMW) that is coming to the landfills about 50% of the waste can be converted into compost and another 30% can be recycled so that only 20% ideally should reach the landfills. This requires segregation of wastes at the source at least in dry and wet parts. The dry garbage can then pass through trammel machines and then segregated further to recover plastics; glass, metals for recycling This should then decrease the load on landfills and thereby emission of GHG gases. Plastics, glass and electronic wastes can be recycled easily after segregation and construction and demolition wastes like ceramic, wood , concrete, asphalt can also be recycled to make grit , aggregates and pre-cast products for lining of roads and pavements. Plastics can be recycled to make blocks that can be used to build roads by laying , these have three times longer life than asphalt roads and can be repaired easily by simply changing blocks , the damaged blocks can be recycled again for use. Metals can be recovered by magnetic separation, density separation and eddy current separation.

V. CONCLUSION

Increase in population has led to increasing urbanization and industrialization and consequently the demand for manufactured products has increased this has led to increase of solid waste which is number one contributor to landfills for example paper, plastic, electronic waste, construction waste, hospital waste etc. eventually end up in the landfills as most of these materials are non-biodegradable. Use of plastics has increased exponentially in the last century and therefore the plastic pollution in urban areas forms a major part of the Municipal waste in the landfills. The decomposition of municipal waste in open landfill sites and various chemical reactions involved lead to production of toxic leachates that seep into the soil in open landfills and reach the groundwater aquifers and connected rivers thus entering human food chain a case for example is the Ghazipur landfill site in Delhi where leachates were found to be reaching as far as 3 to 5 km away from the site and high COD values were reported at Sanjay lake 4 km from the landfill site. Open landfill have no barrier between waste and soil allowing leachates to directly penetrate into the soil as there is no leachate collection system[9]

The new sanitary landfills are engineered to have a leachate collection system and gas discharge system and are covered with alternate layer of soil after the garbage dumping, these improvements although minimise the negative impact still do not rule out the possibility of their leakage after they build up garbage. Management of leachates is therefore the most important aspect of landfill management. The negative effects[7] of the landfills like gas generation may last up to 30 years even after they are shut down. Therefore, even sanitary landfills do not provide a durable solution to avert environmental pollution Segregation of wastes and their recycling is the only durable solution. Thus, circular economy where plastics, glass, construction and demolition wastes are recycled and organic wastes are composted into manures to achieve the desired objective of zero waste to landfill.

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