

A report on

**Impact of Leachate On Ground Water Quality Near
Okhla Landfill Site, New Delhi, India**

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(Environmental Engineering)

by

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Certificate

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Declaration of Originality

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Abstract

The quality of ground water in the areas adjacent to the solid waste disposal sites i.e. Okhla landfill was examined in order to evaluate interactions and the possibility of groundwater contamination as a result of percolation of the leachates generated in the Solid Waste Disposal sites. Leachate generated in the landfills tends to drift from the landfill waste resulting in contamination of groundwater and underlying soil consequently making landfills, the potential source of groundwater contamination.

An integrated approach to the examination was employed in the study. This included Ground water and leachate sampling; and laboratory-based instrumental and experimental analyses. Concentration of various physical parameters and chemical species determined in leachate samples and ground water and includes-pH total dissolved solids (TDS), Chemical Oxygen Demand (COD), Biochemical oxygen demand (BOD), Total Hardness (TH), Calcium Magnesium, chloride (Cl^-), Sulphate (SO_4^{2-}), Phosphate (PO_4^{3-}), heavy metals (Fe, Mn, Cr, Co, Ni, Cu, Zn, As, Cd, Pb). The measured concentrations of TDS (540 mg/l), Fe (0.46mg/L), Ni (0.06 mg/L), Pb (0.063 mg/L), COD (3.2 mg/L) is above the permissible limit in the ground water sample, which indicates that the leachate percolation has influence on the Groundwater quality. Further they can act as tracers for the groundwater contamination. Presence of heavy metals in leachate supports the toxicity data

The physical-chemical concentrations in groundwater samples were not as high as in leachate samples, thus indicating that chemical constituents in leachate are attenuated as they percolate through the aquifer into the groundwater system. Some remedial measures are also suggested to reduce further ground water contamination via leachate percolation.

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CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

Solid wastes are the inorganic and organic waste materials such as product packaging, furniture, clothing, kitchen refuse, grass clippings, paper, bottles, appliances, paint cans, batteries, etc., that are produced in a society, which generally do not carry any values to the first user. Solid wastes, hence, considers both a heterogeneous wastes mass from the urban community as well as homogeneous accumulation of industrial, agricultural and mineral wastes. Since the amount of waste generated increases rapidly, space for permanent disposal becomes crucial. As the production of solid waste is increasing much rapidly than it degrades, therefore land space for disposal has turn out to be more difficult and expensive to achieve. There are several waste management options that can be used to lessen the amounts of waste that requires land disposal. Incineration of solid waste may be used but this is expensive and the emissions are of health worry. This is reason why landfills remains the major solid waste disposal option for most countries. All the collected solid waste is dumped off in low lying areas at the landfill sites by conventional methods of dumping. Since the 1950s, over 12 large landfill sites have been packed with all kinds of toxic and non-biodegradable wastes. Presently, there are 3 landfill sites Gazipur, Okhla and Bhalaswa. None of their bases has been lined hence resulting in continuous contamination of groundwater.

The waste dumped consists of mainly inert materials and domestic garbage .There isn't any proper leachate collection and treatment arrangement at the aforesaid sites and hence leachate generated at these sites mostly percolate in the ground surface in absence of proper lining and the excess quantities of leachate gets accumulated in some low lying areas and some quantity of leachate also comes out of the boundary of landfill and flows into storm water drain or on the road surface which is a very unsafe situation from environment point of view. Leachate produced from the landfill site is highly toxic and responsible for the contamination of surrounding area, ground water and surface water

Solid waste in a landfill is degraded through anaerobic and aerobic processes. Stabilization of the wastes is a very complex phenomena and variable event because of site-specific characteristics of each landfill. The degradation products generated through the stabilization process includes leachate and gas. Landfill gases are generated because of the anaerobic biological degradation of organic materials. Leachate is formed water comes in contact with refuse. Water, mainly comes from precipitation, dissolves soluble inorganics and organics including some of the toxic compounds if present in the landfill materials. Leachate stream may be compared to a complex waste water stream with varying characteristics. A leachate characteristics not only vary because of the different kinds of waste present, but also differs according to the landfill age. Usually leachate from old landfills is rich in ammonia nitrogen due to the hydrolysis and fermentation of the nitrogenous fractions of the biodegradable wastes.

In India, ground water is one of the major source of drinking water and also indispensable source for living beings. Groundwater quality issues has become severe now days. These problems are already critical in cities and towns because the disposal facilities area is not keeping pace with the huge amount of waste that are generated. Thus, it is very common to find large heaps of garbage in disordered manner at most of the place in cities. Open dumping away waste is widely adopted throughout the world to get away of solid wastes. Such Insanitary method of disposing solid waste is a serious threat to human health. Principally, during rainy season, run-off and high humid conditions increase the health hazards [1]. Inefficient solid waste management (SWM) system and improper dumping of MSW (municipal solid waste) on exposed landfills, the ground water and surface water is found to be contaminated in various places at Delhi [2].

The landfill sites, which are not well maintained, are prone to groundwater contamination because of leachate infiltration. Leachate characteristics vary from one landfill to another, and over place and time. In a specific landfill, such variations depend on short and long-term periods due to variations in hydrogeology, climate, and

waste composition [3]. The main environmental problems at any landfill sites are the downward seepage of leachate and its subsequent contamination of the surrounding aquifers [4]. Subsequently, a need arises to formulate reliable and sustainable options to manage such leachate generation. Developments in landfill engineering are designed to reduce leachate production, collection and treatment prior to discharging in open dumping of garbage which further serves as breeding ground for disease vector such as flies, mosquitoes, cockroaches, rats and other pests. High risks of spreading diseases like typhoid, cholera, yellow fever, dysentery, encephalitis, dengue fever and plague may not be ruled out. There are 3 major steps involved in the management of the waste viz. collection, transport and disposal. The collection method currently adopted by the civic authorities is Hauled Container System (HCS) & Stationary Container. Transportation of garbage is carried out using trucks, tippers and refuse collectors with or without a transfer station. As discussed above, disposal of municipal solid wastes is generally done through land filling i.e. burring the waste under soil cover in the mantel of earth surface. The long-term options available in this regard are:

1. Disposal on the earth's surface,
2. Disposal deep below the earth's surface,
3. Disposal at the ocean bottom.

Disposal on the earth surface is mostly adopted method of ultimate disposal of solid waste material, nevertheless it represents the least desirable option from the point of view of waste management, and disposal on land will remain the best practical option for the foreseeable future. When waste is dumped on land, it slowly becomes a part of the hydrological cycle. During infiltration, waste water as well as during runoff of water from the surface numerous contaminants are removed from the waste to the adjacent areas as well as the strata below by the waste through the action of the percolating water known as leachate. The leachate is a highly obnoxious liquid & highly polluting substance. And it can have significant impact on the adjacent environment.

In the past, a large number of studies have been done to know this impact on ground water but still a great scope of further research is there. In the present study, an effort has been made in this direction to clearly understand this impact on ground water due to leachate nearby landfill area.

1.1 Aims and Objective of the Study

The major thrust of this study is to investigate the effects of landfill leachate on groundwater, the objective is proposed to be achieved in the following steps: -

- i) Assessment of contaminants to ground water.
- ii) Identification of the parameters of leachate quality which govern the pollution extent of groundwater.

1.2 Scope and Limitations

The present work is limited to the study of groundwater quality characteristics. To achieve this, groundwater samples were collected from tube wells situated near ESIC Hospital Okhla and were analysed to assess their physico-chemical characteristics. The analysed data has been compared with reference to BIS and WHO water quality standards to investigate the suitability of groundwater for drinking purposes. Although the subjects covered in the overall research work are indisputably wide in context, this specific study was undertaken with certain limitations such as assessment of microbial life forms and their importance on groundwater quality.

The methodology to follow in the present study is to select a site of an active landfill. After selection of site field sampling is required in which groundwater and leachate samples are collected from the site. The samples were then immediately brought to the laboratory and refrigerated. Laboratory study of the samples thus collected to find the ground water quality and the leachate quality was performed.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

Groundwater is considered second to surface water in terms of its significance for human use and the interest devoted to it by the general public and water sector managers [5]. Generally groundwater is a dependable and good quality water source. The history of global rigorous groundwater use is less than 50 years old and much of the modern rise in global water use has been fulfilled by groundwater. Groundwater use in the future will continue resulting in various environmental problems associated with the dehydration of aquifers and the socio-economic problems related to gradually unequal access, particularly in developing countries, to the resource as the groundwater levels drop and the aquifers become contaminated as a side effect of intensive use and generally increased pressure on natural resource. The rapid urbanization has exerted heavy pressure on land and water resources in cities resulting in serious environmental and social problems [6]. The characterization of the water quality includes a careful examination of the delicate interface between Biology, Physics, and Chemistry. The biological methods show the amount of ecological imbalance, while the chemical methods measure the concentration of the pollutants. The characterization and evaluation, as well as formulating methods for reduction of pollution level, requires a thorough study of these three components [7]. The international as well as national contributions on the study of quality of the water, through physical-chemical and heavy metal contamination of the water sources are explained below. An assessment of the comprehensive literature on this subject.

Delivers an insight into the deterioration of the water quality in ground as well as surface water. The variation in heavy metal contamination level seasonally for ground water samples in the Jimeta-Yola area. The aim of the investigation was to find out the seasonal deviation in heavy metal contamination and to see the impact of anthropogenic activities on heavy metal contamination. Samples of groundwater were collected from boreholes and hand dug wells between the rainy season and dry season periods. The ground water samples were examined using TDS/conductivity meter

membrane filtration method and DR/2010 spectrophotometer. Results showed that copper enrichment and chromium hexavalent occurred in the rainy season in the order of Cr^{+6} [8]. Investigation of the concentrations of Zinc and Calcium in different drinking water supplies of Dhaka City, Bangladesh. They concluded that the concentration of Cadmium(Cd) was below the detection limit in source water. A range of 1.03 to 1.58 and 1.71 to 2.24 parts per billion(ppb) in supply water(tap water and tube well water) respectively and that the Zinc content ranged from 0.013 to 0.30, 0.018 to 3.8 and 0.042 to 0.37 mg/L [9].The conclusion of waste water from a landfill disposal site at Koszalin, in Poland, to be one of the reason of enhanced groundwater pollution level, predominantly by heavy metals and that a reduction in the concentrations of Copper, Zinc, Lead and Manganese in the effluents during certain period was shown in the lower levels of concentrations in the ground water [10]. The water quality status of Yamuna for bacteriological analysis in a river in Delhi. Their study reveals the impact of diverse anthropogenic activities as well as the monsoon effect on the bacterial population of river Yamuna in Delhi stretch. Microbial population contributed mainly through human activities prevailed in the entire stretch of Yamuna River with reduction in bacterial counts during monsoon period due to flushing effect [11]. The study of groundwater and soil contamination as a result of sewage sludge land application. He evaluated leaching of chemical compounds (NH_4^+ , PO_4 , SO_4^{2-}) and trace elements (Cd, Cu, Pb, Cr, Ni, and Zn) from sewage sludge and their movement through the soil profile. He revealed that nitrogen compounds, such as ammonium (NH_4^+) and nitrate (NO_3^-) as well as some heavy metals (Cd and Ni) coming from the sewage sludge can reach deeper than 0.8 m and cause the contamination of shallow aquifers [12]. Landfills are the major pollution causing source in the urban environments. The leachates which are generated from the landfills and dumped in open pollute the ground water and possesses the health risks. Because to this landfill are most studied worldwide. Leachate generation and ground water and soil contamination is widely studied all over the world. The groundwater pollution and compositions of landfill leachate at bb landfill, Yemen. They concluded that some bore wells water sample were contaminated with landfill leachate, because the concentration of physico-chemical parameters is above the standard acceptable levels

[13]. Characterization of leachate and groundwater pollution assessment near MSW landfill site. Leachate and groundwater samples was collected from Gazipur landfill-site and from vicinity of landfill area respectively in Delhi so that the possible impact of leachate percolation on groundwater quality can be investigated. They concluded that moderately high concentrations of chemicals in groundwater, probably indicate that groundwater quality is being affected by leachate percolation [14]. Effect of Municipal solid waste leachate on underground water resources has been studied [15]. The contamination of groundwater around two solid waste dumping sites in Lagoos, Nigeria. They were in view that the water around most of the dumpsite areas surpassed the acute and chronic effect levels given by the United States Environmental Protection Agency in 2010 [16], investigated the ground water quality at the vicinity of the waste disposal sites in the eastern part of Kolkata. They came to conclusion that Hardness, Chloride, and total dissolved solids in samples under investigation were having significantly higher value than the stipulated standard values [17]. Various characteristics of leachates from municipal solid waste landfill sites in Inbadan, Nigeria. It has been also reported that the variation in the quality of leachate during dry and wet season. Finally, it has been concluded that SWM has been a very serious problem in urban cities. Disposing wastes to dumpsites for disposal yield leachate, which causes serious problem through polluting the nearby land and water resource [18], also it has been examined the effects on the quality of underground water by solid waste in Benin metropolis, Nigeria. Upon study, they suggested that solid waste needs to be recycled instead of taking them to dump sites directly and there is urgent need for environmental awareness through education campaigns [19]. Chemical, physical and toxicological characteristics of leachate has been investigated [20] and reviewed the literature on the quantity and physico-chemical characteristics of leachates from municipal solid waste (MSW) landfills.

Composition and treatment of leachates had been by studied from sanitary landfills and recommended that leachate treatment method which is being employed for landfill leachate depends mainly on the age of the landfill. For young landfill, biological

treatment is sufficient but for old leachate physical chemical treatment is required [21].

Leachate Pollution Index (LPI), a tool used to quantify the landfill leachate pollution had calculated LPI for Okhla landfill, New Delhi. The Calculated LPI value of 42.181 for the Okhla landfill site was more when compared with the standards set for the treated leachate LPI value (7.378) by the “Municipal solid waste management and handling rules 2000” [22]. From the obtained results, it was determined that a single number index value which reflects the influence of composite significant pollutant variables on pollution by leachate is possible and it can yield a significant, uniform method of evaluating the leachate contamination potential of landfill site at any particular time. The Leachate Pollution Index value of Okhla landfill was comparatively high and therefore proper treatment would be required before the discharge of the leachate.

Potential of leachate contamination of two active and two closed landfill sites was studied in Hong Kong by using Leachate Pollution Index [23]. It has been observed that the leachate produced from the closed landfills can have equal or more contamination potential in contrast to the active landfill sites and hence, the remediation process and post-closure monitoring should be safeguarded at the closed landfills till the leachate produced is stabilized and poses no further risk to the environment.

Analysis of Physico-chemical parameters, heavy metal concentration, microbiological parameters in ground water samples and leachate that has been collected from Gazipur landfill site and its nearby area. High concentrations of nitrate, chloride, sulphate, ammonium, iron, phenol, zinc and COD, BOD in groundwater indicated effect of leachate infiltration [24]. The effect of distance and depth of the well from the pollution source was also studied. By the presence of total coliform and fecal coliform in groundwater they concluded that, aquifer water samples are unreliable for domestic and other uses.

Periodic monitoring of quality of leachate has been conducted at two big dumpsites in Chennai, India and four minor dump sites in Sri Lanka. The leachates were monitored for changes in pH, TDS, DOC, COD, EC, BOD, Ammonium nitrogen, Chloride and heavy metals. Two bigger dumpsites in Chennai showed LPI values of 12 and 10 respectively whereas four smaller dumpsites in Sri Lanka had 13, 18, 21, and 23 LPI values [25]. From the results so obtained it was concluded that smaller dumpsites had high pollution potential associated with it in terms of leachate characteristics.

Landfill leachate and groundwater contamination has been studied at Ibb landfill, five bore wells and leachate samples were analysed which were obtained during wet season. The results showed that out of five boreholes samples, four of them were contaminated; the physical and chemical parameters of water samples were above the standard permissible limits of Yemen's Ministry of Water and Environment [26].

Analysis of heavy metal (Cd, Cr, Fe, Cu, Mn, Pb and Zn) Concentrations in samples of ground water near landfill site in Alimoso State, Nigeria. Except Mn and Cr all other heavy metals were present in water samples, mean concentrations of various measured parameters were outside the WHO permissible limits for drinking purposes [27]. From the study, it has been recommended to the government for a detailed study of the ground water flow direction in the area, so that it can clarify the people to locate well. Adjacent to municipal solid waste landfill area, ground water and leachate samples were analysed for physico chemical and microbiological parameters.

Important parameters in water samples like pH, EC, TDS, Na and Fe were exceeding with WHO limits. High population of *Enterobacteriaceae* has been also found which indicates contamination. But they find out that landfill leachate has a minimal impact on the groundwater as the site consists of clay, which reduces the natural attenuation of leachate into ground water [28].

An attempt has been made to develop water quality index by knowing hydro-geochemical parameters of 148 groundwater samples, which was collected during pre-

monsoon and post monsoon seasons of Thirumanimuttar sub basin in Tamil Nadu. The hydro- geochemical investigation indicated that alkalis (Na and K) exceed alkaline earth (Mg and Ca) and strong acids (SO_3 and Cl) exceed weak acid (HCO_3). From Water quality index rating, pre-monsoon samples were considered as poor quality with higher percentages compared to post-monsoon season, due to agricultural impact and discharge of effluents [29]. The seasonal variation in Heavy metal contamination of groundwater in the Jimeta- Yola area has been investigated. The aims of the study were to determine the seasonal variation in heavy metal contamination and to find out the influence of anthropogenic activities on heavy metal contamination. Samples from ground water was collected from hand-dug wells and boreholes between the dry season and rainy season periods. These samples were analysed using the DR/2010 Spectro-photometer, TDS/conductivity meter and membrane filtration method. The results shown that chromium hexavalent and copper enrichment arisen in the rainy season in the order of Cr^{+6} [30].

Chapter 3

Generation of Leachate

Chapter 3

Generation of Leachate

Leachate is a liquid that drains or ‘leaches’ out from a landfill site. It varies extensively in composition regarding the ages of the landfill and the kind of waste that it contains. It usually contains both suspended and dissolved material. The leachate composition from the transfers station can differ widely depending on several factors, including the degree of compaction, waste composition, climate and moisture content in waste. Leachate generation from landfills effects landfill, operations and design. Leachate generation is affected by waste type, the local weather and the landfill working methodology. It can be visualized that for a landfill to be a bio-chemical reactor with water and solid wastes as the main inputs and leachate and landfill gases as the main output. A leachate control system has been used at all engineered landfills so as to prevent undesirable movement of such outputs, vertically downwards and horizontally into the surrounding soil.

Leachate is produced on account of the seepage of water into landfills and its percolation through the waste as well as by the pressing of the wastes due to its self-weight. Therefore, we can define leachate as a liquid that is produced when water or some another liquid comes in contact with solid waste. Leachate is a very polluted liquid that contains a large number of dissolved and suspended materials. Some part of the precipitation that falls on a landfill site reacts with the solid waste while infiltrating downward. During this infiltration processes, some of the constituent get dissolved in water with the help chemical reactions. The infiltrating water may also dissolve the liquid that is pressed out due to heavy waste weight. It can be observed that even though when no water is allowed to infiltrate through the wastes, a certain portion of polluted liquid always percolate through the waste, expected to be formed due to some biological and chemical reactions. The concentration of chemical compound in such liquid is expected to be very high. The percolating water dilutes these contaminants in addition to formation of leachate. Landfill leachate is widely recognised as one of the most significant source of ground water pollution. Leachate is generated as a result of

the bio-chemical decomposition of organic substances within the deposited waste materials, and the washing out of organic and soluble minerals constituents by precipitation and water runoffs [32-34].

Process Flow of Leachate Formation has been shown below.

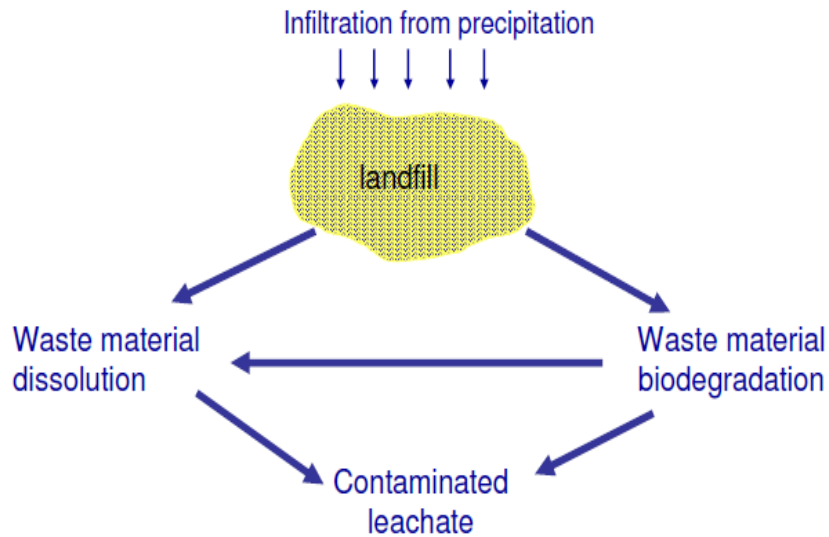


Fig 3.1 Mechanism of Leachate Formation

3.1 Leachate Quantity

Leachate quantity generated in a landfill is directly reliant on on the quantity of infiltrating water. This in turn, is dependent on operational practices and weather. Quantity of leachate generated is controlled by the amount of precipitation falling on a landfill to a large extent, which (precipitation) depends upon a number of climatological factors. Occasionally the landfill base is constructed below the ground Water Table In such types of landfills groundwater intrusion may also surge leachate quantity noticeably due to operational practices.

Leachate quantity generally increases if the waste discharges pore water due to squeeze action by overlying layers of the waste over landfill. Waste continues to absorb water if it is unsaturated until it reaches Field Capacity (FC). Therefore, dry

waste will reduce leachate formation. Nevertheless, in certain cases development of water channel may affect the water to flow over the waste without being absorbed by the it. Hence the quantity of leachate generated is dependent upon a large number of factors few of which can be summarized as follow:

- (i) Landfill surface condition
- (ii) Geology of the landfill site
- (iii) Water availability at landfill site
- (iv) Refuse state

Knowing of each of the above listed factors will helps us to determine the water balance equation, a basic version of which is shown below:

$$L_o = I - E - a * W$$

Where,

L_o = Free Leachate retained at site

E = Evapotranspiration losses occurring

a = Absorptive capacity of the wastes

W = Weight of waste deposited at site

I = Total liquid input

An efficient landfill practice normally demands negative or zero L_o meaning thereby that no leachate is generated

3.2 Leachate Quality

The important factors which effect leachate quality includes waste composition, temperature, elapsed time, oxygen and available moisture. Generally, leachate quality of the same waste type differs from landfills to landfills located at different climate regions. Besides, landfill operational practices have also influential effect on leachate quality. Differences in waste composition are significant in municipal solid waste.

Owing to which, the quality of leachate differs widely. There is variation on leachate quality over time also. As said, leachate quality generated in the first year will be weaker than that generated in succeeding years. The overall leachate quality reaches a peak value after sometimes and then decreases gradually.

The temperature also influences leachate quality at landfill. Temperature affects both chemical reactions and bacterial growth. Sub-zero temperatures freeze some waste mass, which decreases the leachable waste mass and may cause some chemical reactions to stop. Higher temperatures usually cause speeding up of reactions. Water also plays an important role in biodegradation of waste and following leaching of chemicals. Quality of leachate from disposed waste in a wet climate is probable to be different from the leachate quality of the same waste disposed in a dry climate because of availability of different amounts of water.

3.3 Leachate Composition

Leachates are extremely contaminated solution, it encompasses both organic and inorganic components that comes directly through dumped solid waste materials. Leachates are generally known to have significantly some more contaminants physical chemical parameters than many raw sewage or industrial wastes. The quality of leachate varies widely dependent on a sequence of complex but interrelated factors. Though, there are certain constituents that are found to nearly all landfills, yet at different concentrations.

As a general rule, leachate is characterized by high values of ammonia nitrogen, pH, and heavy metals, COD, as well as bad odour and strong colour. At the same time, leachate characteristics also vary with respect to its composition and volume, and amount of biodegradable matter present in the leachate against time. All of these factors do makes leachate treatment very difficult and complicated. In such a landfill that receives a mixture of commercial, municipal, and mixed industrial waste but has no significant quantity of concentrated chemical wastes, a landfill leachate can be characterized as a water-based solution of mainly four groups of contaminants:

inorganic macro components (common cations and anions including sulphate, aluminium, iron, zinc, chloride, and ammonia), dissolved organic matters (alcohols, aldehydes, short chain sugars, acids etc.), heavy metals (Pb, Cu, Ni, Hg), and xenobiotic organic compounds such as halogenated organics,(dioxins, etc.)

As emphasized in the following sections, the parameter levels are used to specify the quality of landfill leachate and its polluting potentials overall. In this study, more emphasis is placed on inorganic parameters due to their solubility; therefore, discussion of organic constituents is very limited

Table 3.1 Leachate Parameters [31]

Constituent Group	Parameters
Physical	pH, Electrical Conductivity, Colour, Redox Potential, Turbidity, Total Dissolved Solids, Suspended Solids, Volatile Dissolved Solids Volatile Suspended Solids Temperature, Odour
Organic	Total Organic Carbon, Phenols, Chemical Oxygen Demand, Tannins, Lignin's, Organic Nitrogen, Hydrocarbons, Ether Soluble, Volatile Acids, Methylene Blue Active Substances, Chlorinated and Another Organic Chemical
Inorganic	Sulphate, Nitrate-N, Nitrite, Sodium, Phosphate Ammonia-N, Chloride, Potassium, Calcium, Hardness, Heavy Metals (Pb, Cu, Ni, Zn, Cd, Fe, Mn, Cr Hg, Ba, Ag).
Biological	Faecal Streptococci, Biological Oxygen Demand Standard Plate Count, Coliform Bacteria, (Total and Thermotolerant or Faecal)

It is a reason for worry that, despite many advancements in the modern landfill technology in terms of leachate production management and migration (that happens mostly in more developed countries), leachate often tends to migrates out of landfill site and percolates to the ground water aquifers or overflows to the areas nearby the disposal sites [32]. Above processes poses a huge threat to the sustainability of the surroundings soil and qualities of water resources. The following sections presents

short reviews of some major constituents which are present in leachates. As stated earlier, due to the limitations in scope, this research work has endorsed more importance to the inorganic chemical and physical components of the leachates. There are only brief mentions of bacteria and viruses, whose contamination level in groundwater are likely to eventually decline and die-off over time as water flows through the soil due to seepage, and hostile environments.

3.1.1 Ions

In landfill leachates, a huge number of ions are reported present, some of the major ones which are often studied and reported by many consist of the cations: Mg^{2+} , Fe^{2+} , Na^+ , Mn^{2+} , Ca^{2+} , K^+ , NH_4^+ , SO_4^{2-} , HCO_3^- , and Cl^- . Also, the amount and fractional distribution of each of these ions in leachate vary significantly depending on a large number of factors, such as; waste composition, the quantity of the infiltrating water, and degree of waste stabilisation. After the leachate is released into the environment, the distribution and amount of each major ion within will be influenced significantly by the interactions of the leachate with the receiving aquifer minerals and water.

3.1.2 Trace Elements and Heavy Metals

Besides to some major ions, a considerable amount of other organic and inorganic elements does exist at small concentrations in the leachates at landfill sites. These are mainly derived from the contents of the waste materials which are deposited in the solid waste disposal site, however a small amount could also be presents from the aquifers solid in the reducing environment of leachate plumes. Some examples of few of which are usually reported trace elements include heavy metals Pb, Zn, Cr, Ni, Cu, and Cd few of these are regulated by some strict water quality standards because of the toxicity effects associated with it. From many researchers, it has been confirmed that in leachates the concentrations of heavy metals are generally very low. Still, they may constitute a substantial environmental threat, even though a very low concentrations (ppb) do get leached into groundwater or surface water resources. Even though their relative abundance in leachate do differs between different landfills, the

characteristically reported heavy metals in leachates include: Cd, Zn, Cu, Pb, Cr and Ni. Even though, when a substantial quantity of metal waste may be present in the landfills leachate, it is assessed that after many years only a small fraction is leached. Heavy metals solubility in leachates is affected by many factors such as: pH, ion exchange capacity and redox potential the waste mass [33].

3.1.3 Dissolved Organic Matter

Study of landfill leachate dissolved organic matters consists of a large number of parameters covering a variety of organic degradation products ranging from humic-like compounds to small fractions of volatile acids to refractory fulvic that may form the bulk of the products of intermediate degradation of some organic waste materials in solid waste disposal sites. The concentrations can be best described using the parameters; Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC). Organic matter in dissolved form can have a vital influence on the attenuation and mobilisation of various contaminants. These act as medium for microbial-mediated redox reactions, and may increase the mobility of heavy metals in solution via complexation with organic ligands and sorption onto Organic colloids [34].

3.2 Migration and Fate of Leachates in Hydrologic

3.2.1 Environment

Landfill leachate upon release into an aquifer environment, undergoes a number of biochemical processes and physical process that attenuate its pollutant concentrations within the groundwater as it travels in the aquifer. The destiny of viruses and microbial contaminants in the environment is mainly affected by filtration and die-off, whereas the co-existing chemical contaminants are attenuated by a number of processes that are presented briefly in the following sections.

3.2.2 Dilution

Even though the process of dilution moderates the concentrations of contaminants by dispensing them across larger volumes of water, dilution will result in a noticeably enhancement in the volume of the impacted groundwater. Dilution process of interaction between groundwater flow and leachate within an aquifer is mainly responsible for the development of leachate plume. Constituents of leachate are subjected to dilution as they migrate from the landfill to form a leachate plume. This is true in the case of conservative species, for example chlorides, where dilution characterizes its only attenuation mechanism.

3.2.3 Degradation

Degradation process in leachate plume takes place when dissolved organic matters go through a microbial-mediated oxidation process so as to form benign end-products. Mostly, this process forms redox conditions in the leachate plume, which has significant influences on the other mechanisms of attenuation within the plume

3.2.4 Dissolution/Precipitation

In a leachate plume, the mechanisms of precipitation of the aqueous species present and dissolution of aquifer minerals are closely related to the dominant redox processes occurring within the leachate plume system. Above mechanisms are important to the mobilisation and attenuation process of major ions in the plume, particularly in relation to Ca^{2+} , Fe^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , S^{2-} and HCO_3^- . The partial pressure of CO is significantly high in leachate which increases the dissolution of carbonate minerals within the aquifer, causing in significant rise of concentrations of Mg^{2+} , HCO_3^- and Ca^{2+} ions in the solution.

3.2.5 Formation of Chemical Complexes

As a process of formation of complexes from the combination of anions, dissolved organic molecules and cations, complexation in leachate plume can act in both ways

as mobilisation or an attenuation process, which depends on the type of complex formed. Principally, the complexation process smoothens the mobility of metals, such as Cr, Pb and Ni, since metal complexes can continue to remain soluble in conditions that normally would cause in their precipitation. Additionally, complexes of the major cations decrease the saturation indices of few minerals, which encourage increased dissolution of the minerals. In terms of attenuation, nevertheless, complexation applies mainly to the condition of surface complexation of soluble cations onto aquifer solids

3.2.6 Sorption Reactions and Element Partitioning

Sorption processes are the surface-related chemical and physical reactions accountable for binding dissolved species to solid phase minerals and organic matters, including absorption, adsorption, chemisorption, ion exchange and surface complexation. Sorption processes represent the principal means of attenuation of organic contaminants in plume of leachate unto aquifer materials.

Dissolved elements will practically completely partition onto organic carbon surfaces when organic carbon fraction mass of the aquifer material is more than 1%. Even though the sorption process provides a mechanism for the dilution of heavy metals, it can increase the transport of the metals in solution which has been adsorbed onto surfaces of organic colloids by decreasing meaningfully their affinity to precipitation or adsorption onto immovable organic matter in the aquifer on the other hand, ion exchange will occur when the weak electrical charge on the surfaces of clay minerals in the aquifer attracts and binds ions of the opposite charge. Though anion exchange is possible under acidic conditions, usually, the mechanism of ion exchange is more or less completely related to cations. It is so because, in natural water pH of neutral range exists in most natural waters, hence clay mineral surfaces are usually negatively charged. In nature, when there are no substantial variations in water chemistry, ion exchange surfaces are frequently saturated with the dominant ion in the system [35].

3.2.7 Redox Transformations

In general terms, redox reactions are processes that include transfer of electrons, through which an electron donor (reductant) gets oxidised and an electron acceptor (oxidant) gets reduced. In ground water systems, redox reactions are assisted primarily by bacterial respiration, in which the energy which is supporting their physiological processes is obtained from the flow of electrons. In nature, pristine groundwater environments are reducing, while pollution related activities create oxidizing conditions. Therefore, as the strongly-reduced leachate gets mixed with pristine, often oxidised groundwater aquifers, gives a complex redox environment. This environment influences intensely both the organic and inorganic biogeochemistry of the aquifer, and generates the chemical framework for understanding the transport pathways and attenuation processes, fate of the contaminants in leachate plume.

CHAPTER 4
PHYSICO-CHEMICAL CHARACTERISTICS
OF GROUNDWATER

Chapter 4

Physico-Chemical Characteristics of Groundwater

This chapter presents the physico-chemical characteristics of groundwater sources nearby Okhla landfill near Employee State Insurance Corporation Hospital. The chapter is based on the findings of quality analyses of groundwater samples collected in the proximity of Okhla landfill solid waste disposal site. Groundwater is used extensively for domestic and commercial purposes, often without any form of treatment in the area.

Against this background, this investigation aims to contribute to revealing the groundwater quality situation in the area, with a view to an evaluation of possible contamination as a result of the indiscriminate locations of SWD sites across the metropolis. In line with the objectives of the research, this chapter forms an important component in the overall process of assessing the interactions between SWD practices and groundwater sources in the study area.

Groundwater samples were collected from borehole nearby Okhla landfill site. These samples were stored in refrigerator at temperatures below 5°C and then transported immediately to the laboratory for analyses of physico-chemical parameters that included; turbidity, pH, total chloride, dissolved solids, total hardness (TH), Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , Cu^{2+} , Fe^{2+} , Mn^{2+} , Pb, Cr, Zn. This chapter discusses the groundwater compositions in comparison with the World Health Organisation (WHO) that has recommended guidelines for the drinking water quality. The key aspects covered in the chapter include: analytical physico-chemical data of groundwater samples studied, and evident variations and possible contaminations in the sampled groundwater sources.

4.1 Groundwater Vulnerability to Pollution

As a natural characteristic of any area, vulnerability of groundwater to pollution means that certain combinations of the geological and the hydrological parameters will give

rise to such a situation where a groundwater aquifer system is more at risk from any source of pollution than other combinations. In nature, all groundwater aquifers are linked hydraulically to the overlying land surfaces through the complexly interwoven pore fringes. Therefore, the degree of vulnerability of any aquifer to contamination depends to a greater extent on the effectiveness of this inter connection. Subsequently, groundwater that quickly and readily receives water and contamination from such land surface is therefore considered to a greater extent more vulnerable than groundwater that receives water and the contaminants more slowly and in lower quantities. In line with this, the WHO has classified groundwater vulnerability into four broad categories, as defined in the below table 4.1.

Table 4.1 Classes of Groundwater Vulnerability to Pollution

Class of vulnerability	Definition
Extreme	Vulnerable to the most water the pollutants with a relatively quick impact on many pollution scenarios
High	Vulnerable to the many pollutants, except those that are highly absorbed and/or that are readily transformed, in many pollution scenarios
Moderate	Vulnerable to some pollutants, but it is only when continuously discharged or leached
Low	Only vulnerable to the most persistent pollutants in very long-term, when are continuously and widely discharged or leached
Negligible	Confining beds are present and hence prevent any significant groundwater flow

Generally, groundwater quality depends mostly on the relative quantity of the contaminants that reaches the aquifer, the contaminant attenuation capacity of the geological system and the travel time of groundwater and contaminants. Moreover, the degree to which the attenuation occurs also depends on the type of rock and soil, the

types of contaminants and their associated activities. Hence, any effort to prevent, remedy and control groundwater contamination in any area requires, among other such things, adequate understandings of the natural intrinsic characteristics of the aquifer that defines its vulnerability to the contamination, as well as the background information of such activities in question.

4.2 Major Sources of Groundwater Contamination

As one of the most pressing global environmental challenges, problems of groundwater contamination are complicated by many varied sources and chemistry. Very often, groundwater contamination does occur as a result of many anthropogenic activities that are subjected to the degree of vulnerability of the targeted aquifer to such activity. The major sources of groundwater contamination include, but are not limited to:

1. Municipal sources that include sewage effluent, septic tanks sewage sludge, sewer leakage, Urban runoff, landfill, latrines.
2. Agricultural sources that encompass pesticides, leached salts, fertilisers, animal wastes.
3. Industrial sources that includes Hydrocarbons, water treatment, plant effluent, process waters.
4. Mining sources that cover liquid mining wastes activities and solid.

To determine the extent of contamination it will requires a multitude of physical, chemical and sometimes biological parameters for both the porous medium and the concerned contaminant. A summary of the major sources of groundwater contamination with a description of some of the associated health risks is provided in the below table 4.2.

Table 4.2 Major Sources of Anthropogenic Groundwater Contamination and Some Key Characteristics

Pollution Category	Pollution Source	Main Pollutant	Potential Impact
Municipal	Sewer Leakage	Nitrate, viruses and Bacteria	Health risk to users, odour and taste, eutrophication of water bodies,
	Septic tanks, cesspools, privies	Nitrate, minerals, organic compounds, viruses and bacteria	
	Sewage effluent and sludge	Bacteria and viruses	
	Storm water runoff	Bacteria and viruses	Health risk to water users
	Landfills	Inorganic minerals,	eutrophication of water bodies, odour and taste, Health risk to users,
		Organic compounds,	
		Heavy metals,	
Bacteria and viruses			
Cemeteries	Nitrate, viruses and Bacteria	Health risk to users	
Agriculture	Feedlot wastes	Nitrate-nitrogen-ammonia, viruses and bacteria	Health risk to water users (e.g. Methemoglobinemia)
	Pesticides and Herbicides	Organic compounds	Toxic/carcinogenic
	Leached salts	Dissolved salts	Increased TDS in Groundwater

	Fertilizers	Nitrogen, phosphorous	Eutrophication of water Bodies
Industrial	Process water and plant effluent	Organic compounds,	Carcinogens and toxic elements (As, Cn)
		Heavy metals	
	Industrial landfills	Inorganic minerals,	odour and taste, Health risk to users, eutrophication of water bodies,
		Organic compounds,	
	Heavy metals,		
	Bacteria and viruses		
	Leaking storage tanks (e.g. petrol stations)	Hydrocarbons, heavy Metal	Odour and taste
	Chemical transport	Hydrocarbons, chemicals	Carcinogens and toxic Compounds
	Pipeline leaks		
Atmospheric Deposition	Coal fired power Stations	Acid precipitation	Acidification of groundwater and toxic leached heavy metals
Mining	Mine tailing and Stockpiles	Acid drainage	May increase concentrations of some compounds to toxic level
	Dewatering of mine shaft	Salinity, inorganic compounds, metals	
Groundwater Development	Salt water intrusion	Inorganic minerals	Steady water quality Deterioration
		Dissolved salts	

4.3 Water Quality Standards and Guidelines

It aimed mainly to protect public health and aquatic lives, hence water quality standards and guidelines is established by every country to normalize the levels of contaminants to be permitted in their various water resources. This consist of the water body's uses, and water quality criteria to protect those uses and hence determine if they are being attained or not, and anti-degradation policies to protect high-quality water body. Generally, issues pertaining to water quality degradation has attracted the attention of many of the researchers and the organisations such as WHO [36] in a struggle to promote a worldwide response to the water quality deterioration. **Annexure I** represent various water quality parameters quality as laid by WHO for drinking purpose.

CHAPTER 5

METHODOLOGY

CHAPTER 5

METHODOLOGY

Due to rapid urbanization, increase in the population and the consumption pattern, the problems of solid waste management in Delhi has been rapidly shooting up. As per Central Pollution Control Board estimate, an average person in the class I city (urban areas having population of 100000 and above), will produces about 0.4 kg of the garbage per day. Per capita waste production in the lower income and the higher income groups is 0.18 kg and 0.80 kg respectively of garbage per day. Inorder to study the groundwater contaminations due to such solid waste disposals in Okhla landfill site having an area of 54 acre is chosen for this present study. This chapter will present the methodology and design of the research. It describes the order of all activities that are logically connected therein. These activities will connect the different sets of informations sourced and utilised in this research programme to the main aims and objectives of the study. The research work involved four main categories of the activity: field works; laboratory-based experimentals and instrumental analysis; analyses of data; and presentation of thesis. All of these activities involve numerous tasks; each task was completed in accordance to the standard operating procedures so as to ensure the best quality outcomes could achieved within the practical and financial constraints of the project.

5.1 Study Area

Delhi is the capital of India and covers over 1483 km² at latitudes 28⁰ 35'N and longitude 77⁰ 12'E which is located at an altitude of 218 m above the mean sea level. The Aravalli Ridge Gangetic Plain Converges at Delhi and hence a there is a mixed geological behaviour with alluvial plains as well as quartzite bedrocks is obtained. The climatic regime of Delhi has a semi-arid type of climatic and is mostly characterized by extreme dry weather conditions with very hot summers and cold winters. It also does experiences the heavy rains during the periods of monsoon with an average rainfall of 714.6 mm. The groundwater level in the Delhi city varies between 15 to 20

m of depth. The temperature of Delhi varies from 45 °C in summer to 4 °C in winters. Delhi, with a population approaching to 18.6 million is assessed to generate about Municipal Solid Waste 9620 MTD/day. In Delhi, there are 5 Municipal Authorities responsible for Municipal Solid Waste generation and management

Table 5.1 Delhi Pollution Control Committee report [38]

Agencies undertaking SWM in Delhi	Quantity of Solid Waste Generated(TPD)
North Delhi Municipal Corporation	4200
South Delhi Municipal Corporation	2850
East Delhi Municipal Corporation	2200
New Delhi Municipal Council	300
Delhi Cantonment Board	70
TOTAL	9620

There are three landfill sites namely Ghazipur, Bhalswa, and Okhla. Bhalswa landfill were Commissioned in the year 1994, Okhla in 1996 and Ghazipur in 1984. All of three landfill sites are not designed in accordance to the schedule 3 of the Municipal Solid Waste Rules which came into effect in the year 2000. Delhi Pollution Control Committee has not given authorization to all three landfill sites. Municipal bodies have informed that they have no other option but to use these sites for disposal of MSW as land is not available in Delhi sites.

5.2 Okhla Landfill

Okhla landfill Phase II, located in south Delhi near Tugalakabad fort at the top of Aravalli ridge, at the bank of the river Yamuna. The geology of Okhla landfill is such that it consists of alluvium (25 %) with patches of the quartzite (75 %). The Okhla landfill is a controlled open dumpsite, which is owned and operated by the Municipal Corporation of Delhi. Okhla Landfill do accept commercial waste and domestic from the Delhi area. The existing Okhla landfill covers a total of 54 acres, and is almost

completely covered with waste height of about 50 m above ground level. The Central Ground Water Authority (2000) had reported that this area because of the shortages of groundwater resource. Sanitary landfill site Okhla receives:

- | | |
|--------------------------|---------------|
| 1. Municipal Solid Waste | : 450 MT/day |
| 2. Malba | : 600 MT/day |
| 3. Silt | : 200 MT/day. |
| 4. Ash/Reject | : 600 MT/day. |

150 MT/day of the waste is processed at compost plant Okhla and 1250 MT/day Waste to Energy Plant at Okhla.

5.2.1 Sampling Stations

To characterize the quality of ground water sample, it was collected from the bore hole at under construction building site adjacent to ESIC hospital Okhla phase 1. This is approximately at 200 meters from Okhla landfill site. To evaluate the pollution source for the ground water, leachate sample were collected from Okhla landfill site and analysed as per the procedures.



Fig.5.1 Sample location map showing leachate samples, and groundwater sample locations

5.3 Materials and Methods

Material and methods are key component of any research. The outcome of any research mainly depends on materials and methods used in research. Present study encompasses the critical issue involved in our day to day life. Different types of waste generated in urban areas are creating numerous problems to the human civilization. Hence, to study such problems proper selection of material and method was necessary, because any ignorance in such work can disrupt the research outcomes. Therefore, in present investigation proper selection of material and methods was carried out keeping in view, the research objectives and time framework for the research. The methods were identified from renowned journals, books, thesis or any such published and authentic material obtained from different sources like research institutes, university libraries, college libraries, internet etc. During use of different materials, care was taken to use it as accurate as it can give the more accurate results.

5.3.1 Sample collection

- I. Groundwater sampling
- II Landfill leachate sampling

5.3.2 Groundwater sampling

Groundwater sample was collected nearby Okhla landfill site from a bore hole located adjacent to ESIC Hospital at under construction building. “Guidelines for Water Quality Monitoring” [38], by Central Pollution Control Board was kept in mind at the time of sampling. Groundwater samples were collected in 2 litre capacity polyethylene containers. Before collection, as part of the quality control measures all the bottles were washed and then rinsed with de-ionized water. Just before doing final water sampling, the bottles were rinsed three times with the bore well water at the point of collection of sampling. Each collected sample container bottle was then labelled in accordance to sampling location and all the samples were then transported to the laboratory and stored at a temperature of 4°C in refrigerator for further physico-chemical, and heavy metal analyses.

5.3.3 Landfill leachate sampling

Landfill leachate sample was collected from solid waste dumping site (Okhla Landfill) in a plastic bottle of 2 litre capacity. The sample was carefully transferred to laboratory to analyse physico chemical parameters and heavy metals content.



Fig.5.2 Generated Leachate Flowing Over Landfill

Table 5.2 List of parameters analysed and methodology followed

Parameters	Methodology
pH	pH meter
Total dissolved solids as (TDS)	gravimetric method
Dissolved oxygen as DO, BOD	Winkler's method
Total hardness as (TH)	EDTA titrimetric method
Chloride as (Cl ⁻)	Argentometric method
Sulphate as (SO ₄ ²⁻)	Spectrophotometric method
Phosphate as PO ₄ ³⁻	UV- Spectrophotometric method
Chemical Oxygen demand as (COD)	Dichromate reflux method
Heavy Metals	Inductively coupled plasma mass spectrometry (ICP-MS)

5.4 Analytical Methods

The groundwater sample and leachate were analysed for physico-chemical parameters in accordance to **APHA** [39] that included: pH, total dissolved solids (TDS), turbidity, total hardness, colour, TH, Ca^{2+} , Mg^{2+} , SO_4^{2-} , PO_4 , Cl, BOD_5 , COD, Cr, Fe^{2+} , Mn^{2+} , Co, Ni, Cu, As, Cd, and Pb ions. Various instrumental experiments and techniques were used to analyse the different physical and chemical components. Summaries of these methods have been explained;

5.4.1 pH – Instrumental Method

pH was measured in the laboratory with the help of a digital pH meter. Difference in electrical potential between a reference electrode and a pH electrode is measured by pH meter, and so the pH meter is sometimes referred as a "potentiometric pH meter". The differences in the potential relates to the acidity or pH of the solution. This pH meter finds many applications ranging from laboratory experimentation to quality control.

5.4.2 Turbidity – Instrumental Method

About 200ml of the ground water sample was placed in a beaker and was allowed to settle at the room temperature. It was then mixed thoroughly so as to disperse the solids and was allowed to settle until air bubbles had disappeared. The sample then poured into the turbidimeter tube. The turbidity value has been read directly from the instrument scale and then recorded to the nearest whole number in Nephelometric Turbidity Units (NTU).

5.4.3 Total Dissolved Solids – Evaporation Method

50 ml of sample was filtered and then evaporated in a water bath using a pre-weighed porcelain dish. Initial and final weights of the evaporation dish were recorded using the analytical balance and the results expressed as mg/L

5.4.4 Total Hardness – EDTA Titrimetric Method

Total Hardness is determined by titrimetric method in which 100 ml of the ground water sample was measured in a conical flask. Buffer solution of 2 ml was added and then solution was titrated against 0.01N (EDTA) Ethylene Diamine tetra acetic acid using Eriochrome black T indicator (EBT) until the faint pink colour changed to blue at the end point amount at which titrant i.e. EDTA is determined. It is expressed in mg/L equivalent CaCO_3

5.4.5 Chlorides – Argentometric Method

Chlorides are determined by Argentometric method in which 25 ml of the ground water sample was measured and later few drops of Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was added as an indicator. The solution was then titrated against 0.01N Silver Nitrate (AgNO_3) solution until the yellow colour changed to reddish at the end point, and the result was expressed in mg/L.

5.4.6 Sulphates- Spectrophotometric Method

Sulphates is determined by Spectrophotometric method in which Sulphate ions (SO_4^{2-}) do precipitates in an acelic acid medium with barium chloride (BaCl_2) so as to form barium sulphate (BaSO_4) crystals of uniform size. Light absorption of the BaSO_4 suspension is measured by spectrophotometer and the sulphate concentration is determined by comparison of reading with standard curve.

5.4.7 Phosphate- Spectrophotometric Method

Phosphates are determined by Spectrophotometric method. In the present experiment, ground water sample and leachate sample was analysed using spectrophotometer. The principle of this method involves the formation of molybdo phosphoric acid, which is reduced to the intensely coloured complex, molybdenum blue. This analytical method

is extremely sensitive and is reliable down to concentrations below 0.1 mg phosphorus per litre.

5.4.8 Bio-chemical Oxygen demand as (BOD₅) - Winkler's method

The Bio-chemical Oxygen Demand determination is a test in which standardised laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents and polluted waters (APHA). The test measures the oxygen required for the biochemical degradation of organic material (carbonaceous demand). The method consists of placing a sample in a full, airtight bottle and incubating the bottle under specified conditions for a specific time. Dissolved oxygen (DO) is measured initially and after incubation, the BOD is calculated from the difference between the initial and final DO. Normally a 5-day BOD test period is used where samples are incubated in the dark (to restrict algal growth) at 20°C

5.4.9 Chemical Oxygen Demand

The COD is defined as the amount of a specified oxidant that reacts with a sample under controlled conditions. The quantity of oxidant consumed under controlled conditions is expressed in terms of its oxygen equivalence. Organic and inorganic components of a sample are subject to oxidation but in most cases the organic component predominates and is of the greater interest. COD is a defined test, in other words, the extent of sample oxidation can be affected by digestion time, reagent strength and sample COD concentration (APHA) In the COD reactor digestion method a sample is digested for two hours, at 150°C, with potassium dichromate (K₂Cr₂O₇), which is a strong oxidising agent. Oxidisable organic compounds then reacts with K₂Cr₂O₇, reducing the dichromate ion (Cr₂O₇²⁻) to a green chromic ion (Cr³⁺).

5.4.10 Heavy metals concentration (ICP-MS Analysis)

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry which is capable of detecting metals and several non-metals at

concentrations as low as one part in 10^{15} (part per quadrillion, ppq) on non-interfered low-background isotopes. This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions. Compared to atomic absorption spectroscopy, ICP-MS has greater speed, precision, and sensitivity. However, compared with other types of mass spectrometry, such as thermal ionization mass spectrometry (TIMS) and glow discharge mass spectrometry (GD-MS), ICP-MS introduces many interfering species: argon from the plasma, component gases of air that leak through the cone orifices, and contamination from glassware and the cones. Heavy metals concentration like, Iron(Fe), Copper(Cu), Arsenic(As), Cobalt(Co) Manganese(Mn), Cadmium(Cd), Lead(Pb), Total chromium(Cr), Nickle(Ni) and Zinc(Zn) were analysed by ICP-MS ICP-MS (inductively coupled plasma-mass-spectrometry) is a technique to determine low-concentrations (range: ppb = parts per billion = $\mu\text{g/L}$) and ultra-low-concentrations of elements (range: ppt = parts per trillion = ng/L). Atomic elements are lead through a plasma source where they become ionized. Then, these ions are sorted on account of their mass. The advantages of the ICP-MS technique above AAS (Atomic Absorption Spectroscopy) or ICP-OES (inductively coupled plasma optical emission spectrometry) are:

- Extremely low detection limits
- A large linear range
- Possibilities to detect isotope composition of elements

In this research work concentration of heavy metals was calculated through ICP -MS, values of those heavy metals have been presented in **ANNEXURE II**

Chapter 6

Results and Discussion

Chapter 6

Results and Discussion

6.1 Introduction

In order to evaluate the potential impact of leachate generated through solid waste disposal (SWD) sites on the quality of local groundwater sources, adequate understanding of the characteristics of generated leachate is required. Concentrations of the components therefore must also be identified. This is the basis upon which this chapter was developed. The primary aim of this chapter is to provide an overview of the physico-chemical characteristics of the leachate and ground water samples studied around Okhla landfill site. It also highlights the contaminant strengths in the leachates relative to their potential for groundwater contamination and is presented according to the various parameters investigated. Further, it addresses specifically the individual chemical characteristics of leachate and ground water sample.

It can be stated that inadequate protection of groundwater resources from anthropogenic contamination represents one of the greatest challenges facing the present generation, especially the populations in cities of less-developed countries. Unlike the situation in most parts of the more-developed regions, where public perceptions of groundwater protection are geared towards a more preventive approach, groundwater protection measures in less-developed regions are often non-existent or are initiated at a stage where severe contamination has already occurred. Once groundwater becomes contaminated, the clean-up process is complicated and often time-consuming; thus, it is essential for these communities [in less-developed countries] to experience a paradigm shift from the existing scenario towards approach to preventative and more sustainable solutions.

The key objectives of groundwater protection strategy are to preserve the sustainability and quality of the sub-surface water resources, being a strategic source of water supply and supporter of terrestrial ecosystems, by controlling its quality degradation and over exploitation.

6.2 Physico-chemical characteristics of leachate

Physico-chemical compositions of the leachate samples studied, indicates the nature of the SWD sites. Table 6.1 below presents a summary of the studied leachate composition.

Table 6.1 Summary of Physico-Chemical Compositions of Leachate Samples

Parameter	Unit	Value
pH	No unit	7.9
Appearance	-	Dark brown
Turbidity	NTU	325
Total dissolved solids	mg/L	11445
Total hardness	mg/L	8875
Sulphate (SO ₄ ²⁻)	mg/L	670.5
Phosphate(PO ₄ ³⁻)	mg/L	34.9
Chloride(Cl ⁻)	mg/L	16324
BOD ₅	mg/L	9870
COD	mg/L	16460
Ca	mg/L	140.449
Mg	mg/L	68.432
Fe	mg/L	11.189
Mn	mg/L	0.326
Cr	mg/L	0.262
Co	mg/L	0.118
Ni	mg/L	0.50
Cu	mg/L	0.461
Zn	mg/L	1.680
As	mg/L	0.0264
Cd	mg/L	0.0515
Pb	mg/L	0.559

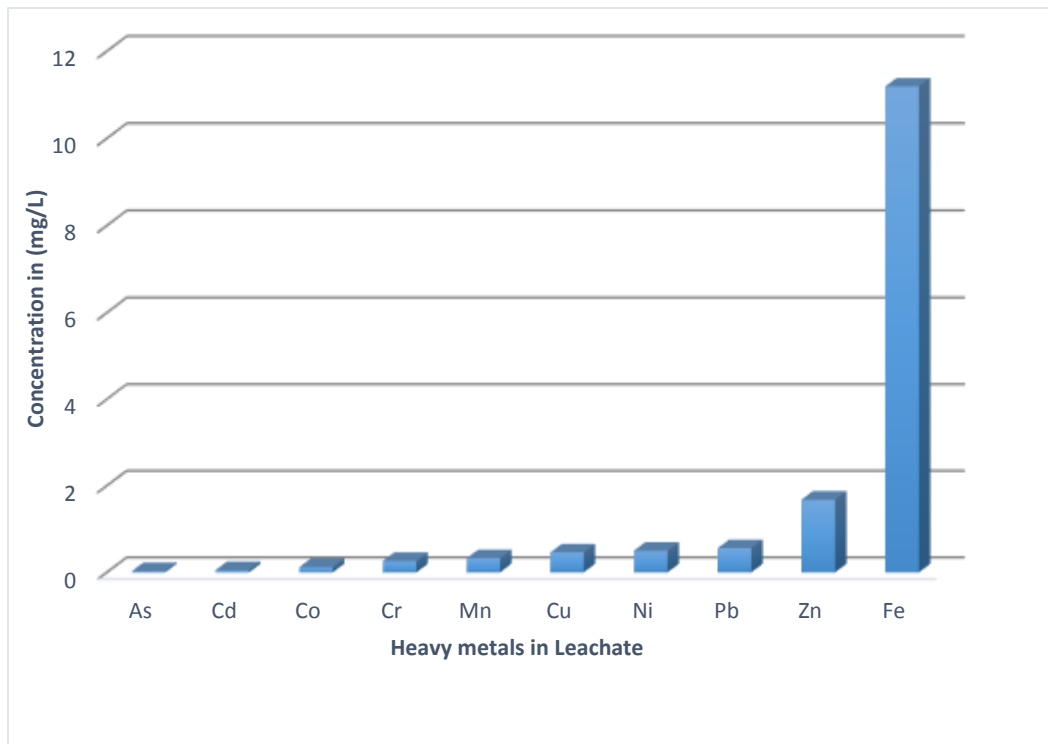


Fig 6.1 Heavy Metal Concentration in Leachate Sample (determined by ICP-MS)

6.3 Leachate pH

In leachates, pH is controlled mainly by a series of chemical reactions. The most significant reaction is the degradation of organic materials to produce small amounts of ammonia that dissolves in the leachate to form ammonium ions and carbonic acid and carbon dioxide the carbonic acid then dissociates with ease to give bicarbonate anions and hydrogen cations, which had influence on the level of pH of the system. Moreover, leachate pH is also affected by the partial pressure of the produced CO₂ gas that is in contact with the leachate. In this study, pH values were found to be 7.9 therefore the samples can be said to be alkaline. Moreover, the observed alkaline pH in the samples indicates that the methanogenic fermentation stage has prevailed throughout the disposal sites. Because of the selected SWD sites are relatively old [aged over 20 years], the alkaline pH values obtained are consistent with the anticipated methanogenic fermentation stage of the biochemical decomposition of

leachate. Usually, within old disposal sites that remain active, the bulk of the waste mass has reached the methanogenic stage of biochemical decomposition and generates leachate with near neutral to alkaline pH values. Nevertheless, pH alone does not necessarily have any direct negative effect on the ecosystem, but it does highlights certain interactions of other chemical constituents in the solution that potentially poses a threat. pH influences the chemical processes (dissolution, precipitation, sorption, complexation and redox reactions). Subsequently, it is one of the most important operational leachate and water quality parameters.

6.4 Total Dissolved Solids

Total Dissolved Solids in the leachate sample of this study came out to be 11445 mg/L. TDS parameter is usually influenced by the total amount of dissolved organic and inorganic materials present in the solution, and hence used to demonstrate the degree of salinity and the mineral contents of leachates. This total mineral content does further reflect the overall pollutant and strength of load of the leachate. The high concentration of total dissolved solid can alter both chemical and physical characteristics of receptor groundwater

6.4.1 Major anions (SO_4^{2-} , PO_4^- , Cl^-)

The concentration of inorganic elements present in leachates is mainly dependent on the ease of leaching the inorganic constituents present in waste and the stabilisation process in the landfill. In this research, the samples were found to have very high concentrations of all the major anions (sulphates, chlorides, and phosphate). Concentration of Chloride (Cl^-) is the highest, while Phosphate concentration is the lowest. Relatively high concentration of chloride in leachate samples reflects the significant presence of soluble salts in the waste materials of the study area. The concentrations of chloride in the samples were found to be significantly high as 16324 mg/l. Unlike chlorides, concentrations of sulphates was found out to be 670.5 mg/l. Sulphate in landfill leachates is mainly sourced from the decomposition of soluble

waste such as construction wastes or ash, Organic matter, synthetic detergents and inert waste. Conc. of Phosphate in the leachate sample were found out to be 34.9mg/l.

6.4.2 Major Cations (Ca and Mg)

The constituents Ca^{2+} and Mg^{2+} are considered in general to be the major cations mostly present in leachates. Derived from the waste material via mass transfer processes, concentration of these cations in leachate is hence specific to the composition of the waste mass and the prevailing phase of stabilisation in the landfill. Calcium (as Ca mg/l) and Magnesium (as Mg mg/l) came out to be 140.449 and 68.432 respectively. In leachates, these are sourced mainly from the degradation of organic materials and the dissolution of inorganic wastes such as plaster, concrete and tiles.

6.4.3 BOD and COD

Biochemical Oxygen Demand and Chemical Oxygen Demand of the leachate sample under analysis came out to be 9870 mg/l and 16460 mg/l respectively. This high COD and BOD values does indicate the high organic strength in the leachate of landfill sites. The presence of high values of COD in the leachate may cause severe contamination of groundwater resources.

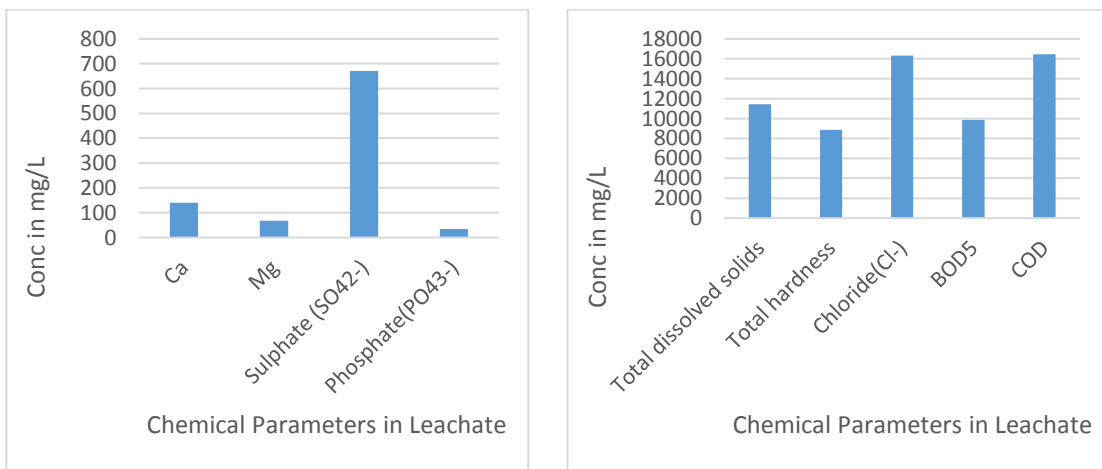


Fig 6.2 Chemical Parameters Concentration in Leachate Sample

6.5 Heavy Metals

Dissolved metals can be present in the form of free ions (e.g. Mn^{2+}) in leachate or may form complexes with organic or inorganic ligands. The free heavy metal ions presence in leachate is not only affected by the amounts present in the waste mass, but also the degradation processes within the disposal site; these are predominantly dependent on pH. With the increase in solubility of most heavy metals under acidic conditions in the fermentation stage and decrease in the methanogenic stage under neutral to alkaline conditions, samples are expected to have significantly low concentrations of these metals due to the prevalence of relatively high pH. High concentrations of Fe (11.189mg/L), Zinc (1.680mg/L) and Chromium (0.262 mg/l) was found in the leachate sample. Heavy doses of chromium salts even though are rapidly eliminated from human body, could corrode the intestinal tract. Zinc with concentrations of 1.680 mg/L indicates that the landfill is receiving waste batteries and fluorescent light bulbs. With regards to plant and aquatic life it is a matter of concern. High levels of Iron (11.189mg/L) in samples indicate that iron and steel scraps are also dumped in the landfill which may change the colour of groundwater. Manganese (Mn) with a mean concentration 0.326 mg/l was observed in all the leachate samples. Manganese is considered to be a neurotoxin and long-term exposure through contaminated water is hazardous for human health. The major anthropogenic source of iron (Fe) and other iron-containing alloys in Groundwater is waste from steel industry which is dumped in the landfill site without prior treatment. The steel industry generally dumped their effluents and scraps in nearby landfills that contain very high concentrations of iron; over time, the iron seeps into groundwater from landfills through rainwater. The presence of Pb (0.559 mg/l) in the leachate samples indicates the disposal of lead batteries, chemicals for photograph processing, lead -based paints and pipes at the landfill site. Cu (0.461 mg/l), Ni (0.50 mg/l) and as (0.0264 mg/l) was also present in leachate sample.

6.6 Physico-chemical Characteristics of ground water

Groundwater samples were collected bore hole which is located in under construction building adjacent to ESIC HOSPITAL Okhla Phase 1 about 200 meters from landfill site. The underground water of this area is used for domestic and other purposes. The water samples were collected from the above sites in plastic sampling bottles. The samples were brought to the laboratory and then analysed for various physico-chemical parameters such as pH, TDS, total hardness, calcium, magnesium, chloride, sulphate, phosphate, and Heavy metals by following standard methods cited in APHA [39]. Table below shows the physical and chemical characteristics of groundwater sample.

Table 6.2 Physico-chemical Characteristics of Groundwater sample

Parameter	Unit	Value
pH	No unit	6.8
Appearance	-	Colourless
Turbidity	NTU	2
Total dissolved solids	mg/L	540
Total hardness	mg/L	390
Sulphate (SO ₄ ²⁻)	mg/L	145
Phosphate (PO ₄ ³⁻)	mg/L	0.95
Chloride(Cl ⁻)	mg/L	245
COD	mg/L	3.2
Ca	mg/L	85.680
Mg	mg/L	35.450
Fe	mg/L	0.46
Mn	mg/L	0.00253
Cr	mg/L	0.00375
Co	mg/L	0.000425

Ni	mg/L	0.06
Cu	mg/L	0.0291
Zn	mg/L	1.177
As	mg/L	0.00317
Cd	mg/L	0.00036
Pb	mg/L	0.063

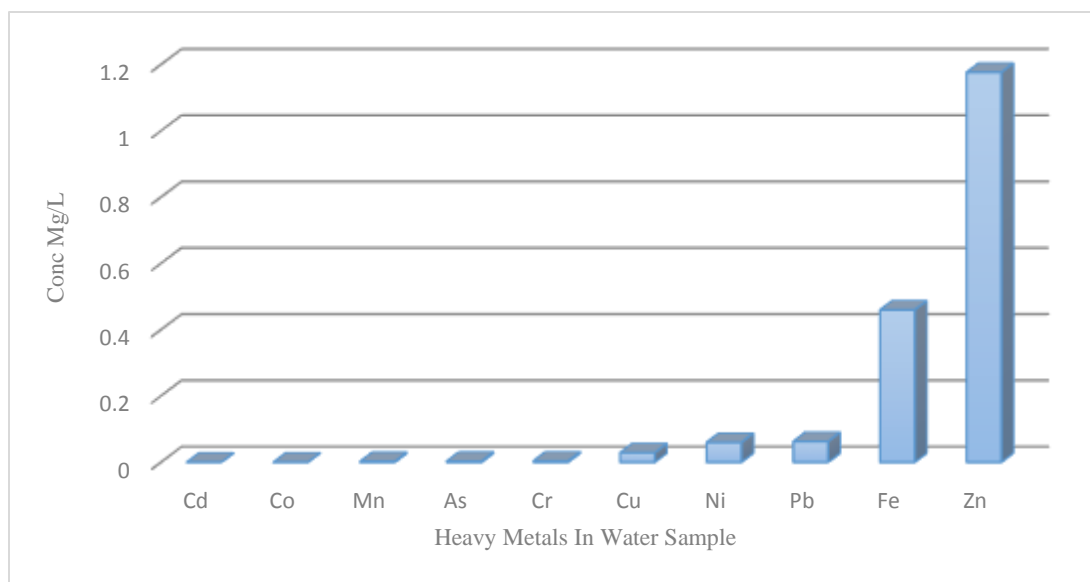


Fig.6.3 Heavy Metals Concentration in Ground water sample

The pH of all the groundwater samples obtained through pH meter was 6.8 which is within the permissible limit as per BIS limits. Moreover, the influx of contaminants from anthropogenic and natural activities like percolation of solid waste leachates and other land uses can also considerably affect the pH values. However, the pH values were within what would be considered a relatively normal band. samples were slightly acidic. Generally, acidic pH indicates the possible effect of contamination due to anthropogenic and natural sources or both.

TDS indicates the general nature of water quality or salinity. TDS obtained in this study was 540 mg/l. This high value of TDS may be due to the leaching of various

pollutants into the groundwater. The high concentrations of TDS decrease the palatability and may cause gastro-intestinal irritation in human and may also have laxative effect particularly upon transits (WHO).

The total hardness (TH) of water samples came out to be 390 mg/L, the desirable limit for hardness of water is 300 mg/L therefore the water in the bore-wells is very hard. Calcium hardness in ground water sample came out to be 85.680 mg/L. The desirable limit for calcium is 75 mg/L. The concentration of calcium in ground water samples is high than desirable. Calcium often comes from carbonate based minerals, such as calcite and dolomite. The excess of calcium causes concretions in the body such as bladder stones and kidney and irritation in urinary passages. Magnesium hardness in the bore-well water was 35.450 mg/L. The desirable for magnesium is 30 mg/L. Hence, we observe that concentration of magnesium is beyond desirable limits. High concentration may cause laxative effect. Chloride content of water sample came out to be 245 mg/L. An excess of Cl^- in water is usually taken as an index of pollution and considered as tracer for groundwater contamination. High Cl^- content of groundwater is likely to originate from pollution sources such as domestic effluents, fertilizers, and septic tanks, and from natural sources such as rainfall, the dissolution of fluid inclusions. Increase in Cl^- level is injurious to people suffering from diseases of heart or kidney (WHO, 1997).

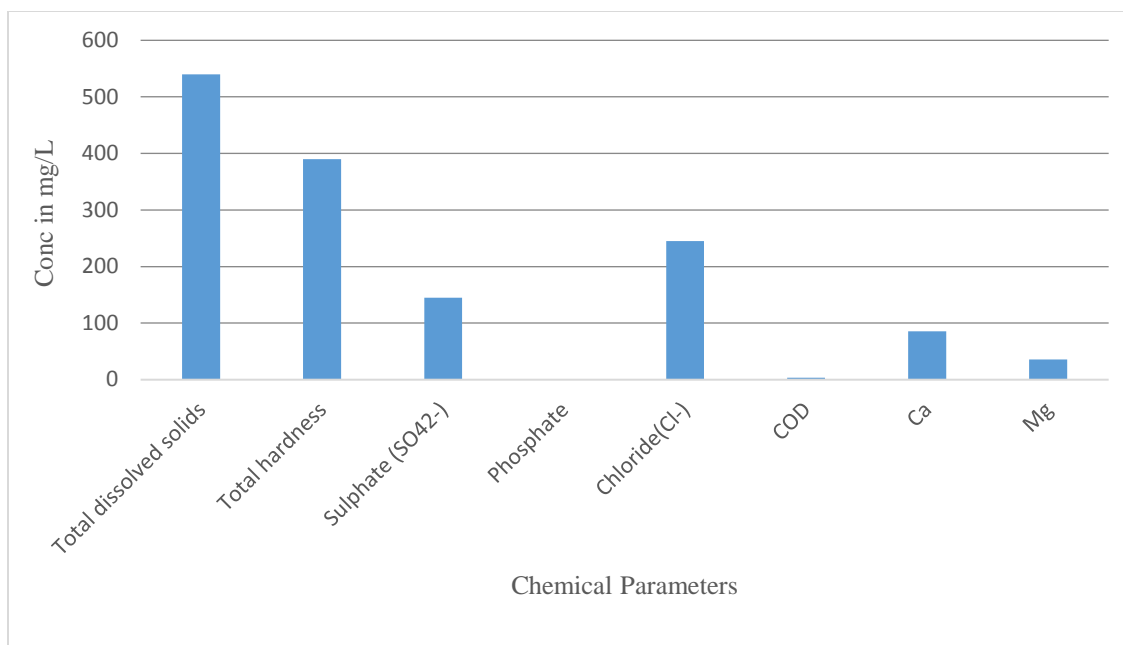


Figure 6.4. Chemical parameters Concentration in Ground Water Sample

The moderately high concentration of Cl⁻, SO₄²⁻, and Fe etc. in groundwater sample near landfill deteriorates its quality for drinking and other domestic purposes. As there is no natural or other possible reason for high concentration of these pollutants, it can be concluded that leachate has significant impact on groundwater quality near the area of Okhla landfill site. COD is a measure of oxygen equivalent to the organic matter content of the water susceptible to oxidation by a strong chemical oxidant and thus is an index of organic pollution. The COD level in the groundwater sample was 3.2 mg/l thereby indicating the presence of organic contaminants in the water and hence can be used as organic indicators to assess the pollution of ground water caused by landfill.

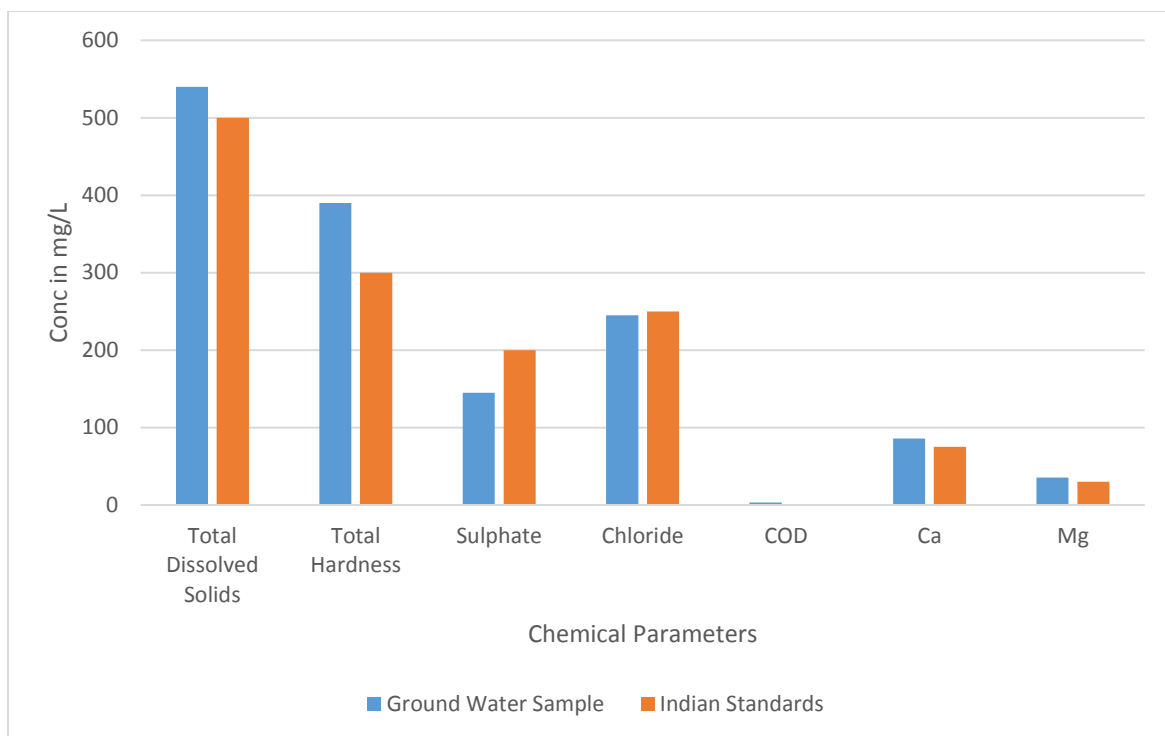


Fig 6.5 Comparison of Chemical Parameters Concentration in Ground Water Sample With Indian Standards

The metals Pb, Cr, Cd and Ni are characterized as toxic one for drinking water. The concentration of few heavy metals was found to be quiet low in groundwater samples. This likely indicates that this metal would have been adsorbed by the soil strata or by the organic matter in soil. The hypothesis that the heavy metals originate from the landfill is also justified because there is no known natural source of these heavy metals in the study area. High concentration of heavy metals (Fe, Zn, Ni, Pb) was observed, which is hazardous for health.

CHAPTER 7

CONCLUSIONS

Chapter 7

Conclusions

The significance of freshwater resources to the survival and efficient functioning of ecosystem cannot be over emphasised. Furthermore, groundwater represents a very important component of available freshwater resources. It is also central to water supply systems in many parts of the world. Groundwater pollution in urban areas is a growing environmental problem worldwide. A major source of groundwater pollution is the indiscriminate disposal of domestic and industrial wastes, which are principal components of the urbanisation process. As it is technologically difficult and economically expensive to treat a contaminated aquifer, groundwater protection measures must be sought beforehand SWM in less developed countries faces many challenges that need to be addressed urgently. The existing common practice of indiscriminate disposal in those regions is one of the most visible environmental challenges the region faces. The liquid leachate formed in the disposal sites represents a major source of environmental contamination, including groundwater aquifers that are used extensively for drinking and other purposes. Management of solid waste in urban areas represents a growing environmental challenge faced in most parts of the world. The occurrence and physico-chemical characteristics of leachate samples collected from disposal sites in Okhla were assessed comprehensively in order to determine their polluting potentials on the environment. Significantly, varied physico-chemical characteristics were revealed, which, in turn, indicate the diverse characteristics of the different SWD sites. Because the selected SWD sites were neither engineered nor properly managed and regulated, there is a high tendency of leachate migration to the soil and water resources. This may result in contamination of the soil, surface water and subsurface water resources, which, in turn, poses a significant threat to the environment and public health.

It was observed that solid waste generated in the study area is not properly managed, especially in relation to the final disposal practice, as there is no single engineered sanitary landfill in the region. A survey of all existing disposal sites in the study area

confirmed that they are all poorly managed and lack systematic design, operational competence and overall management; therefore, it is difficult to even estimate the quantity of solid waste received. Thus, the indiscriminate manner in which solid waste is disposed of, poses significant risks to the environment and public health.

From the groundwater quality assessments conducted in this research, the physico-chemical characteristics of the groundwater around selected SWD sites revealed significant contamination. This is reflected in the high concentrations of many parameters including: chlorides, heavy metals which were often found to be above the WHO guideline threshold values. These parameters are used typically as indicators of contamination. The level of contaminants in the groundwater samples exhibited a reasonable level of correlation with the quality of leachate sample from the SWD site. These correlations imply that the deterioration in quality of shallow groundwater sources examined in the study area have, to a certain extent, been influenced by the leachates composition.

However, the results in isolation do not confirm that the pollution of groundwater sources examined have been contaminated by a particular source of pollution, let alone the leachates that has been generated from the surrounding SWD sites, which are the main suspects in this study. The concentration of TDS, TH, SO_4^{2-} , Cl^- was comparatively high with respect to WHO Water Quality Standards in the sampling site near to the dumping yard. The high concentration of these parameters shows that there is a ground water contamination from leachate percolation in the study area. Calcium and Magnesium concentration are above the limits of Indian Standard for drinking water (BIS-10500:1991) and WHO. The higher concentration of TDS shows the infiltration of landfill leachate has occurred to the ground water and polluted the water. High concentrations of chloride in groundwater direct impact of anthropogenic input on groundwater quality.

The high concentration of heavy metals and other cations was observed around the Okhla landfill. The groundwater samples nearby Okhla landfill contain higher

concentration of few heavy metals and other cations than recommended by BIS and WHO standard for drinking water. The spatial, distributions of all these heavy metals specify possible leaching of contaminant from landfill.

Few heavy metals such as Co, As, Cd seems to have least impact from Okhla Landfill, this might be due to its position on quartzite belt where clay is the major constituent of soil. It is a well-known fact that clay has high sorption capacity. That is why contaminant flow through the unsaturated zone is being slowed in this case. Nevertheless, there is a limit of sorption capacity and once that is saturated soil itself will start emancipating the contaminant with infiltrating water. Thus, even if the situation is little better it has high probability that in future it will deteriorate with time and impact will shift towards moderate to high impact It is to be noted that all parameters detected in landfill leachate samples were also found in ground water samples. The physical-chemical concentrations in groundwater samples were not as high as in leachate samples, thus indicating that chemical constituents in leachate are attenuated as they percolate through the aquifer into the groundwater system.

It is, therefore, very expected that the leachates have had a significant impact on the quality of ground water sources inspected in the study area. This highlights the need for a more sustainable management of groundwater resources, SWM and proper sanitation systems in the region in order to safeguard the public health and environmental quality. It should be noted, though, that establishment of causal link (between leachates and underlying aquifers) with greater accuracy requires further research in the area in order to collect more temporal and spatial data for in-depth statistics and analyses.

7.1 Suggestions

- Study of ground water quality carried out at the vicinity of Okhla Landfill in Delhi helped to suggest some optimistic approach so that possible damage can be minimized up to a certain extent and possible precaution to be taken for future planning of landfill sites.
- Okhla landfill may be closed as soon as possible so that further source of contaminant can be abridged since it has crossed its capacity.
- Proper management should be taking on to sort out or remove hazardous solid wastes before dumping so that leachates from Okhla landfill can be reduced and will not pollute ground water.
- Proper lined sanitary landfill sites besides with segregation of wastes and incinerators Techniques need to be established which are effective in keeping the ground water and surface water free from leachates enriched with pollutants.
- People living around the landfill site should be educated about possible impacts of using contaminated water.
- Extraction of the leachate collected at the base should be done so that and it can be recycled, thereby reducing the amount of leachate entering enter the aquifer lying below.
- Requiring stricter structural and design conditions for the landfills and surface impoundments, including two or more liners, leachate collection system between and above the liners, and continuous groundwater monitoring

7.2 Future Scope

In my thesis, through research activities a number of serious issues relating to the interactions between the quality of adjacent groundwater resources and Solid Waste Disposal activities in Okhla, Delhi has been reported. The following points has been recommended for future research activity.

1. There is a necessity for more research activity to be directed towards increasing the understanding of sources of pollution in Okhla, Delhi. This urgency is required so that contaminants can be identified and prioritised depending upon their types and sources associated that pose the serious threat to quality of groundwater in this susceptible area. Once known, such contaminants and their sources should be prioritised in future research activity and monitoring.
2. There is a need of suitable scientific monitoring programmes for assessing the quality of groundwater in this area, and therefore be designed with a selection of few key parameters and sampling frequency that will helps us to study the effect on the groundwater across temporal and spatial scales.
3. More research work is required so that the hydrogeological situation of the area under study can be understood. Such information is important to the effective assessment of groundwater pollution, particularly from SWD sites.
4. It is additionally necessary to evaluate the possibilities of groundwater contamination as a result of some other sources that haven't been covered during this study. There is an immediate need to evaluate the extent of the problem and, eventually, develop some guidelines for the detection and assessment of contamination caused by such sources. The overall consequence of the immediacy of disposal sites to one another and hence their combined interactions and effects on groundwater resources needs to be assessed in the

study area due to the observed high density of disposal sites in the area. They can have a major impact on the determined concentrations of contaminants found

- 5 An apparent social push toward indiscriminate and uncontrolled Solid Waste Disposal practice conjointly wants more rationalisation so as to know the pull factors that encourage such behaviour. This challenge must be researched further so as to develop a sustainable Solid Waste Management strategy that includes the socio-cultural practices of the area

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ANNEXURES

Annexure 1

Characteristics	Requirement (desirable limits)	Undesirable Effect Outside the Desirable Limit	Permissible limit in the absence of alternate sources	Remarks
Colour,Hazen Unit ,max	5	Above 5,consumer Acceptance Decreases	25	Extended to 25 only, if toxic substances are not suspected, in absence of alternate sources
Odour	Agreeable	-	Agreeable	a) Test cold and when heated b) Test at several dilutions
Turbidity, NTU, Max	5	10	Above 5, consumer acceptance decreases	-
Dissolved Solids mg/L, Max	500	Beyond this palatability decreases and may cause gastro intestinal irritation	2000	-
pH value	6.5 to 8.5	Beyond this range the water will		

		affect mucous membrane and/ or water supply system	No relaxation	-
Total hardness as CaCO ₃ mg/L max	300	Encrustation in water supply structure and adverse effects on domestic use	600	-
Copper (as Cu), mg/l, max	0.05	Astringent taste discoloration and pipes	1.5	-
Chlorides (as Cl ⁻) mg/l, max	250	Beyond this limit, taste, corrosion	1000	
Iron (as Fe) mg/l, max	0.3	Beyond this limit taste/ appearance are affected, has adverse effect on domestic uses and water supply structures, and promotes iron bacteria	1	-
Manganese (as Mn) mg/l,	0.1	Beyond this limit taste/ appearance are affected ,has adverse effect on domestic uses and water supply	0.3	-

		structures		
Zinc (as Zn) mg/l, max	5	Beyond this limit it can cause tringent Taste in water	15	-
Sulphate (as SO ₄ ²⁻) mg/L, max	200	Beyond this causes extended Gastro intestinal Irritation when Magnesium or Sodium are present	400	May be extended upto 400 provided that Mg does not exceed 30
Alkalinity as CaCO ₃ mg/l, max	200	Beyond this limit taste becomes unpleasant	600	-
Calcium (as Ca) mg/l, max	75	Encrustation in water supply structure and adverse effects on domestic use	200	-
Magnesium (as Mg), mg/l, max	30	Encrustation in water supply structure	100	
Arsenic (as As), mg/l, max the	0.01	Beyond this water becomes toxic	0.05	
Lead (as Pb), mg/l, max	0.01	becomes toxic Beyond this, the water becomes toxic	No relaxation	

ANNEXURE II

Concentration of Heavy Metals from ICP-MS analysis

Sample	Type	CalBlk	CalStd	CalStd	CalStd	CalStd	CalStd	Sample	Sample	Sample
	Level	1	2	3	4	5	6			
	Sample Name	blank	10ppb	20ppb	50ppb	100ppb	200ppb	blank	sample water	leachate
	Dilution	1	1	1	1	1	1	1	1	1
24 Mg [He]	Conc. [ppb]	0	11.331	20.99	50.81	101.8	198.8	0.5733	35450.9435	68432.32
	Conc. RSD	N/A	3.7116	3.23	1.309	0.534	0.42	29.9	2.62257963	3.225409
43 Ca [He]	Conc. [ppb]	0	8.2822	16.26	52.61	95.87	201.9	0.3741	85680.2578	140490
	Conc. RSD	N/A	37.818	32.64	6.832	4.4	6.093	62.49	2.01692893	3.083073
52 Cr [He]	Conc. [ppb]	0	8.2251	18.18	47.92	98.88	201.4	0.1602	3.75548785	262.0716
	Conc. RSD	N/A	0.7688	1.649	2.313	0.861	1.295	18.594	1.80337283	4.421166
55 Mn [He]	Conc. [ppb]	0	9.2592	19.7	48.82	98.92	200.9	0.0935	2.53239761	326.1577
	Conc. RSD	N/A	0.3439	0.65	0.938	0.766	0.446	25.572	1.90129652	8.134675
56 Fe [He]	Conc. [ppb]	0	10.633	19.1	48.4	98.92	201	0.7826	460.10402	11189.59
	Conc. RSD	N/A	2.1267	1.193	2.034	1.094	0.743	4.6536	1.66123385	3.142612
59 Co [He]	Conc. [ppb]	0	9.2011	19.43	48.78	100.6	200.1	0.0518	0.42550393	118.2203
	Conc. RSD	N/A	0.8156	1.411	1.642	1.138	0.288	4.8564	1.3491083	2.308166
60 Ni [He]	Conc. [ppb]	0	9.2101	19.45	48.69	99.36	200.7	0.0214	60.3918755	500.0056
	Conc. RSD	N/A	0.8726	1.316	2.43	0.746	1.499	100.08	8.0669847	2.047832
63 Cu [He]	Conc. [ppb]	0	9.1289	19.38	48.82	98.99	200.9	0.008	29.171451	461.8725
	Conc. RSD	N/A	0.9704	1.56	2.033	1.645	1.66	207.61	4.11505521	2.733543
66 Zn [He]	Conc. [ppb]	0	11.253	20.77	49.21	100.4	199.9	<0.000	1177.02833	1680.504
	Conc. RSD	N/A	6.7603	2.882	0.669	0.494	1.401	N/A	2.03671315	4.516492
75 As [He]	Conc. [ppb]	0	8.2666	17.75	47.04	98.75	201.7	0.1144	3.17196452	26.46137
	Conc. RSD	N/A	0.503	2.338	2.241	1.39	1.054	25.61	10.2590385	3.535573
111 Cd [He]	Conc. [ppb]	0	8.8166	18.53	48.18	98.01	201.7	0.0412	0.36519919	51.54739
	Conc. RSD	N/A	1.9417	1.42	3.114	1.287	0.913	42.435	41.8094542	7.24827
206 Pb [He]	Conc. [ppb]	0	8.3792	17.52	45.84	95.65	203.5	0.131	63.129367	559.3058
	Conc. RSD	N/A	0.5854	0.888	2.124	1.3	1.739	12.508	3.30693631	4.303334