



**GROUNDWATER POLLUTION AND PUBLIC HEALTH  
RISK ANALYSIS IN THE VICINITY OF REPPi SOLID  
WASTE DUMPING SITE, ADDIS ABABA CITY  
ETHIOPIA**

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## **ACRONYMS**

AACGSBPDA	Addis Ababa City Government Sanitation, Beautification and Park Development Agency,
BOD	Biochemical Oxygen Demand,
COD	Chemical Oxygen Demand,
CI	Confidence interval,
DO	Dissolved Oxygen
ECA	Economic Commission of Africa,
EDTA	Ethylene Diamine Tetra Acetic Acid
GPs	General Practitioners,
KPa	Kilo Pascal,
LCS	Leachate Collection System
MCL's	Maximum Contaminant Levels,
MSW	Municipal Solid Waste,
PVC	Poly Venial Chloride,
SS	Suspended Solids,
SW	Solid Waste,
SWM	Solid Waste Management,
UNDP	United Nation Development Programme,
UNICEF	United Nation International Children Fund,
USEPA	United State Environmental Protection Authority,
VOCs	Volatile Organic Compounds,
WHO	World Health Organization

## **ABSTRACT**

**Background:** *The daily waste generation in Addis Ababa city from each individual is expected to be 0.252Kg. Current waste generation in the city is 2,940 m<sup>3</sup>/day of which 80% is collected and disposed on dumping site every day. This open dumping site has no liner system and other groundwater pollution and public health risks control mechanism.*

**Objective:** *To analyze groundwater pollution and public health risks in the vicinity of Reppi solid waste dumping site Addis Ababa City, Ethiopia.*

**Methods:** *A cross sectional study was conducted in Reppi solid waste dumping site from April 10 to 25/ 2007 to analyze associated risks to the groundwater and the public health in its vicinity. For groundwater issue leachate, nearby well water and far away spring water samples were collected based on the distance difference and for public health issue. Based on standard sampling procedures 316 in the near by community and 316 from the controlled group were used for the study. Extreme care was taken to avoid alteration of chemical composition of samples during sampling. The study parameters for leachate, and groundwater quality were determined in Addis Ababa City Environmental Protection Authority and Ethiopian Geological Survey Water Laboratories. It includes physicochemical parameters such as P<sup>H</sup>, chloride, total hardness, alkalinity, TDS, TSS, DO, BOD, COD, Nitrate, Ammonia, Phosphate and trace metals. Standard methods were used for the analysis of the samples. The public health parameters were collected using pre designed questionnaires.*

**Result and discussion:** *Physicochemical analysis of leachate and groundwater showed that more than 95% of parameters in nearby well water analysis is more higher than the far away spring water and much exceeded WHO drinking water quality standard. This may be due to contaminants transport from dumping site to ground water. More than 95% risk ratio Public health risks were found in the nearby residents.*

**Conclusion:** *From this study we can conclude that there is an increase in risk to ground water and public health that is reported near Reppi solid waste dumping site. There fore the concerned authority should take appropriate intervention measures to groundwater and the health of the community.*

# CHAPTER-I

## 1.1. INTRODUCTION

Addis Ababa, the capital city of Ethiopia, enjoys a mid Afro-Alpine climate with an average temperature of 16<sup>0</sup>C. It is the diplomatic capital for Africa (AU, UNECA), regional head quarters like UNDP, UNICEF, UNHCR, FAO, etc. The population of the city is 3,035,135, and living in 10 sub-cities and 99 kebeles divided for administrative purpose. It is center for modern economic and social activities because of the infrastructure services are found relatively in better situation than other cities of Ethiopia. However, its development is too slow to meet the demands of the increasing population due to both natural growth and rural urban migration. In particular, the complete inadequacy of the solid waste management is major environmental problem in Addis Ababa [1].

The daily waste generation in the city is estimated to be 0.252 kg/capita [1]. The current daily waste generation of the city is 2,940m<sup>3</sup> or 765 tones and of this municipal waste about 80 % (2,352 m<sup>3</sup>/day) is collected [1]. The remaining 20 per cent of waste is disposed off through informal means, except smaller percentage going to incineration, dumped on open sites, drainage channels, rivers and valleys as well as on the streets. The rivers that cross the city, are widely used as disposal sites, although the hygiene and environmental sanitation regulation issued by the Addis Ababa city administration [Pro.No.1, 1994] prohibits people from disposing waste along roads, avenues, rivers, ponds, and other sites. Due to lack of proper means of discharging their day to day waste, it becomes difficult to implement the proclamation, directives and rules that result a continuous violation of regulation by the people.

The rapid population growth rate of 3.8 percent is also resulting in a rise of approximately 5 per cent of urban waste generation [1]. This implies that the current waste collection and disposal capacity of the city could not match with the growing population and generation of waste. These environmental problems also have socio-economic consequences. Poor environmental quality of cities can deprive citizens of a good quality of life as it affects their

health and consequently, adversely affect productivity and economic development. Various concepts have been developed over the years to provide the basis for improving the solid waste conditions in developing countries like Ethiopia. Among them, integrated solid waste management (SWM) provides a framework, which has been very successful in various countries.

Inadequate municipal and industrial solid waste collection and disposal creates a range of environmental problems in Addis Ababa. A considerable amount of waste ends up in open dumps or drainage system, threatening both surface water and ground water quality and which provides a breeding ground for disease carrying pests. Open air burning of waste, spontaneous combustion in dumping site, and incinerating plants that lack effective treatment for gas emissions are causing air pollution. The situation is exacerbated in slums where households cannot make use of garbage collection containers. Lack of the most basic solid waste services in crowded, low-income neighbors is a major contributor to the high morbidity and mortality among the urban poor, in particular Addis Ababa city vulnerable individuals. The adverse effect of inadequate solid waste service on productivity and economic development of the city expected to be significant.

The present SWM system in Addis Ababa relies not entirely on the municipality, the community has also developed a mechanism (organizing street boys) to dump in the refuse tank and/or solid waste collection trucks by collecting from door to door which is expected to provide the full range of solid waste collection and disposal. This is proving to be an impossible task, and except for privileged areas, the services offered are found to be largely inadequate. This approach neglects the many activities and actors that waste management comprise to tackle a range of problems associated with waste management in order to achieve socially and environmentally responsible waste management. An integrated approach to SWM seems to be the best option and could well hold the key to effective and sustainable waste management system in developing cities such as Addis Ababa.

As effort to improve solid waste management, the city administration has transferred the service provision of solid waste management to the newly established Addis Ababa City Sanitation, Beatification and Park Development Agency (since January 2003], with objective

to make the city naturally balanced, green and favorable environment through integrated solid waste management and urban recreational area development. The agency improves collection coverage from 68% to 80% of daily solid waste generation in the city.

### **1.1.1 Organization**

The dumping site is publicly owned and is managed by Addis Ababa City Sanitation, Beautification and Park development Agency since 2003. The agency concerns operation and management of the site, which consists mainly of activities relating to receipt of the waste, processing and burial, on-going site preparation and restoration. Also, since the collection and transportation of waste are the responsibility of sub cities solid waste management team, the dumping site operation and management is equally the responsibility of all ten-sub cities but mainly by AACGSBPDA.

### **1.1.2 Incoming waste: type and amount**

The incoming wastes originate mainly from households and commercial areas, but there are also some wastes that are brought to the dumping site from industries and municipal services. However, before being carried to the dumping site, the wastes undergo with out compaction and sorting at transfer stations since the city does not have transfer station.

Latest figures show that about 765 tons of wastes are being produced daily and that figure is expected to increase significantly in the coming years. It has been estimated that about 80 % of the wastes can be classified as municipal waste [1]. In 2004/5, about 333 000 m<sup>3</sup> entered the dumping site.

Solid waste segregation at the point of generation is not carried out, if it is practiced this action will have reduce the volume of waste going to the dumping site. 80% of the waste produced is dumped with a low percentage being reused or recycled. Since once in the dumping site, paper, garden and food waste decompose under microbial action into various gases, water and other compounds, it can be deduced from table 1.1 that more than 80% of the wastes are biodegradable.

Table 1.1: Solid waste composition disposed every day by 2004

	Constituent	%
1	Vegetable	4.2 %
2	Paper	2.5 %
3	Rubber and plastics	2.9 %
4	Wood	2.3 %
5	Bone	1.1 %
6	Textiles	2.4 %
7	Metals	0.9 %
8	Glass	0.5 %
9	Combustible leaves	15.1 %
10	Non-combustible Stone	2.5 %
11	Miscellaneous waste	65.0 %
	Total	100 %

Source: from current status of solid waste of Addis Ababa city (2004)

### **1.1.3 Physical, Geographical and environmental conditions**

#### **1.1.3.1 Dumping site description**

The dumping site is approximately square in shape with an area of about 25 hectare. The south side of the dumping site is bounded by ring road of the city. Other boundaries are straight with out fence and other means of protection for man as well as for animals. Dumping area is compartmentalized into 2 zones: 1 filled zone and 2 others in exploitation zone. The filled cell occupies an area of about 20 hectare and has piled up to a height of 5 m. The height of the landfill from the bottom of the cell is today is expected to be 11 meters above ground level.



Figure 1.1: Features of Addis Ababa solid waste dumping site 'Reppi'(Photo by sanitation and beautification team of Nifas Silk Lafto sub-city 2007)

## 1.2. STATEMENT OF THE PROBLEM

Classical unlined sanitary landfills and open dumps are well known to release large amounts of hazardous and otherwise deleterious chemicals to nearby groundwater, surface water and soil also to the air, via leachate and landfill gas. It is known that such releases contain a wide variety of potential carcinogens and potentially toxic chemicals that represent a threat to public health. However, little quantitative information exists on the total hazard that landfills represent to those who live or otherwise use properties near the landfill.

Epidemiological studies of the "exposed" populations near un controlled landfill sites in the United States have not detected a clearly discernable increase in the incidence of cancer in those populations. This is to be expected because of the insensitivity of epidemiological methods for detecting small increases in cancer incidence in limited populations over the normal lifetime cancer risk for the US population of one cancer in three people. It would be rare that a sufficient number of individuals near landfill sites would experience an average increased cancer risk of 1 in 1,000 [5].

Leachates have been implicated as environmental pollutant such as air, soil, surface water and groundwater pollution worldwide. The knowledge of the quantity and composition of leachates usually gives an insight into appropriate, effective and sustainable treatment approach. Some studies documented the physical, chemical and trace metals characteristics of leachates from the major repository of municipal solid wastes in different sites. Integrated samples of leachates can be collected during wet and dry periods and analyzed for P<sup>H</sup>, Suspended Solids (SS), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Ammonia, Nitrate, Phosphate, Sulphate and trace metals among others [6].

The leachate from MSW dumping site is a highly concentrated "chemical soup," so concentrated that small amounts of leachate can pollute large amounts of groundwater rendering it unsuitable for use for domestic water supply. In addition to potential carcinogens and highly toxic chemicals, MSW leachate contains a variety of conventional pollutants that render a leachate-contaminated groundwater unusable or highly undesirable due to tastes and odors, reduced service life of appliances such as dishwashers, water heaters, plumbing, fabric

(clothes), etc. Furthermore, both gas and leachate from uncontrolled MSW landfills contain many organic chemicals that have not been characterized with respect to specific chemical content or their associated public health or other hazards. These "non-conventional pollutants" include more than 95% of the organics in MSW leachate [5].

Given the highly concentrated nature of MSW landfill leachate, that a large portion of the organics in MSW leachate are of unknown character and hazard, and that a comparatively few chemicals are regulated, it should not be assumed the fact that a leachate-contaminated groundwater meets all drinking water MCL's (maximum contaminant levels) means that the water should be considered safe to consume. Furthermore, once a groundwater is contaminated by MSW landfill leachate of the type produced in today's Subtitle D landfills, it and the associated aquifer cannot be cleansed so as to render water that can be considered reliable for consumption and certain other uses. The contaminated portion of the aquifer must be abandoned for future use as a domestic water supply source and for conjunctive use storage of surplus surface waters for use during drought periods. Therefore, it is prudent public health and water resource management policy to assume that any contamination of groundwater by MSW landfill leachate represents a significant threat to public health and the environment and should cause termination of the use of the water for domestic water supply purposes [5].

The amount of leachate produced from the sanitary landfill depends on the moisture content of the solid waste and quantity of water entering the fill. Once the solid waste has reached its capacity to hold water, the leachate that is formed can create serious water pollution problem. Detailed investigation on the quality of water that may enter a landfill through the soil cover and the on the quantity and quality of the leachate that may leave the fills and enter an aquifer or stream frequency of water infiltration and the rate of evaporation and transformation for covered material [7].

The land disposal of municipal and industrial solid waste is the potential source of surface as well as groundwater contamination. Buried waste is subjected to leaching by percolating rainwater and surface water or by ground water contact with the fill. The generated leachate can contain high level of BOD, COD, Nitrate, and Chloride. Alkalinity, trace metals and even toxic matter that can degrade the quality of ground water. In addition, the biochemical

decomposition of the organic matter in waste generates gases such as methane, carbon dioxide, ammonia, hydrogen sulfide, that can migrate through unsaturated zone in to adjacent terrain and cause potential hazard [8].

Gas emissions from solid waste dumping site also contain large amounts of obnoxious and otherwise deleterious chemicals that are highly detrimental to nearby property owners and users. The methane in disposal site gas releases, while odorless, poses a threat of explosions in enclosed structures and contributes to the greenhouse gases that promote global warming. Both methane and CO<sub>2</sub> in dumping site gas can also be highly detrimental to vegetation on and near the dumping site cover. The obnoxious odors that are emitted from MSW dumping site can persist for a mile or more from the dumping site. Such odors provide a tracer for non-odorous as well as odorous hazardous chemicals in gaseous emissions. Because of the large amounts of non-conventional pollutants in dumping site gas, the detection of dumping site odors on offsite properties should warn of a significant public health threat. Odors and other adverse conditions created by dumping site operations cause property values to decrease within a mile or so of the dumping site [9].

MSW in a "dry tomb" landfill will be a threat to public health, groundwater resources, and the environment forever. The effectiveness of landfill liner systems in preventing leachate migration is compromised after installation, and will deteriorate over time allowing increasing amounts of leachate to pass through the liner into the groundwater system hydraulically connected to the bottom of the landfill [5].

The municipal solid waste stream of today and of the future potentially contains less industry-derived hazardous chemicals than the classical sanitary landfill. However, it does, and will continue to, contain large amounts of highly hazardous and otherwise deleterious chemicals that will render groundwater contaminated by such leachate unusable for domestic water supply purposes [10].

Solid waste disposal are the source of hazardous leachate, which migrates from the site in to nearby system, groundwater, home, schools and playgrounds. The primary pathways of community exposure were inhalation of volatilized chemicals emitted from the dumping site

and contaminated water and, to a lesser extent, direct contact with contaminated soil and water. Drinking water may not consider being potential exposure pathway because most nearby residents may commonly use public pipe water system. Several studies revealed that the concern of impacts of exposure to nearby residents chemicals emanated from landfill can cause still birth, low birth weight, congenital malformation, Cancer and other public health problems [11, 12, 13, and 14].

Studies on solid waste disposal sites would greatly benefit from a more interdisciplinary approach, drawing from the fields of landfill engineering, environmental engineering, toxicology, and epidemiology. Improvements in the base of toxicologic, environmental engineering and epidemiologic data on effects of chemicals exposure would improve our understanding of possible risks of the migration of these chemicals from landfill sites into the environment. Therefore, this study was aimed to find the groundwater and the public health risks with in the vicinity of Addis Ababa city solid waste disposal site, Reppi.

### 1.3. SIGNIFICANCE OF THE STUDY

Addis Ababa City Sanitation, Beautification and Park development Agency is responsible for organizing the prevention of risks of solid waste disposal site on the public health and the groundwater in its vicinity. The agency should therefore practice best available technology mainly modern landfill technology in such away that it should be out of residential area and free of environmental and public health impact.

Even though this study is focused on Addis Ababa city solid waste disposal site impacts on ground water and public health, its finding will provide scientific and technological facts for all responsible bodies, such as:

1. Provision and monitoring modern landfill so as to prevent unwanted environmental pollution and public health problems,
2. Identification of the requirements for construction of new landfill,
3. Provision of base line data for new landfill construction and to change the existing dumping site,
4. Provision of facts for major regulatory and concerned authorities so as to consider legal requirements for landfill project:
  - Environmental protection Authorities,
  - Water Work Authority,
  - Ministry of Health,
    - ✓ Directorate of Environmental Health
    - ✓ Directorate of Disease Prevention and General Safety, Occupational Health
5. Other water and public health concerned organizations.

## **1.4. OBJECTIVES**

### **1.4.1 General objective of the thesis**

Improper municipal solid waste and many industrial solid waste disposal landfills emit large amounts of landfill gas and leachate to the environment and are very good media for the breeding of disease vectors. Such emissions and breeding of vectors can have significant adverse impacts on public health and groundwater quality of the area near the landfill. Therefore, this study was aimed to analyze groundwater pollution and public health adverse risks of the Addis Ababa municipal solid waste-dumping site with in its vicinity.

### **1.4.2 Specific objectives of the study:**

- ❖ To draw ultimate solution for the collection and treatment of leachate accurately,
- ❖ To compare the public health risks at the dumping site with the community living further away,
- ❖ To identify source, parameters and impacts of leachate,
- ❖ To indicate the relationship between the dumping site management, groundwater and public health risks,
- ❖ To provide base line information for new landfill design for capital towns of different regional state in the country,
- ❖ To make the results available and give reference data to groundwater impacts assessment,
- ❖ To recommend the mitigation measures to tackle the prevailing problem at Reppi.

## **CHAPTER II**

### **LITERATURE REVIEW**

Landfills have served for many decades as ultimate disposal sites for all types of wastes: residential, commercial and industrial [15]. Physical, chemical, and biological processes interact simultaneously to bring about the overall decomposition of the wastes. One of the by-products of all these mechanisms is chemically laden leachates [18]. The major environmental problem experienced at landfills is the loss of leachates from the site and the subsequent contamination of groundwater [15].

Modern landfills have liners at the base, which act as barriers to leachate migration. However, it is widely acknowledged that such liners deteriorate over time and ultimately fail to prevent the movement of leachates into an aquifer [16]. It can take years before groundwater pollution reveals itself; and chemicals in the leachates often react synergistically and often in unanticipated ways to affect the ecosystem.

#### **2.1 LANDFILL LEACHATE**

There are three important attributes that distinguish any source of groundwater contamination: the degree of localization, the loading history, and the kinds of contaminants emanating from them. A sanitary landfill is a point source of groundwater pollution and produces a reasonably well-defined plume in many instances [17].

The loading history describes how the concentration of a contaminant or its rate of production varies as a function of time at the source. Leachates rates at a landfill site are controlled by seasonal factors or by a decline in source strength as components of the waste such as organics, biodegrade [17].

Many factors influence leachate composition; these include the types of wastes deposited in the landfill, the amount of precipitation in the area and other site-specific conditions. The rates of biological and chemical activities taking place in the landfill can also affect leachate quality by altering the way that waste dissolves in or migrates with leachates [16].

## 2.2 LEACHATES EFFECTS

Leachates contain a host of toxic and carcinogenic chemicals, which may cause harm to both humans and the environment [16]. Leachate-contaminated groundwater can adversely affect industrial and agricultural activities that depend on well water. For certain industries, contaminated water may affect product quality, decrease equipment lifetime, or require pretreatment of the water supply, all of which cause additional financial expenditures. The use of contaminated water for irrigation can decrease soil productivity, contaminate crops, and move possibly toxic pollutants up the food chain as animals and humans consume crops grown in an area irrigated with contaminated water [19].

## 2.3 FORMATION OF LEACHATE PLUME

Gravity causes leachates to move through the landfill, to the bottom and sides, and through the underlying soil until it reaches the groundwater zone or aquifer (see figure 2.1).

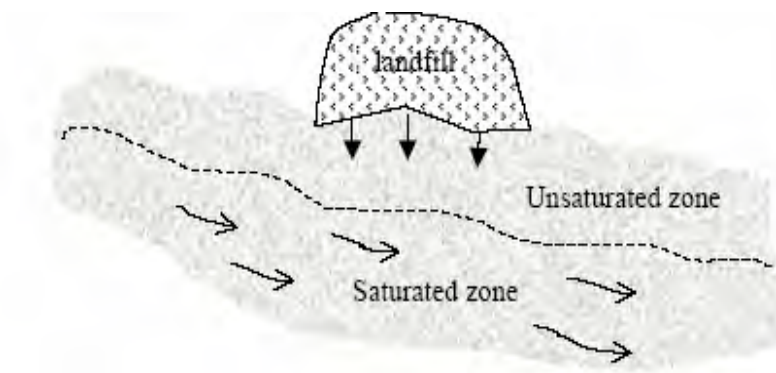


Figure 2.1: Movement of leachates from landfill to groundwater Saturated zone (www.groundwater.com)

As leachates move down the subsurface, they mix with groundwater held in the soil spaces and this mixture moves along the groundwater's flow path as a plume of contaminated groundwater as shown in figure 2.2.

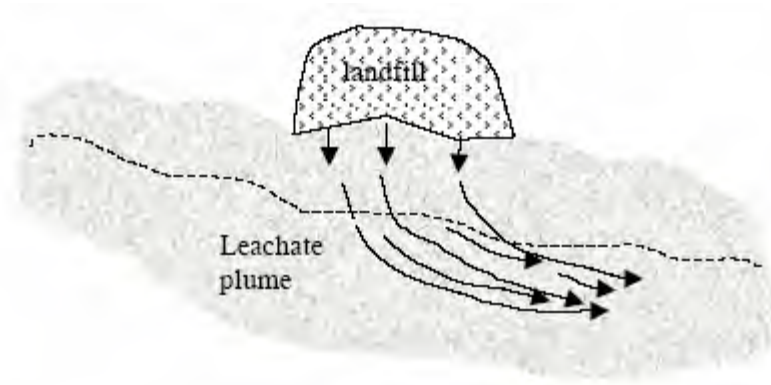


Figure 2.2: Formation of leachate plume (www.groundwater.com)

The leachates contaminants first enter the unsaturated zone and eventually are transported to the groundwater table in the saturated zone. Figure 2.3 gives an overview of the zones that exist underground. It is noted that the figure is valid for arid and semi arid zone.

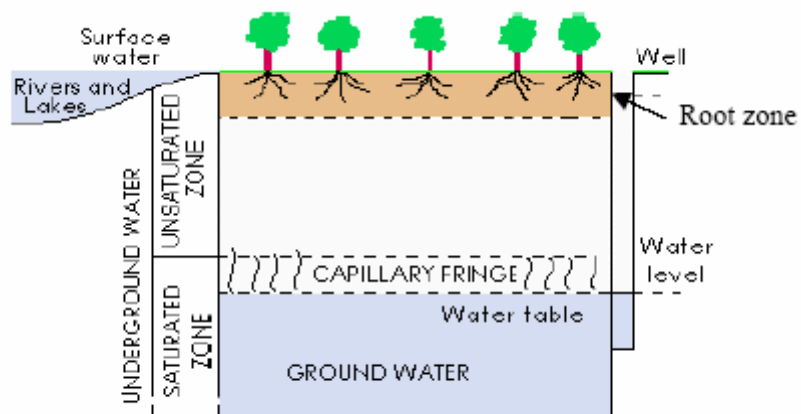


Figure2.3: Subsurface vertical stratigraphy (www.groundwater.com)

## 2.4 REVIEW OF CONTAMINANT TRANSPORT THEORY

Contaminant transport in aquifers cannot be determined if there is no information concerning where the water is moving. The flow of groundwater is dictated by Darcy's law, which states that the velocity of flow is proportional to the hydraulic gradient [17]. The Darcy's velocity of groundwater flow is defined as follows:

$$\frac{Q}{A} = q = -K \frac{\partial h}{\partial l}$$

Where,

$q$  is the volumetric flow rate per unit area of connected space, [LT-1]

$k$  is the hydraulic conductivity, [LT-1]

$\frac{\partial h}{\partial l}$  is the hydraulic gradient (change in hydraulic head per unit length) [LL-1]

Darcy's law is valid for laminar flow, which is the case for most porous material. Darcy's law is valid for horizontal and vertical flows in the saturated and the unsaturated zone. The direction of the flow depends on the formation of the geological units, the aquifer systems, hydraulic properties, topography, recharge and the presence of water supplies. The speed at which groundwater flow depends on the size of the spaces in the soil or rock and how well the spaces are connected. These materials are permeable because they have large connected spaces that allow water to flow through them [18]. Groundwater must satisfy the equation of continuity; water is conserved in flow through porous media. The equation of continuity for non-steady state conditions in a confined or unconfined aquifer is

$$\frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} = \frac{\partial(\rho \eta)}{\partial t}$$

Where,

$\rho$  is the water density, [ML<sup>-3</sup>]

$v_{x,y,z}$  is the specific discharge in the longitudinal, lateral, and vertical directions, [LT<sup>-1</sup>]

$\eta$  is the Porosity of the porous medium

$t$  is time, [T]

## 2.5 CONTAMINANT SOLUTE TRANSPORT MECHANISM

Advection and dispersion are the two major transport processes that determine the maximum extent of the leachates plume spread and the geometric character of the concentration distribution. *Advection* is mass transport due simply to the flow of water in which the mass is dissolved. The direction and rate of transport coincide with the groundwater. Dispersion is a process of fluid mixing that causes a zone of mixing to develop between fluids of one composition that is adjacent to a fluid with a different composition [17].

Transport and reaction of the contaminant in the porous medium can be represented by the equation below

$$\frac{\partial C}{\partial t} = \underbrace{\frac{\partial}{\partial x_i}(u_i C)}_{\text{Advection}} + \underbrace{\frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C}{\partial x_j} \right)}_{\text{Dispersion}} \pm \underbrace{\sum_{m=1}^n r_m}_{\text{Reaction}}$$

Where,

$C$  is the Solute concentration, [ML<sup>-3</sup>]

$t$  is the Time, [T]

$u_i$  is Velocity in three dimensions, [LT<sup>-1</sup>]

$x_i$  is Longitudinal, lateral, and vertical distance, [L]

$D_{ij}$  is Dispersion coefficient tensor, [L<sup>2</sup>T<sup>-1</sup>]

$r_m$  is Physical, chemical, and biological reaction rates, [ML<sup>-3</sup>T<sup>-1</sup>]

Advection is by far the most dominant mass transport process in shaping the plume while hydrodynamic dispersion is usually a second-order process, except in some cases involving fractured rocks. The magnitude and direction of advective transport are controlled by: hydraulic conductivity distribution within the flow field, the configuration of the water table, the presence of sources and sinks (e.g. wells), and the shape of a domain. All of these parameters are important in controlling the ground water velocity, which drives advective transport. When there is no dispersion or reactions, the plumes have a uniform concentration equal to the source concentration. A reduction in hydraulic conductivity reduces the extent of the plume by simply reducing the ground water velocity [17].

On the other hand, dispersion can cause important changes in the shape of a plume. Dispersion mixes the contaminant with an increasing proportion of the uncontaminated water and the plume size increases, the maximum concentration decreases [17]

## **2.6. ATTENUATION**

In the unsaturated zone, both air and water fill the pores between soil particles [18]. The slow movement of leachates in that zone causes attenuation of certain leachate chemicals. Positively charged lead, zinc, cadmium and mercury metals, are easily attenuated. As leachate containing these metals flows through soil, the metals stick or adsorb to the soil and is removed from the leachate. Other leachate pollutants, such as VOCs and acids are not easily attenuated, and they move unimpeded through soil, see figure 2.4 [19].

The composition of a soil and the characteristics of its binding sites affect its attenuation capability. Different soils have different abilities to attenuate and exchange chemicals. Once the binding sites of the soil particles become full, they can hold no more chemicals and henceforth, pollutants will move through the soil towards the groundwater [17].

As they fill to capacity, the binding sites become choosier. Only preferentially bound chemicals, or those that form tight bonds with soil, will be attenuated, and chemicals that bind loosely to soil will be replaced, refer to figure 2.5. For example, as leachate flows through soil, lead particles in the leachate can easily replace manganese that is adsorbed on soil because lead

is more preferentially bound than manganese. In this situation, lead would be removed from the leachate and stick to the soil, but manganese would leave the soil and re-enter the leachate, posing a continued threat to groundwater. In general, the more rapidly a reaction removes a contaminant the smaller the plume will be at a given time. Ion exchange can also produce the same dramatic attenuation in concentration. In ion exchange processes, the coefficient of selectivity is a determining factor. When the selectivity (preference among ions), is small, there is no exchange and the contaminant moves due to mass transport alone. However as selectivity increases, the plume becomes smaller as exchange retards spreading. In some instances, the geo-chemical processes have the capability of immobilizing particular contaminants at the source [17].

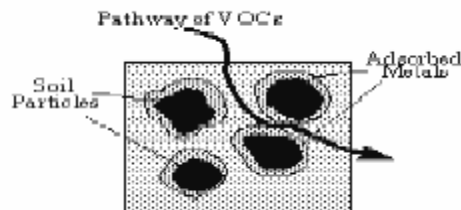


Figure 2.4: Soil attenuation (www.foe.org//ptp)

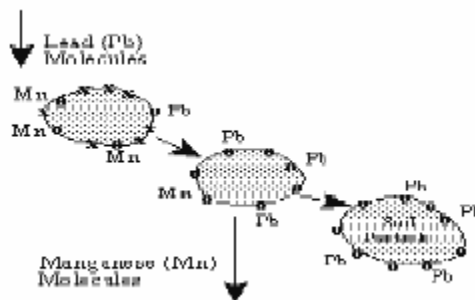


Figure2.5: Preferential adsorption of certain chemicals (www.foe.org//ptp)

## **2.7 GROUND WATER POLLUTION AND HEALTH EFFECTS OF DUMPING SITES**

The presence of chemicals in groundwater and drinking water is an important factor in determining the risk posed by landfill sites. However, it does not tell us what effect, if any, the consumption of contaminated water has on human health. There are studies of adverse health effects prompted by the contamination of well water used for drinking water and other domestic uses by hazardous substances from waste disposal sites (mainly sites where chemical waste drums were buried). Literature on contaminated water and potential health effects are more extensive than that presented in this section, which focuses only on water contamination directly related to the disposal of waste. The 1991 review by the US National Research Council gives a more comprehensive review of studies on contamination of domestic water supplies and health effects and concludes that although the available literature is scanty and not conclusive, drinking water contamination could lead to adverse health effects [20].

A number of studies followed the contamination of two drinking-water wells in Santa Clara County, California, with chlorinated solvents that had leaked from an underground waste storage tank. Residents living near one of the contaminated wells reported a cluster of adverse pregnancy outcomes, mainly spontaneous abortions and congenital heart defects. A first investigation confirmed a significant excess of cardiac anomalies in the service area of the water company that operated the contaminated well compared to those among residents of an unexposed area. The excess was found within the potentially exposed time period and not in an unexposed time period after the well was closed. The authors conclude that the solvent leak was an unlikely explanation for the excess of cardiac anomalies found because the excess occurred mainly in the first 12 months of the exposed time period, and there was a significant ( $p = 0.03$ ) deficit of cases during the second 8 months corresponding to the time when exposure was thought to be more certain. However, it is unclear when the leak started and the potentially exposed period was defined beforehand as the full 20 month period. An exposure study estimating monthly concentrations of solvents in each census tract found no difference in probability of exposure between women with adverse pregnancy outcomes and women with normal births and subsequent studies investigating water consumption in Santa Clara County

report significant associations between reported tap water consumption and risk of cardiac defects and spontaneous abortions [21].

Leakage from an industrial dump of chemical waste drums in New Jersey caused contamination of groundwater and well water with organic chemicals (including benzene, toluene, trichloroethylene, and lead) [22], found higher self-reported prevalence of respiratory disease and seizures but not cancer, liver illness, and skin disease in people living in a high-exposure area estimated on the basis of groundwater flow patterns. Residents in the high-exposure area used private drinking-water wells, eat homegrown food, and smoked more often than populations living in unexposed areas, and when these factors were adjusted for, differences in health outcomes disappeared. Adjusting for possible exposure routes such as local food consumption and use of private wells may have led to over adjustment, however, which would explain why no differences in health outcome were found.

For the future planning and regulation of landfill sites it is important to know which types of sites are most likely to entail risks. Landfill sites may differ enormously in the conditions that render them hazardous, and conditions that determine the exposure to and resulting health risks posed by any waste site are likely to be unique to that particular site. Such conditions may include the types, quantities, and age of the waste present; hydro geological and meteorological factors; and site management and engineering practices. We have not in this review attempted to relate technical aspects of waste disposal to health effects. Much of the existing epidemiologic work investigates large, old sites, uncontrolled dumps, and sites where heavy off-site migration of chemicals was detected. On the basis of current evidence, we cannot extrapolate findings for these individual sites to landfill sites in general or conclude which landfill sites are more likely than others to affect the health of nearby human populations [23].

Migration of hazardous substances into groundwater is often an important environmental concern in relation to landfill sites, which may represent a public health problem, especially when a site is located near aquifers supplying public drinking water. However, in many situations the drinking water supply of residents near waste sites does not originate from the local area. For people living in the vicinity of these sites, other routes of exposure may be of more concern. Landfill sites may be a source of airborne chemical contamination via the off-

site migration of gases and via particles and chemicals adhered to dust, especially during the period of active operation of the site. Very little is known about the likelihood of air exposure from landfill sites through landfill gases or dust. At some of the sites described below, low levels of volatile organic chemicals have been detected in indoor air of homes near landfill sites [24] and outdoor air, in areas surrounding sites and in on-site landfill gas [25]. Other possible routes of exposure include contamination of soil, ground, and surface water, which may lead to direct contact or pollution of indoor air in the case of evaporation of Volatile Organic compounds (VOCs) into basements of nearby houses. Contamination via the food chain may sometimes be of concern for nearby residents in the case of consumption of homegrown vegetables. Drinking water is a possible route of exposure only if water for domestic use is locally extracted. If this is the case, other domestic water uses (bathing, washing) may also lead to exposure via inhalation of evaporated VOCs and/or direct contact [24].

A general problem in studies of cancer incidence is the long latency period between exposure and clinical manifestation of the cancer. Studies may not always allow for a long enough latency period, which reduces their power to pick up long-term effects. Moreover, because of the long latency period, a considerable number of people may have migrated into or out of the exposed areas between time of exposure and time of diagnosis, which will lead to misclassification of exposures. Studies of chromosome changes (chromosome aberrations and sister chromatid exchanges) are undertaken with the assumption that such changes are related to the mechanisms underlying cancer and possibly birth defects. Chromosomal changes are studied as biomarkers of early response or effect of exposure to mutagenic and carcinogenic chemicals. Sorsa et al. point out that theoretically it is reasonable to assume that chromosome damage is directly related to cancer etiology, but the number of agents clearly shown to induce such damage in humans is still limited. Increased frequencies of chromosome changes may indicate exposure to mutagens and carcinogens, but it is not clear at present how well they predict cancer risk [26].

It is also relatively easy to collect accurate information on birth weight from birth certificates. However, a large number of risk factors are associated with low birth weight (including smoking, socioeconomic status, nutritional factors, parental height) and these may act as

confounding factors, giving biased estimates of association with residence close to a site. Birth defects have fewer established risk factors than other reproductive outcomes such as low birth weight, and studies of birth defects may therefore be less affected by confounding factors, although unknown risk factors could still play a confounding role. Also, birth defects represent an etiologically very heterogeneous set of conditions; analyses of the total malformation rate (all defects combined) have the advantage of larger numbers but may not be sensitive enough to pick up increases in risk of specific defects. The grouping of malformations into groups that are etiologically similar is difficult because of lack of knowledge on causes of specific defects. Grouping therefore always entails a compromise between large enough numbers and etiologic specificity.

Large quantities of toxic materials (residues from pesticide production) were dumped at the landfill of Love Canal, New York State, during the 1930s and 1940s, followed by the building of houses and a school on and around the landfill in the 1950s. By 1977 the site was leaking and chemicals were detected in neighborhood creeks, sewers, soil, and indoor air of houses. This led to one of the most widely known and publicized incidents of environmental pollution from landfill. Exposure of Love Canal residents, although not well understood, may have occurred via inhalation of volatile chemicals in home air or via direct contact with soil or surface water [27]. The drinking water supply was not contaminated. Chemicals detected at Love Canal were primarily organic solvents, chlorinated hydrocarbons and acids, including benzene, vinyl chloride, PCBs, dioxin, toluene, trichloroethylene, and tetrachloroethylene. Several studies were conducted to detect whether Love Canal residents suffered adverse health effects.

Infants and children have been the subject of other Love Canal studies. A cross-sectional study reported an increased prevalence of seizures, learning problems, hyperactivity, eye irritation, skin rashes, abdominal pain, and incontinence in children living close to the Love Canal site compared to controls from other areas, as reported by the parents of the children. It has been noted in previous reviews [28] that this study was conducted in 1980, 2 years after the residents of Love Canal had become aware of the hazardous waste problem, when media and public interest were high, and people were being evacuated. This makes it likely that differential reporting of health problems biased the results. However, a similar population of children

(spending 75% or more of their childhood in the Love Canal area) had significantly shorter stature for their age than control children after allowing for factors such as birth weight, socioeconomic status, and parental height [29] found an excess of low birth weights (less than 2500 g) during the period of active dumping (1940-1953) in areas of Love Canal where exposure had been highest. Rates of low birth weight between 1960 and 1978 after the site had been closed were comparable to those in upstate New York as a whole. It is not clear whether exposure from Love Canal was highest during the active dumping period or during the period after the site was closed, when the building of houses near the site increased and the landfill was leaking. A study in 1985 by Goldman et al [29] reported a 3-fold risk of low birth weight for children exposed during gestational life to the Love Canal area compared to that for control children born elsewhere from 1965 to 1978. Data were analyzed separately for homeowners and renters so that groups of similar socioeconomic status were compared, and after allowing for confounding factors, the risk of low birth weight was significantly increased for homeowners only. This finding is difficult to interpret because there are no strong reasons to believe that homeowners would be more susceptible than renters to the effects of toxic chemicals. In the same study an increased risk of birth defects was observed for both homeowners and renters. Information on birth defects relied mainly on reports from parents. Some recall bias can therefore be suspected, in particular for defects of lesser severity, but this is unlikely to account for the entire association found for major birth defects.

Berry and Bove studied birth weight at the Lipari Landfill in New Jersey, a site for municipal and industrial waste. Leachate from the site migrated into nearby streams and a lake adjacent to a residential area. Inhalation of volatile chemicals emitted from the landfill and contaminated waters was thought to be the most important exposure pathway. The site closed in 1971 after complaints of residents, but the heaviest pollution was estimated to have occurred during the late 1960s to the mid-1970s. The study found a convincing increase in proportion of low birth weight babies (< 2500 g) and a lower average birth weight in the population living closest (within a radius of 1 km) to the landfill in the time period when potential for exposure was thought to be greatest (1971-1975) compared to these factors in a control population. Although information on some confounding variables such as smoking, alcohol consumption, and socioeconomic status was not available, mothers in the exposed area were more highly educated and therefore appeared to be of higher socioeconomic status. One would expect

higher birth weights in areas of higher socioeconomic status, so as the authors point out, confounding by socioeconomic status does not explain the lower birth weights found. In time periods before and after heavy dumping and off-site pollution, birth weights were higher in the area closer to the site than in the control area, which supports the hypothesis that pollution from the waste site may have been related to low birth weights in the community close to the site [30].

A range of reproductive effects including low birth weight was studied around the large BKK hazardous waste disposal site in Los Angeles County, California [31]. After previous investigations of vital records found that trends in low birth weight and neonatal deaths corresponded closely with times and quantities of dumping at the landfill. Results for the whole study period showed no increase in adverse reproductive effects, but during the period of heaviest dumping, birth weights were significantly lower in exposed areas than in control areas using odor complaint frequency zones to classify exposure. All results were adjusted for education, income, and race. The decrease in mean birth weight found in the high-odor complaint zone was small (59 g) compared to that in the Lipari Landfill study (192 g) and was less than a third of birth-weight reductions caused by smoking during pregnancy [30]. Odor complaint frequency zones corresponded better with vinyl chloride monitoring data and meteorology around the site than did census tract areas or distance-based (< 0.7 miles) exposure zones, and this was therefore thought to be the most accurate method for classifying exposure. Using census tract or distance-based exposure zones, smaller decreases in mean birth weight were found (35.2 g,  $p = 0.02$  and 20.4 g,  $p = 0.25$ , respectively).

Miron Quarry, a large (the third largest in North America) municipal solid waste site in Montreal, Quebec has prompted studies on both reproductive outcomes (low birth weight and preterm births) [25]. Gas from the site was the main environmental and health concern and a range of VOCs, including a number of recognized or suspected human carcinogens, had been detected in the gas. An excess of 20% in low birth weight was found among babies of mothers who were living in the high-exposure area adjacent to the landfill at the time of delivery, taking account of confounding factors such as education and age of the mother. No excess was found in the low-exposure zone compared to a control area. Exposure zones were based on proximity to the site and accounted for the direction of dominant winds. Control areas were selected that

were similar to exposure areas on a number of socio-demographic variables so as to limit the potential for confounding. The cancer study used the same exposure zones and control areas and increases were found in incidences of cancers of the stomach, liver, prostate, and lung for men, and stomach and cervix/uterus for women. Incidences of cancers of other organ sites were not increased in the exposed areas. Age and sex were the only confounders that could be controlled for directly and the authors admit that area matching for socio-demographic factors was based on fairly broad zones. The landfill started operation in 1968 and cancer incidence was studied between 1981 and 1988, which allowed a maximum latency of only 20 years among those residents in the area throughout the period [25].

In Mellery, Belgium, gases containing a complex mixture of VOCs escaped when the clay seal of a landfill site cracked. Because some of the detected chemicals were known mutagens and/or carcinogens, damage to chromosomes was studied and an increase in chromosome damage (sister chromatid exchanges) was found among Mellery residents but not in unexposed subjects in subgroups of both smokers and nonsmokers [31]. In children 8-15 years of age, a more marked difference was found between exposed and unexposed groups than among adults. The findings indicated exposures similar to those of occupationally exposed populations. The adult unexposed comparison subjects were recruited from a volunteer blood donor list and may therefore have comprised a group with risk behavior and exposure to possible risk factors for chromosome damage different from those of the general population. They also reported less occupational exposure than the Mellery inhabitants. It is unclear how occupational exposure was defined and results have not been adjusted for it. A follow-up study after site remediation reduced the concentration of the atmospheric pollutants to background levels reported that chromosomal damages in Mellery children had returned to background levels and were no longer different from those for unexposed populations [31]. At the Drake Superfund Site, an industrial chemical dump in Pennsylvania, widespread on- and off-site contamination of groundwater, soil, and surface water with organic (benzene, chlorinated benzene, phthalates) and inorganic (arsenic, mercury) compounds prompted a cancer mortality and birth defects study and Air monitoring near the site identified a small number of organic compounds, but the main exposure route was thought to be direct contact with surface waters and soil in recreational areas near the site.

Budnick et al.[32] found an increase in mortality from bladder cancer (cancer of primary a priori concern because of aromatic amines detected on and off site) in the male population of one of the counties surrounding the waste site compared to average mortality rates in the entire state and the United States. Bladder cancer in females did not show such an effect. The authors point out that an occupational effect for males working in the Drake chemical plant may explain the fact that the association was found in men only. No excess in risk of birth defects was found.

A number of other community health surveys have investigated a wide range of health problems, including respiratory symptoms; irritation of skin, nose, and eyes; gastrointestinal problems; fatigue; headaches; psychological disorders; and allergies. These studies have been conducted in response to concerns from the public, often triggered by smells and odors from the sites. In a number of studies, self-reported health problems were increased in exposed populations (people living close to the waste sites) compared to control populations [33]. The majority of these health surveys rely on residents reporting symptoms and diseases through questionnaires or interviews.

Two recent studies around the French landfill of Montchanin used records of prescribed medication and cases from general practitioners [34] to define health outcome, in order to avoid biases related to self-reporting of symptoms. Exposure classification in both studies was based on an individual index, taking into account the concentration of airborne pollutants and daily activities of study subjects. High concentrations of VOCs were detected in areas near the site and both leachates and air from the site were reported to be highly toxic in 1988 and 1989, shortly after site closure. Consumption of drugs prescribed for most conditions from 1987 to 1989 did not show a trend with exposure level, although a slight trend was found for drugs taken for ear, nose, and throat, and pulmonary conditions. In the second study, patients with conditions thought to be associated with dump emissions were compared to other GP patients and an association was found for respiratory symptoms and psychological disorders. Again, consulting a doctor for such conditions and subsequent diagnosis of the conditions by the physician may be related to fears of adverse effects from the landfill rather than to toxic chemical effects.

A number of reports are available of geographical comparison studies initiated after high rates (clusters) of specific diseases were reported in the vicinity of landfill sites. For example, increased rates of leukemia found in communities nearest a toxic waste dump in North-Rhine Westfalia, Germany, supported a GP report of a cluster near the site [35]. A cluster of childhood cancer reported by residents near a landfill site in Walsall, England, was not confirmed in a geographical comparison of rates in the ward containing the site to expected rates based on the regional average. Only short reports of these two investigations have been published. Concerns from residents and a GP about increased rates of congenital abnormalities (specifically gastroschisis, a defect in the abdominal body wall) among the population living near the Welsh landfill of Nant-y-Gwyddon were supported by the finding that rates of congenital abnormalities in exposed wards were almost 1.9-fold those in unexposed wards over the period from 1990 to 1996 . However, rates in the exposed wards were already high (1.9-fold those of unexposed wards) between 1983 and 1987 before the site opened, and it is unlikely, therefore, that these increased rates were due to the landfill. Four cases of confirmed gastroschisis indicated significant 9-fold excess in rates of gastroschisis among exposed wards between 1989 and 1996. A cluster of bladder cancer cases in one town in Illinois in the United States, was observed by researchers and subsequently linked to the presence of two contaminated wells close to a landfill site [36].

Shaw et al conducted a study on the risk of congenital malformations and low birth weight in areas with landfills, chemical dumpsites, industrial sites, and hazardous treatment and storage facilities in the San Francisco Bay, California area. Census tracts were classified as a no hazardous site in area, b hazardous site in area but no evidence of human exposure, and c hazardous site and plume in the area with evidence of potential human exposure. A small increase (1.5-fold) in risk was found for heart and circulatory malformations in the areas with potential human exposure. This increased risk was present across chemical classes and exposure routes. Risk of other malformations or low birth weight was not significantly increased. Results were adjusted for some potential risk factors (maternal age, race, sex of child, birth order) but not for socioeconomic status [37].

Vrijheid review evaluates current epidemiologic literature on health effects in relation to residence near landfill sites. Increases in risk of adverse health effects (low birth weight, birth

defects, certain types of cancers) have been reported near individual landfill sites and in some multisite studies, and although biases and confounding factors cannot be excluded as explanations for these findings, they may indicate real risks associated with residence near certain landfill sites. A general weakness in the reviewed studies is the lack of direct exposure measurement. An increased prevalence of self-reported health symptoms such as fatigue, sleepiness, and headaches among residents near waste sites has consistently been reported in more than 10 of the reviewed papers. It is difficult to conclude whether these symptoms are an effect of direct toxicologic action of chemicals present in waste sites, an effect of stress and fears related to the waste site, or an effect of reporting bias. Although a substantial number of studies have been conducted, risks to health from landfill sites are hard to quantify. There is insufficient exposure information and effects of low-level environmental exposure in the general population are by their nature difficult to establish. More interdisciplinary research can improve levels of knowledge on risks to human health of waste disposal in landfill sites. Research needs include epidemiologic and toxicologic studies on individual chemicals and chemical mixtures, well-designed single- and multisite landfill studies, development of biomarkers, and research on risk perception and sociologic determinants of ill health [38].

## CHAPTER III

### MATERIALS AND METHODS

#### 3.1 STUDY SITE

By considering the previous studies and by the fact that residents and groundwater are well exposed to pollutants the study sites were selected. According to Poul Elliot (2001) the site selection was conducted below 2 km [11] of Addis Ababa city solid waste disposal site, Reppi, and based on convenience site selection strategy for controlled study Nifas Silk Lafto sub-City Kebele 15, which is 12km far from the dumping site, was selected. (See figure 3.1)

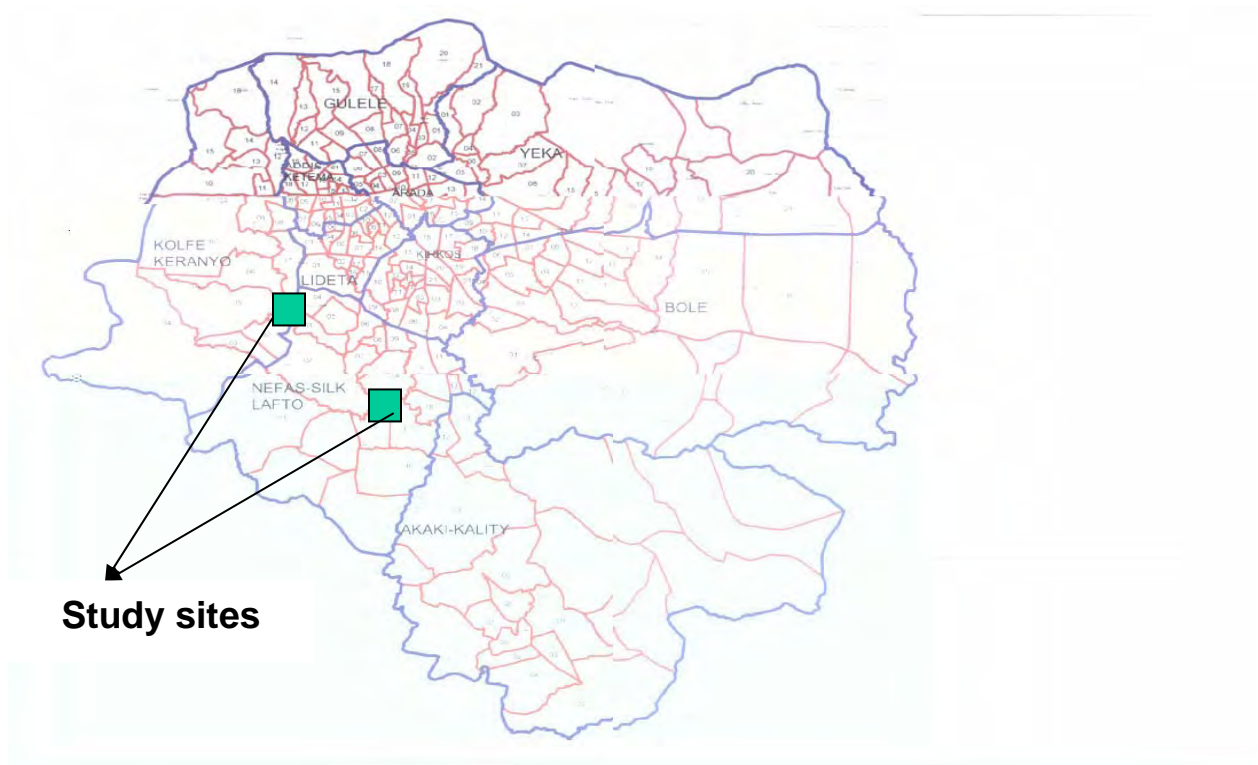


Figure 3.1 Study sites (www.addisababacitymap.com)

## **3.2 STUDY PERIOD AND DESIGN**

Cross-sectional study was conducted in Addis Ababa city solid waste disposal site from April 10-25/ 2007 to determine the public health and groundwater risk analysis in the vicinity of study area.

## **3.3 STUDY POPULATION FOR PUBLIC HEALTH ISSUE**

### **3.3.1.1 Source and Study Population**

The source population for this study was Addis Ababa city residents. Based on the standard sampling technique the study populations for this study include were those who live in 2km from the boundary of Addis Ababa city solid waste dumping site and the same study population size from 12km away from dumping site that is Nifas Silk Lafto sub –city Kebele 15 residents were included in the study.

### **3.3.1.2 Study Population Sampling**

Representative samples were sampled based on standard method of randomization for study population. For public health variables, the proportionality (p) value has been taken to be 0.5 since there are not relevant findings that state proportionality of public disease occurrence in the study site vicinity. Then some marginal error (d) (5%) in the estimate of proportion (p) of housing units was agreed on and there might be a small risk ( $\alpha$ ) (0.05) that is willing to incur that actual error would be larger than (d). Simple random sampling is assumed, and p is taken as normally distributed.

According to Cochran [39], the formula that connects total sample size housing unit (n) with the desired degree of precision is given below.

$$n = \frac{NZ^2 pq}{d^2(N-1) + Z^2 pq}$$

Where;

n = Total sample size of housing unit,

N= Total number of housing units in the study area,

Z= standardized normal variable and its value that corresponds to 95 % confidence interval equals 1.96,

P=0.5 since there not relevant findings that states proportionality of disease occurrence in its vicinity,

q = 1-p,

d= degree of accuracy or estimation (= 0.05),

$\alpha$ = level of significance and it is taken as 5 %

According to the two nearby kebeles information about 2000 total housing units (N)near the landfill with in 2km away from the boarder of the landfill, the total number of samples of housing units (n) is determined using the above formula.

$$n = \frac{2000(1.96)^2 \times 0.5 \times 0.5}{(0.05)^2 (2000 - 1) + (1.96)^2 (0.5 \times 0.5)} = 322$$

The expected number of housing units to be taken for this study was 322 but because of the non-cooperativeness and absence of some householders during sampling and data collection days, the response rate was assumed 98% and thus the actual sampling size for this study was 316.

### **3.4 STUDY VARIABLES**

#### **3.4.1 Leachate characteristics and groundwater chemical quality**

The following leachate and ground water parameters were selected for this study. They were Temperature, P<sup>H</sup>, Total Dissolved Solids (TDS), Total Suspended Solids, Biochemical Oxygen Demand (5 day BOD), Chemical Oxygen Demand (COD), Nitrate (as N), Ammonia (N), Copper, Nickel, Lead, Chromium (total), Cadmium, and Chlorides, total phosphate, sulfate, Alkalinity, and electric conductivity.

### **3.4.2 Health variables**

The following health variables were considered in the study,

- ❖ Abortion,
- ❖ Birth weight,
- ❖ Toxic dust ( respiratory, dermal and eye problems ),
- ❖ Odors ( respiratory problems),
- ❖ Playground and school,
- ❖ Disease vectors including Flies, Cockroach, Spider, Rats, Mosquitoes and Scavenger Birds, Canine animals (including cats, dogs, hyena, fox etc),.

## **3.5 SAMPLES COLLECTION, TRANSPORTATION AND STORAGE OF LEACHATE, AND GROUNDWATER**

### **3.5.1 Sample collection**

Leachate samples were collected from the well dug in the center of the site and groundwater samples for laboratory analysis were collected from privately owned well and naturally occurring spring, which are found 300 meter and 12 kilometer distance from the boarder of dumping site respectively.

### **3.5.2 Ground water and leachate sample collection equipment**

The equipments used to withdraw samples from leachate, landfill shallow well and one spring were selected based on consideration of the parameters (chemicals) to be analyzed in the sample. To ensure the sample is representative of groundwater information, it was to keep physical or chemical alterations of the sample to a minimum. USEPA (1992a) provides review of the issues involved in selecting ground-water sampling equipment, and a summary of the application and limitations of various sampling mechanisms. Sampling materials and equipment were selected to preserve sample integrity. Sampling equipments that were used bottles and jar can made of poly venial chloride (PVC). Sample collection equipments were not

altering analyte concentrations and composition. To avoid altering sample quality, the samples were transferred from the sampling equipment directly into a prepared container.

### **3.5.3 Sample Preservation**

In groundwater and leachate sampling, every attempt was made to minimize changes in the chemistry of the samples. To assist in maintaining the natural chemistry of the samples it was preserve these preservation methods that will be used generally include P<sup>H</sup> control, refrigeration and protect from light.

### **3.5.4 Sample Storage and Shipment**

Storage and shipment of groundwater and leachate samples were performed in manners that maintain sample quality. Samples were cooled to 4°C as soon as after samples were collected. These conditions were maintained until the samples were received at the laboratory.

Transportation arrangement was maintain proper storage conditions and provide for effective sample pickup and delivery to the laboratory. Sampling plan was coordinated with the laboratory so that appropriate sample receipt, storage, analysis, and custody arrangements were provided.

## **3.6 LABORATORY PROCEDURES**

As can be seen in annex III all physicochemical parameters were determined based on American standard methods for examination of water and wastewater [40]. The available standard procedures and apparatuses listed were used.



Figure3.2: - Sanitarian Tesfaye Bogale during leachate and well water sample collection

### **3.7 STATISTICAL ANALYSIS**

Parametric analyses of variables were followed by comparative procedures to identify statistically significant evidence of contamination. The method was included estimation and testing of contrasts between each compliance groundwater sample and leachate sample for each constituent.

The statistical performance standards were used to provide a means to limit the possibility of making false conclusion from the sample analysis data. The specified error level of 0.01 for individual sampling area compression for probability of type I error (indication of contamination when it is not present or false positive) essentially means that the analysis is expected predicted with 99% confidence that significant increase in contaminant levels is evident when in fact there increase is present. In addition to that public health data was analyzed by considering relative risk of exposed group and non-exposed group.

### **3.8 SAMPLE ANALYSIS AND INTERPRETATION**

#### **3.8.1 Leachate and groundwater sample**

Standard method was used for physicochemical analysis for leachate, well water and spring water samples. The purpose of ground water and leachate sampling and analysis were aimed to compare physicochemical properties water and leachate quality with internationally accepted protocols (standards). Sample collection, shipment, storage and analysis were conducted in the study period.

Samples were collected based on standard procedures to detect significant changes in ground water chemistry due to operation of solid waste disposal facility (dumping site). These data quality objectives were addressed:

- ❖ Accuracy and precision of methods used in the analysis of samples, including measurements

- ❖ Quality control and quality assurance procedures used to ensure the validity of the result. Example use of blank samples, record keeping and data validation

### **3.8.2 Public Health Data**

Public health data were collected using pre designed questionnaire (annex II). The collected raw data were compiled and analyzed based on set variables or the objectives of the study and the results is presented using descriptive measures and finally interpreted in to valuable information and is displayed in tables and in graphs. Percentage is used to express the difference among characteristics in the study. Some statistical methods were carried out so as to associate variables.

### **3.9 ETHICAL CONSIDERATION**

Data collection as well as leachate and groundwater sampling were proceed after a written consent obtained from Addis Ababa University Chemical engineering department, Addis Ababa city administrative council, Addis Ababa city Sanitation, Beautification and Park development agency and Kebele administrative found in the nearby dumping site and oral consent from the study population.

### **3.10 PRE-TEST**

The questionnaires were tested on randomly chosen households for its reliability and validity before it was used for actual data collection. This helped data collector to be more familiarized with the contents of the questionnaires and also helped me to think the following points:

- ❖ Acceptability of the different approaches during data collection and interviewing,
- ❖ Acceptability of the questions which was asked,
- ❖ Sequences in the questionnaire,
- ❖ Willingness of respondents to collaborate the study,
- ❖ Wording of questions (clear or not), and
- ❖ Space for answer.

## CHAPTER IV

### RESULT

#### 4.1. GROUND WATER AND LEACHATE SAMPLE RESULTS

Before samples were collected site selection for leachate sample and groundwater samples was carried out. After sampling sites selected leachate sample was collected at the center of dumping site from shallow well as can be seen in figure 3.1 and the color of leachate sample looks black and the ground water samples were collected from private owned well located in the southern direction at 300m from the boarder of dumping site. The well water table range 1.8 to 4.5m in one full day, since the water was used for construction of building and the other controlled sample was collected from naturally occurred spring in east direction at distance 12km from dumping site the color were bright yellow and colorless respectively as can be seen in figure 4.1.



Figure 4.1: Samples collected for laboratory analysis from leachate, nearby well and spring water (from left to right).

On site measurement were conducted for the temperature, DO, conductivity and P<sup>H</sup> of leachate and ground waters using standard devices and the result obtained from the measurement for leachate was 24.4<sup>o</sup>C that is similar with the ambient temperature and the temperature of well water and spring samples were 24.3<sup>o</sup>C and 24.7<sup>o</sup>C respectively. The P<sup>H</sup> value of the leachate, well water and spring water in the on site were 9.23, 9.48 and 9.15 respectively.

Leachate produced in the dumping site and groundwater physicochemical characteristics; nutrients and heavy metals were determined in Addis Ababa city Environmental Protection Authority and in Ethiopian Geological Survey Water Laboratory. Tables 4.1, 4.2, 4.3 displayed the physicochemical characteristics, nutrient concentration and some important trace heavy metals concentration with their respective samples.

Table 4.1: Physicochemical characteristics of leachate and groundwater samples

Parameters	leachate mg/l	Well water mg/l	spring water mg/l	WHO standards mg/l
P <sup>H</sup>	9.23	9.48	9.15	6.5-8
SS	29	11	Nil	@
TDS	5658	2154	132	600-1000
Alkalinity (HCO <sub>3</sub> <sup>-</sup> )	5364	1465	173	@
Chloride	520	256	186	250
Sulfate	502	398	64	300
BOD	160	20	30	0.8 to 5
COD	210	54	67	<10
DO	NA	2.6	2.8	7 - 14
Conductivity (μsc/cm)	2126	154	32	@

@ = Not found in the available WHO standards documents

NA = Not applied

Table 4.2: Nitrogen and phosphate concentration in leachate and groundwater samples

Parameters	Leachate mg/l	Well water mg/l	Spring water mg/l
Ammonia (as N)	0.4	0.1	0.02
Nitrate (as N)	0.66	0.42	0.03
Total Phosphate	6	2	Nil

Table 4.3: trace metals composition of leachate, well and spring water samples

Parameters	Leachate (mg/L)	Well water Conc.(mg/L)	Spring water Conc.(mg/L)	WHO standards (mg/L)
Lead	0.09	0.076	0.06	0.010
Nickel	0.07	0.04	0.01	0.020
Copper	1.40	0.40	1.40	2.000
Cadmium	0.13	0.10	Nil	0.003
Chromium	0.30	0.20	Nil	0.050

Table 4.4: Risk based drinking water criteria and near by well concentration.

Element	Risk-based drinking water criteria (mg/l)		Well water concentration (mg/l)
	WHO	U.S.EPA	
Cd	0.010	0.010	0.1
Cr	0.050	0.100	0.2
Ni	0.020	0.100	0.04
Cu	2.000	1.3000	0.4
Pb	0.010	0.015	0.09

WHO - World Health Organization (41)

USEPA – United States Environmental Protection Authority (42)

## 4.2. PUBLIC HEALTH RESULTS

Due to uncertainty in quantifying dumping site emission, uncontrolled type of disposal practice and lack of facilities in the site, it is difficult to estimate the health risks on the nearby residents of the dumping site. Although there is conflict findings on health effects of solid waste dumping site this section display some important public health findings.

Based on the data collected from the nearby community and controlled site community combined respiratory tract, dermatological and sight problems were assessed and the finding was 91.5%, 75.6% and 84.8% respectively for exposed population and unexposed group findings were below 10%. In the study population there were no significant abortion and congenital problems. Table 4.5 showed combined respiratory, dermal and sight problems in the exposed and unexposed communities.

Table 4.5: Comparison of public health problems to those who live in the near by dumping site and controlled group

Conditions	Comparison group	N <sup>o</sup> of events (n=316)	% of problems
Combined respiratory problems	Near site residents	289	91.5
	Control group	28	8.8
Combined Skin problems	Near site residents	239	75.6
	Control group	16	5.1
Red, itchy eyes	Near site residents	268	84.8
	Control group	22	6.9

96% interviewed respondents near the dumping site were confirmed all children less than 10 years play with condoms and other used medical utensils including syringes and needles and dust and noise nuisance were considerable problems to the entire exposed group but it was not in the controlled community. Among interviewed near the dumping site households 92% under 5 years children were with diarrhea and 5% in the controlled community. Among 15 live births in exposed group 40% infants in last one year was under weight and among 12 live birth in non exposed group only 8% of live birth were also under weight see figure 4.2.

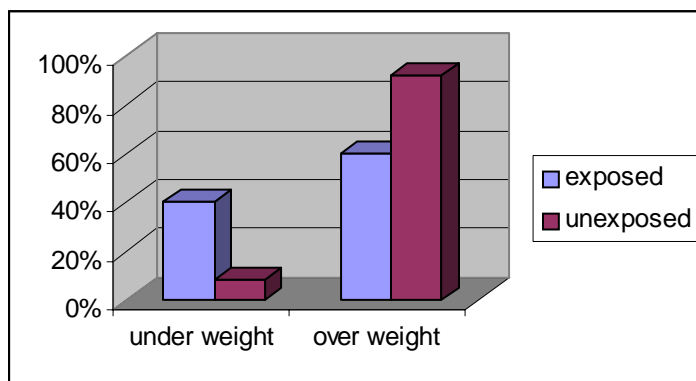


Figure 4.2: Birth weight of infants from study population in the last one year.

Study population for the disease vectors including dogs, other canine animals, flies, cockroach, mosquito, rat and scavengers were interviewed. Almost all disease vectors were a considerable problem in the vicinity of dumping site as can be seen in table 4.6.

Table 4.6: Prevalence of disease vectors with in the vicinity of dumping site and controlled site

Vectors	Near landfill site (n = 316)		Far landfill site (n = 316)	
	No	%	No	%
Dogs	313	99	29	9.2
Canines except dogs	302	95.6	6	1.9
Flies	316	100	28	9
Cockroach	304	96.2	23	7.3
Mosquito	303	95.9	None	0
Rats	316	100	13	4.1
Scavenger	299	94.6	None	0

## CHAPTER V

### DISCUSSION

Since there is no design information obtained from the Addis Ababa City Solid Waste Dumping Site, Reppi, the concentration of organic compound, nutrients, Temperature, P<sup>H</sup>, Alkalinity, trace metals and hardness were determined based on American Public Health Association standard methods for the examination of water and wastewater [40]. However, as can be deduced from tables 4.1, 4.2, 4.3 the maximum concentration of the stated materials are most likely found in the leachate and near by ground water.

The characteristics of leachate and ground water are shown in Tables 4.1, 4.2, and 4.3. High concentration of pollutants prevailed in leachate and well water except copper. Leachate and well water produced during sampling higher concentration of pollutant particularly of conductivity, SS, TDS, Alkalinity, Phosphate, lead were found this may be due to the emission from mixed waste but BOD and COD of spring water were greater than nearby well water this may be due to contaminant of waste from its catchments area and due to its stagnation. This could be attributed to groundwater and surface water ingress from the dumping site that promote volatilization of pollutants from active decomposition of waste mass in to leachate emanated from disposal site to the near by ground water source.

Turbidity, as can be seen in figure 4.1, and suspended solids (11mg/l in well water) indicated that the presence of organic and inorganic solids that can provide adsorptive site for certain chemicals and/or biological agents.

The dissolved oxygen in the leachate was not detected and in the groundwater was quit low and cannot support desired aerobic organisms in the study sites. This may upset the ecosystem, encouraging development of septic conditions and lead to proliferation of anaerobic biota that may produce anaerobic condition in the groundwater. The ammonia value in the leachate (0.4 mg/l) provides evidence of its release from decomposition of nitrogenous substances in the dumping site.

There is no set standard for ammonia in wastewater and in leachate aimed for discharge in to aquatic environment in Ethiopia even though it is highly toxic and lethal to aquatic species even at low concentrations. The same is true for nitrate and phosphate concentration standard in Ethiopia.

The background level of phosphorus in groundwater was not found. The level of phosphorous measured in leachate and well water in and near the dumping site is 6 and 2 mg/l; which is much exceeded the value of 0.15 mg/l. There is little potential for phosphorus to leach through the soil into the groundwater. This is because soil particles have a large capacity to fix phosphorus in forms that are immobile in soil. Most soils filter out soluble phosphorus as water passes through the soil profile into groundwater. In instances, where relatively high values of phosphorus were obtained in leachate, see table 4.2, an overload or a bypass of the filtration process could have occurred, thus allowing relatively higher concentrations of phosphorus (2 mg/l) into groundwater. There is no indication that the amount of phosphorous leached is increasing as more wastes are being added to the landfill since there may be a source for phosphorous from near by farming land.

Natural concentrations of nitrates in groundwater are very low, since plants take up most of the nitrogen near the ground surface before it can reach the water table. However, background levels of nitrates in the leachate and nearby well recorded at the dumping site are relatively high (0.7 and 0.4 mg/l). This might be explained by the fact that the land is contaminated by leachate nitrate and that contamination might have been brought by the application of fertilizers from the residents farming land. Nitrate is a concern because it does not break down quickly in the soil and does not stick to soil particles. Instead, it travels rapidly with the groundwater and can seep a long way from its source.

In this study, groundwater and leachate concentrations of trace metals such as Cadmium, Chromium, Lead, Nickel and Copper were determined in Ethiopian Geological Survey Laboratory and in Addis Ababa city environmental protection authority. As can be seen in tables 5.1 these analytes are identified, as have several potentially significant groundwater and public health challenges that require urgent attention and additional study. Table 4.3 displayed composition of trace metals with respect to sampling.

The concentrations of these analytes in leachate and groundwater are shown in Table 4.3 for information purposes. Daily minimum, average, and maximum, water table of the nearby well depths in this study were 1.8 m, 2 m, and 4.5 m, respectively. Mercury (Hg) and Arsenic (As) were not included in the table because these elements could not be identified in the available laboratories. Some trace metals were found above their respective standard in the nearby well water sample. Lead in the leachate and groundwaters were greater than the WHO international standard by 90% and 76% respectively and when we compare the nearby well and faraway spring the concentration in the well is greater than the spring. This may be due to the contamination resulted from the disposal site leachate.

Of these heavy metals analytes, the concentrations of lead (Pb), nickel (Ni), and chromium (Cr) and cadmium (Cd) in well water exceeded WHO or U.S. Environmental Protection Agency health based drinking water criteria (table 4.4). This may be due to the dumping mixed waste in the site that includes lead battery and petroleum compound, cadmium, chromium, and Nickel. Copper concentration in the controlled spring exceeded from other samples this is due to its source from its catchments area and from rock formation in its vicinity.

There is sufficient evidence from human epidemiologic studies linking increased mortality from liver, kidney, bladder, and lung cancers to drinking heavy metals contaminated water;

Table 5.1: Health effects of selected metals found in leachate

Cadmium	Probable carcinogen and teratogen; embryo toxic; CNS, reproductive and lung/respiratory effects; kidney damage
Lead	Probable teratogen, Kidney, and brain damage, CNS and reproductive effects, blood cell disorder
Chromium	Carcinogenic, probable mutagen, lung/respiratory effects, allergic Sensitization, eye irritation
Nickel	Probable carcinogen, possible teratogen, lung/respiratory effects, allergic sensitization, eye and skin irritation, liver and kidney damage

SOURCE: Adapted from the poisoned well [Sierra Club Legal Defense Fund, 1989]

The characteristics of leachate result in table 4.4 agrees with the study done in Abidjan, Nigeria [6], which was not sensitive enough to delineate the WHO drinking water guideline. This can be

revealed that the contamination of nearby well is due to leachate contamination from an engineered solid waste dumping site.

From study results of heavy metals in the groundwater it might reveal that, if residents used groundwater for domestic purpose for long time, the community may be in danger for diseases listed in the above table 5.1.

The study finding demonstrated in table 4.5, 10.3 fold increased respiratory morbidity from respiratory tract problem among exposed group (residents near the dumping site) compared with controlled group (residents live far away the site). The relative risk of dermatological problem among current exposed to the dumping site compared with unexposed group was 14.9 and the sight problem compared the exposed group with non exposed group was 12.2. Thus, living in the near by dumping site is much strong risk factor for morbidity from respiratory tract, dermatological and sight problems than unexposed to the dumping site. This revealed that the potential public health impact of living near the site on morbidity would be far greater than living far away from the dumping site.

A potential exposure to ambient air pollutants from the dumping site was defined in terms of a set of geographical exposure zones proximal to the site. A set of reference areas distal from the site was selected to be similar to these exposure zones with out considering socio-demographic factors. Risk ratio for respiratory tract problem with distance was 10.3 (99% of CI).As Goldberg MS [25] revealed that low birth weight was significantly elevated in the exposed zone proximal to the site.

The study finding in the nearby community indicated that children under 10 years play with infectious waste and mainly with condom. Several literatures reported that HIV could be transmitted through blood transfusion and sharp equipment mainly through syringe and needles in addition to that contacting with body fluid mainly with blood, orgasm, and sperm cell. Though HIV can live for seconds but occasionally it may be as long as 10 to 15 minutes [43]. This may revealed that those children playing with condom and infectious waste are in danger for HIV infection. In addition to that they are in danger for indirect transmissible diseases. Of the interviewed respondents in exposed group 92% were revealed under 5 children were with diarrhea this is due to exposure to contaminants and disease victors from dumping site.

As can be seen from the Table 4.6 more than 95% of the population lives near the dumping area are infested with canine animals this is due to the fact that stray dogs and other similar canine animals are scavengers for left over food and other wastes. This infestation will be big problem for the transmission of hydrophobia (rabid disease). And more than 96% near the residents are infested by flies and cockroach. This infestation revealed that those live near the dumping site are in danger for feco-oral disease transmission with relative risk of 12 as compared with population far away from the dumping site. In addition to that almost 96% of nearby community are well exposed for the occurrence of malaria due to the mosquitoes breeding. The last but not the list, rat infestation is pronounced problem in near by community (100% exposure rate). This revealed that the community in the site is exposed for communicable diseases such as Hantavirus Pulmonary Syndrome (HPS), Murine Typhus, Rat-bite fever (RBF), Salmonella enterica serovar, Typhimurium, Leptospirosis, and Eosinophilic Meningitis.

## **CHAPTER VI**

### **CONCLUSION**

The presence of large quantities of mixtures of potentially hazardous chemicals in solid waste dumping sites close to residential area has increasingly caused some significant groundwater and public health concerns. Concerns have led to a substantial number of studies on groundwater and public health effects associated with solid waste dumping sites. From this study we can conclude that there is an increase in risk to ground water and public health that is reported near Reppi solid waste dumping site. Although biases and confounding factors cannot be excluded as explanations for this finding, the finding revealed that high risks are associated with groundwater pollution and public health near the dumping sites. In general Reppi solid waste dumping site worth nothing to the environment as well as to the public health in its vicinity. This indicated that Addis Ababa city Government is practicing an out of site out of mind or problem principle with out giving due regard for the environment and public health.

## **CHAPTER VII**

### **RECOMMENDATION**

The result indicated that the dumping site is producing many potent contaminants to the environment and to the people nearby which has made using the site for a dump is completely unacceptable. The following are therefore recommended.

1. The government with other environmental and public health concerned organizations should give prior attention to the problem of dumping site, with regard to public health and ground water risks.
2. The operation of dumping site must be stopped as soon as possible so as solve groundwater and public health problems and new engineered landfill should be constructed with proper collection and treatment of leachate. Before closing the present dumping site temporary disposal options should be considered and that should be free of environmental pollution and public health risks.
3. There should be rules, regulations and scientific standards regarding well engineered landfill design and other means of solid waste disposal technology.
4. There should be monitoring well to the new landfill for continuous monitoring of leachate contamination to the ground water.

## **ANNEX-I**

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## ANNEX II-QUESTIONNAIRS

**Subcity** -----

**Kebele**-----

**House Number**-----

1. Is there any dust nuisance in the indoor environment of the household?

Yes  No

2. Is there any respiratory illness in the family member of the house?

Yes  No

3. Was there any one who dead due to respiratory problem?

Yes  No

4. Is there any toxic smoke from the landfill in the indoor environment?

Yes  No

5. Do you think there will be fire hazard from landfill?

Yes  No

6. Do you face any skin rash problem in your family member?

Yes  No

7. If Q6 is yes, age of individual with the skin problem-----

8. Do you see any children in your vicinity play with hospital waste?

Yes  No

9. Which of the following do your problem in your vicinity?

- |              |                    |
|--------------|--------------------|
| A. Snake     | E. Rodents         |
| B. Scorpions | F. Scavenger Birds |
| C. Spiders   | G. Coack roach     |
| D. Flies     | H. Mosquitoes      |

10. Which Canine animals are commonly found in your vicinity?

- |          |          |
|----------|----------|
| A. Cats  | E. Other |
| B. Dogs  |          |
| C. Foxes |          |

D. Hyena

11. Was there diarrhea (bloody, watery, etc) in under 5 children in the last month?

Yes  No

12. Was there stillbirth in you family member in the last one year?

Yes  No

13. Is there any one in your family with congenital malformation?

Yes  No

14. Was there an intermittent of the face, hands, and feet in the family members?

Yes  No

15. Do you have infants in you home?

Yes  No

16. If Q15 is yes when and where does the mom give birth?

A. Hospital

B. Health center

C. Clinic

D. Home

17. If the give birth in health institutes state whether it is under weight or over weight

Under weight  Over weight

## ANNEX III LABORATORY PROCEDURE

### 1. P<sup>H</sup>

P<sup>H</sup> was determined based on site measurement using P<sup>H</sup> meter.

P<sup>H</sup> is the way of expressing the hydrogen ion activity. Measurement of P<sup>H</sup> is one of the most important and frequent used tests in water and wastewater analysis such as:-Acid base neutralization, Water softening, Precipitation, Coagulation, Disinfections, Corrosion control.. Acids and bases were originally distinguished by their difference in taste and latter by the manner in which they affect certain materials that come to be known as indicators. With the discovery of hydrogen by Cavendish in 1766, it soon becomes apparent that all acids contained the element hydrogen. Chemists soon found that neutralization reaction between acids and bases always produced water. From this and other related information, it was concluded that bases contained hydroxyl groups.

At a given temperature the intensity of the acidic or basic character of a solution is indicated by P<sup>H</sup> or hydrogen ion activity.

$$PH = - \log [H^+].$$

P<sup>H</sup> scale is usually represented as ranging from 0 to 14, with P<sup>H</sup> 7 at 25°c representing absolute neutrality.

The minus sign is used because most of the concentration encountered is less than 1M, and so this delineation gives a positive number. The aim of this section is to determine the P<sup>H</sup> of the various forms of water and wastewater by visual comparison method and electrode method.

The basic principle of electrometric P<sup>H</sup> measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 Kilo Pascal.

Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode commonly is used. The electromotive motive force (emf) produced in the glass electrode system varies linearly with  $P^H$ . this linear relationship is described by plotting the measured emf against the PH of different buffers. Sample PH is determined by extrapolation.

### **Apparatus & Reagent**

1.  $P^H$  meter: -Consisting, glass electrode, reference electrode potentiometer and temperature compensating device.

❖ Potentiometer: A cerimit is completed when the electrodes are emerged reads as a form of  $P^H$  or milliVo HS.

❖ Reference Electrode: A half-cell that provides a constant electrode potential mostly calomel and silver that is silver- chloride electrodes.

❖ Glass electrode: A special glass containing a fixed concentration of HCl or a buffered chloride solution in contact with an internal reference electrode

❖ Beaker: Preferably use polyethylene

❖ Stirrer: Use either a magnetic or mechanical

❖ Flow chamber: For continuous flow measurement or for poorly buffered solution.

Preparation of buffer solution to calibrate the electrode before measuring the  $P^H$ . After preparation the buffer solution should be replaced after 4 weeks and stored in polyethylene bottles.

Measurement of pH is one of the most important and frequent used tests in water chemistry. pH measurements are affected by temperature in two ways: mechanical effects that are caused by changes in the properties of the electrodes and chemical effects caused by equilibrium changes.

## **2. CONDUCTIVITY.**

Electric conductivity was measured in the field based on the stated procedures and using equipments. Conductivity (K) is a measure of the ability of the aqueous solution to carry an electric current. This ability depends on: - Presence of ions, their concentration, mobility, and temperature, Valence.

Solutions of most inorganic compounds are relatively good conductors. Conversely molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

Conductance is defined as the reciprocal of resistance, R.

$$G = 1/R$$

Where the unit of R is Ohm and G is  $\text{ohm}^{-1}$  (some times written mho).

Conductance of a solution is measured between two spatially fixed and chemically inert electrodes. To avoid polarization at the electrodes surfaces the conductance measurement is made with an alternating current signal.

The conductance of a solution G is directly proportional to the electrode surface area, A  $\text{cm}^2$ , and inversely proportional to the distance between the electrodes, L cm. the constant proportionality, K such that:

$G = K (A/L)$ , is called conductivity or specific conductance. In the international system of units (SI) the reciprocal of ohm is the siemens (S) and conductivity is reported as millisiemens per meter (ms/m).

$$1 \text{ ms/m} = 10\mu\text{mhos/cm.}$$

The conductivity of a solution is a measure of its ability to carry an electric current. It varies with temperature and depends on the presence of ions and their total concentration, mobility, and valence. In practice, conductivity can be used as a measure of the dissolved solids in water, and the greater the dissolved solids the greater the ability of the water to carry electric current. Conductivity may also be referred to as specific conductance. The conductivity of deionized water is typically between 0.5 and 3.0  $\mu\text{S/cm}$ , and that of potable water ranges between 50 and 1500  $\text{S/cm}$ . Wastewater conductivity may be as high as 10,000  $\mu\text{S/cm}$ .

Establish degree of mineralization to assess the effect of the total concentration of ions on chemical equilibrium, Physiological effect on plants and animals, and corrosion effect.

- ❖ Assess degree of mineralization of distilled water and deionized water.
- ❖ Determine the amount of ionic reagent needed in certain prispitate. and neutralization reactions.

- ❖ Estimate the amount of total dissolved solids in a sample by multiplying conductivity by an empirical factor. This factor may vary from 0.55 to 0.9 depending up on the soluble components of the water and the temperature measurement.

The aim of this section is to determine the conductivity of the various forms of water and wastewater by electrode method.

## **Procedures.**

### **Measurement of conductivity at sample site**

- ❖ Turn on the conductivity meter.
- ❖ Place the conductivity probe in the conductivity standard solution and verify the meter is responding accurately.
- ❖ Obtain approximately 200 mL of sample and place in a 250 mL beaker.
- ❖ Place the probe in the sample solution and measure the conductivity. Record your data in  $\mu\text{S}/\text{cm}$ .
- ❖ Estimate the TDS (in mg/L) by multiplying the conductivity by a conversion factor of 0.55.

## **3. ALKALINITY**

Alkalinity was determined based on the following procedures and using reagents and equipments.

Alkalinity is a measure of the capacity of a water and wastewater sample to neutralize strong acid. In natural waters this capacity is attributable to bases such as  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{OH}^-$  as well as to species often present in small concentrations such as silicates, borates, ammonia, phosphates, and organic bases. Alkalinity in natural waters affects a wide range of processes such as coagulation in water treatment operations, buffering capacity of lakes and rivers, and ammonia stripping, to name a few.

## Reagents and apparatus

- a). Standard sulfuric acid or hydrochloric acid 0.1N: dilute 2.8 mL conc.  $\text{H}_2\text{SO}_4$  (specific gravity 1.834-1.836, 96-99% w/w  $\text{H}_2\text{SO}_4$ ) or 8.3 mL Conc. HCl (specific gravity 1.174-1.189, 36-37% w/w HCl) to 1000 mL standardize against the standard NaOH solution prepared for Acidity determination.
- b). Standard sulfuric acid or Hydrochloric acid, 0.02N; Dilute 200.00 mL 0.1000N standard Acid to 1000 mL with distilled water.
- c). Mixed bromocresol green-Methyl Red indicator solution: Dissolve 0.02g Methyl red and 0.1g bromocresol green in 100ml 95% ethyl alcohol.
- d). Phenolphthalein solution, alcoholic pH 8.3 indicator: Dissolve 8g phenolphthalein in 500 mL 95 % ethyl or isopropyl alcohol and add 500mL distilled water.
- e). Sodium thiosulfate 0.1N.

## Procedures

### Titrimetric method:

Measure the appropriate sample volume for the indicated alkalinity ranges and transfer

If necessary, remove the residual chlorine by adding 1 drop of sodium thiosulphate to each flask and mix.

Add two drops of phenolphthalein indicator solution and mix. If the sample turns pink, Carbonate or hydroxide is present, proceed with step. If the sample remains colorless, the water contains bicarbonate or is acid. Skip steps 4 and 5 and go on to step 6.

If the sample turns pink, gradually add sulphuric acid titrant from the burette, shaking the flask constantly until the pink just disappears.

Record the milliliters acid consumed

To the same sample, add 2 drops of mixed bromocresol green or methyl red indicator solution.

Titrate with small volume of sulphuric acid titrant until the color changes from greenish blue to light pink

Record the milliliters acid consumed. Calculate the total volume of acid used in the p-Alkalinity titration (If step 4 is carried out) and the M-Alkalinity titration.

**Calculation:**

$$\text{Alkalinity mg/L as CaCO}_3 = \frac{A \times N \times 50,000}{\text{ml sample}}$$

Where

A= ml standard acid used and

N= normality of standard acid

#### **4. CHLORIDE**

Chloride, in the form of chloride ion ( $\text{Cl}^-$ ), is one of the major inorganic anions in water and waste water. In potable water, the salty taste produced by chloride concentrations is variable and dependent up on the chemical composition of water.

Human excreta particularly the urine contains chloride in amount about equal to the chlorides consumed with food and water. This amount averages about 6gm of chlorides per person per day and increases the amount of chloride in municipal waste water about 15mg/l above that of the carriage water. Thus, waste water effluents add considerable chlorides to receive streams. Many industrial wastes contain appreciable amounts of chlorides.

Before the development of bacteriological testing procedures, chemical tests for chloride and nitrogen, in its various forms, served as the basis of detecting contaminations of ground water.

In many areas the level of chlorides in natural waters is an important consideration in the selection of supplies for human, industrial, and agricultural use. Where brackish waters must be used for domestic purposes, the amount of chlorides present is an important factor in determining the type of desalting apparatus to be used. The chloride determination is used to control the pumping of ground water from locations where intrusion of sea water is a problem.

In areas where the discharge of salts water brines and industrial wastes containing high concentrations of chlorides must be controlled to safe guard receiving waters, the chloride determination serves as to excellent advantage for regulatory purpose.

Chlorides interfere in the determination of chemical oxygen demand. A correction is made on the basis of the amounts present or else a complexing agent such as Mercury sulfate can be added. High chloride content may harm metallic pipes and structures, as well as growing plants.

The purpose is to determine amount of chloride water and waste water by using the argentometric Method.

### **Reagent.**

a). Potassium chromate indicator solution:

Dissolve 50g  $K_2CrO_4$  in a little distilled water. Add  $AgNO_3$  solution until a definite a red precipitate is formed. Let stand 12h filter and dilute to 1L with distilled water.

b). Standard silver nitrate titrant, 0.0141N:

Dissolve 2.395g  $AgNO_3$  in distilled water and dilute to 1000mL. Standardize against 0.0141N NaCl solution.  $1.00mL = 500 \mu g Cl^-$ , store in a brown bottle.

c) Standard sodium chloride. 0.0141N: Dissolve 824g NaCl (dried at  $140^{\circ}C$ ) in distilled water and dilute to 1000 mL,  $1.00mL=600\mu g Cl^-$ .

d) Special reagents for removal of interference:

Aluminum hydroxide suspension: dissolve 125g Aluminum potassium sulfate or aluminum ammonium sulfate, in 1L distilled water. Warm to  $60^{\circ}C$  and add 55mL conc.  $NH_4OH$  slowly with stirring. Let stand about 1hr transfer to a large bottle, and wash precipitate by successive additions, with thorough mixing and decanting with distilled water, until free from chloride.

### **Procedure**

#### **Argentometric method**

Measure the appropriate sample volume for the indicated chloride range using the following table and transfer to a 250 ml Erlenmeyer flask or porcelain casserole.

Brink the total volume to 100 mL with distilled water If the sample size is less than 100 mL Prepare a color comparison blank by placing distilled water in a similar flask and the volume must be equal to that of the sample.

Add 1 mL potassium dichromate indicator solution to the blank and the sample; and mix. To the color comparison blank carefully add from a burette drop by drop silver nitrate titrant until the yellow color changes to a brownish tine. Record the mL silver nitrate titrant consumed. If the sample turns yellow, gradually add silver nitrate titrate from a burette. Shake the flask continuously and continue adding the titrant until the sample turns the same. Record mL silver nitrate titrant consumed

### Calculation

$$\text{mg Cl/l} = (A-B) \frac{X N X 35,450}{\text{Ml of sample}}$$

Where

A= Ml nitration for sample

B= mL titration for blank and

N= normality of silver nitrate

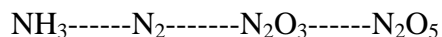
Mg NaCl/L = (mg Cl/L) x 1.65

## 5. AMMONIA NITROGEN

Ammonia nitrogen was determined based on the following procedures and using the listed reagents and apparatus

The compounds of nitrogen are great interest in environmental engineering because of the importance of nitrogen compounds in the atmosphere and life process of all plants and animals.

The chemistry of nitrogen is complex because of the several oxidation states that nitrogen can assume and the fact that changes in oxidation states can be brought about by living organisms. The chemistry of nitrogen of interest in water and wastewater can be summarized as follows.



All these forms of nitrogen are biochemically interconvertible and are components of the nitrogen cycle. The oxidation state changes brought about by bacteria under anaerobic conditions prevail.

The two major factors that influence selection of the method to determine ammonia are concentration and presence of interferences. In general, direct manual determination of low concentrations of ammonia is confined to drinking waters, clean surface or ground water, and good quality nitrified wastewater effluent. In other instances, and where interferences are present or greater precision is necessary, a preliminary distillation step is required.

### **Reagent and apparatus**

- a). Zinc sulfate solution: dissolve 100g  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and dilute to 1L with water.
- b) Stabilize reagent (Rochelle salt solution): Dissolve 50g potassium sodium tartarate tetrahydrate in 100 mL distilled water. Remove ammonia usually present in the salt by boiling off 30 mL of solution. After cooling, dilute to 100 mL.
- c) Nessler reagent: Dissolve 100g  $\text{HgI}_2$  and 70g KI in a small quantity of water and add this mixture slowly, with stirring, to a cool solution of 160g NaOH dissolved in 500mL water. Dilute to 1L. Store in rubber stoppered borosilicate glassware and out of sunlight to maintain reagent stability for up to a year under normal laboratory conditions. Check reagent to make sure that it yields the characteristic color with 0.1mg  $\text{NH}_3\text{-N/L}$  within 10min after addition and does not produce a precipitate with small amounts of ammonia within 2h. (Caution: Toxic care to avoid ingestion).
- d) Stock ammonium solution: dissolve 3.819g anhydrous  $\text{NH}_4\text{Cl}$ , dried at  $100^\circ\text{C}$  in water and dilute to 1000mL, 1mL = 1.00mgN = 1.22mg  $\text{NH}_3$ .
- e) Standard ammonium solution: dilute 10mL stock ammonium solution to 100mL with water, 1.00mL = 10.00  $\mu\text{g N}$  = 12.2 $\mu\text{g NH}_3$ .
- f) 6N NaOH solution .

## Procedure

### Direct Nesslerization Method

1. Prepare series of standards by transferring the following amounts of standard ammonium chloride solution to a 50 mL volumetric flask stoppered graduated cylinder and dilution to 50mL with ammonia free distilled water.
2. Nesslerize the standards by adding 1.0ml Nessler's reagent to each flask with a safety pipet.
3. Stopper and invert several times
4. Read the absorbance 425 nm at least 10 minutes after adding Nessler's reagent
5. Plot a calibration curve absorbance versus concentration

### Calculation

$$\text{mg/L NH}_3\text{-N} = \frac{\mu\text{gNH}_3\text{-N}}{\text{Ml of sample}}$$

$$\text{mg/L NH}_3\text{-N} = (\mu\text{gNH}_3\text{-N} \times 1.22) / \text{Ml of sample}$$

$$\text{mg/L NH}_4\text{-N} = (\mu\text{gNH}_3\text{-N} \times 1.29) / \text{Ml of sample}$$

## 6. NITRATE NITROGEN

Determination of nitrate ( $\text{NO}_3^-$ ) is difficult because of the relatively complex procedures required the high probability that interfering constituents will be present, and the limited concentration ranges of the various techniques.

An ultraviolet (UV) technique that measure the absorbance of  $\text{NO}_3^-$  at 220 nm is suitable for screening uncontaminated water (low in organic matter) Screen a sample, if necessary then select a method suitable for its concentration range and probable interferences. Nitrate may be determined by ion chromatography. Applicable ranges for other methods are: nitrate electrode method 0.14 to 1400 mg  $\text{NO}_3^-$  -N/L cadmium reduction method 0.01 to 1.0mg  $\text{NO}_3^-$  -N/L stannous chloride method .001 to 10mg  $\text{NO}_3^-$  -N/L hydrazine reduction method 0.01 to 10mg  $\text{NO}_3^-$  -N/L automated cadmium reduction method 0.5 to 10mg  $\text{NO}_3^-$  -N/L. For higher  $\text{NO}_3^-$  -N/L concentrations, dilute into the range of the selected method.

Colorimetric methods require an optically clear sample. Filter turbid sample through 0.45 - $\mu$ m-pore-diam membrane filter. Test filters for nitrate contamination.

Start  $\text{NO}_3^-$  determinations promptly after sampling. If storage is necessary, store for up to 24 ha at 4 $^\circ$ C. NOTE: when sample is preserved with acid,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  cannot be determined as individual species.

The main purpose is to determine the nitrate concentration for various forms of water and wastewater by phenoldisulfonic acid method.

### **Reagent and apparatus**

- a). standards silver sulfate solution: Dissolve 4.40g silver sulfate free from nitrate in distilled water and dilute to 1000 mL ,1.00 mL = 1.00 mg /L
- b). Phenoldisulfonic acid reagent: Dissolve 25g pure white phenol in 150 mL conc.  $\text{H}_2\text{SO}_4$ .Add 75 mL fuming  $\text{H}_2\text{SO}_4$  (15% free  $\text{SO}_3$ ) stir well and heat for 2 hour on a hot water bath.
- c). Ammonium hydroxide Conc: if this can not be used, prepare 12N KOH solution by dissolving 673 g KOH in distilled water and diluting to 1 liter
- d). EDTA reagent: Rub 50 gm disodium ethylendeiamine tetracetate dehydrate with 20mL distilled water to form a thoroughly weight paste add 60 ml concentrated ammonium hydroxide( $\text{NH}_4\text{OH}$ ) and mix well to dissolve the paste.
- e). Stock nitrate solution: dissolve 9.7218g anhydrous potassium nitrate and dilute to 1000 mL with distilled water 1 mL = 100  $\mu$ g N.
- f) Standard Nitrate solution: Evaporate 50.0 mL stock nitrate solution to dryness on a steam or water bath dissolve the residue by rubbing with 2.0 mL phenoldisulfonic acid reagent, and dilute to 500 mL with distilled water,1.00 mL= 10.0  $\mu$ g N= 44.3  $\mu$ g  $\text{NO}_3^-$
- g). Reagent for treatment of unusual interference:
  - a. Aluminum hydroxide suspension-prepares as in for chloride determination but wash KHO free of ammonia, chloride nitrite, and nitrate
  - b. Sulfuric acid 1N dilutes cautiously 28 mL conc.  $\text{H}_2\text{SO}_4$  to 11 with distilled water.
  - c. Potassium permanganate 0.1N: dissolve 0.316g  $\text{KMNO}_4$  in distilled water and dilute to 100 mL.
  - d. Dilute hydrogen peroxide solution: dilute 10 mL of 30% hydrogen peroxide to 100 mL with distilled water.

e. Sodium hydroxide 1N: dissolve 40g NaOH and dilute to 1 Liter with distilled water.

## **Procedure**

### **Phenoldisulfonic Acid method**

- ❖ Determine the chloride content of the water sample and treat 100 ml with an equivalent amount of silver sulfate solution (1mL for 1 mg Cl ) to precipitate the chlorides
- ❖ Remove the precipitated chloride either by centrifugation or by filtration coagulating the AgCl by heat If necessary.
  
- ❖ If the sample has color of more than 10 unit (on platinum cobalt scale), decolorize by adding 3 mL aluminum hydroxide suspension to 150 mL sample; stir very thoroughly; allow to stand for a few minutes; then filter, discarding the first portion of the filtrate Pipette a suitable quantity of the sample or the clarified filtrate in to an evaporating dish and neutralize to approximately PH=7
  
- ❖ Evaporate to dryness over a hot water bath.
- ❖ Add 2 mL phenoldisulfonic acid reagent and rub the residue thoroughly to insure dissolution of all solids. If needed heat on the water bath a short time to dissolve the entire residue
- ❖ Dilute with 20 mL of distilled water and add with stirring about 6 to 7 mL of NH<sub>4</sub>OH or about 5 to 6 mL KOH solution (12N) until maximum yellow color is developed
- ❖ Remove any resulting flocculent hydroxides by filtration or add the EDTA reagent drop wise with stirring until the turbidity re dissolves
- ❖ Transfer the filtrate of clear solution to a 50-mL volumetric flask or graduated cylinder. Rinse the dish, glass rod and filter paper with distilled water, adding the rinsing to the flask or cylinder until all the colored solution has been transferred.
- ❖ Dilute to the 50-mL mark with distilled water, and mix thoroughly
- ❖ Measure the absorbance at a wave length of 410 nm against a blank prepared from the same volumes of reagents as used for the samples.

- ❖ Construct a calibration curve in the range 0-2mg/L NO<sub>3</sub>-N by adding 0,0.2, 0.5,1.0,3.0,5.0, and 10 mL of standard nitrate solution to separate evaporating dishes and treating them in the same way as the sample.

Determine the µg of NO<sub>3</sub>-N in the sample by reference to the calibration curve

**Calculation:**

$$\text{mg/L NO}_3\text{-N} = (\mu\text{g NO}_3\text{-N}) / \text{mL sample}$$

$$\text{mg/L NO}_3 = (\mu\text{g NO}_3\text{-N} \times 4.427) / \text{mL sample}$$

## 7. PHOSPHATE

Phosphorus is an essential nutrient for algal growth, and when in excess it is one of the leading causes of eutrophication. The primary sources of phosphorus in natural systems include wastewater treatment facilities, runoff of fertilizer from agricultural operations, detergents and some natural sources. Under summer growing conditions, it has been established that the critical level for inorganic phosphorus is approximately 5 µg /L.

Orthophosphates and polyphosphates are the most common forms of inorganic phosphorus found in natural waters. Orthophosphates contain a single phosphorus molecule, and common orthophosphates include trisodium phosphate (Na<sub>3</sub>PO<sub>4</sub>), disodium phosphate (Na<sub>2</sub>HPO<sub>4</sub>), monosodium phosphate (NaH<sub>2</sub>PO<sub>4</sub>), and diammonium phosphate ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>). Polyphosphates contain multiple phosphorus molecules, and examples include sodium hexametaphosphate (Na<sub>3</sub>(PO<sub>3</sub>)<sub>6</sub>), sodium tripolyphosphate (Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>), and tetrasodium pyrophosphate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>). Polyphosphates hydrolyze in natural waters to the ortho form, typically in the time frame of several hours to days.

Several techniques are available for the determination of phosphorus in natural water samples, including gravimetric, volumetric, and colorimetric methods. Gravimetric and volumetric methods are best when the concentration of phosphorous is high. In most environmental engineering applications, this is not the case, and colorimetric methods are preferred. The method detection level for phosphate by colorimetry is approximately 0.1 mg/L as phosphorous, or 0.01mg/L if an extraction step is included, and thus it is the most common technique used for the analysis of water and wastewater.

The objective of this laboratory is to determine the concentration of phosphorus in water using the stannous chloride colorimetric method.

## Reagent and apparatus

a). Glassware: (200mL volumetric flask [1 per analysis ], 500mL or 250 mL Erlenmeyer flasks [1 per standard], 10mL Mohr pipette, 2-3 clean spectrophotometric cuvettes, 100mL graduated cylinder (1), 250mL beaker (1-2 per analysis ), timer.

b). Spectrophotometer: (capable of operating at a wavelength of 690nm).

a). Phenolphthalein Indicator: dissolve 0.2g phenolphthalein into 200mL deionized water and 200mL ethanol.

b) Ammonium Molybdate Reagent: Dissolve 25g  $(\text{NH}_4)_6 \text{MO}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 175 ml distilled water. Cautiously add 280 ml con.  $\text{H}_2\text{SO}_4$  to 400 mL distilled water. Cool, add molybdate solution, and dilute to 1liter.

c.) Stannous Chloride Reagent: Dissolve 2.5g of fresh stannous chloride in 100mL glycerol (also known as glycerin). Heat on a hot plate (lowest setting) and stir with a stirring rod to enhance dissolution. This reagent is stable and requires neither preservatives nor special storage.

d). Stock phosphate solution: Dissolve in distilled water 0.7165 anhydrous  $\text{KH}_2\text{PO}_4$  and dilute to 100mL; 1.00ml = 500 $\mu\text{g}$   $\text{PO}_4^{3-} - \text{P}$

e). Standard Phosphate Solution: Dissolve 219.5mg of potassium biphosphate ( $\text{KH}_2\text{PO}_4$ ) and dilute to 1000mL (1mL=50.0  $\mu\text{g}$   $\text{PO}_4^{3-} - \text{P}$ ).

f). Strong-acid solution: slowly add 300 mL conc.  $\text{H}_2\text{SO}_4$  to about 600 mL distilled water. When cool, add 4.0 mL conc  $\text{HNO}_3$  and dilute to 1L.

## Procedure

### Stannous Chloride method

1. Take a 50 mL sample in a 250 mL Erlenmeyer flask and dilute to 100 mL with distilled water.
2. Add 1 drop (0.05 mL ) of phenolphthalein indicator solution .
3. If a pink color develops, add strong acid solution one drop at a time until the pink color disappears. Then add 1 mL extra of the acid solution .

4. Boil the acid –treated sample gently for 90 minutes, adding distilled water from time to time to keep the volume between 25 and 50mL.
5. Cool to room temperature.
6. Stirring the sample constantly and sodium hydroxide solution until a faint pink color reappears.
7. Transfer sample to a 100 mL volumetric flask or graduated cylinder
8. Rinse the flask, glass beads, and stirring rod with distilled water and add the wash to the flask/cylinder and dilute to the 100 mL mark with distilled water.
9. Complete the determination as described for orthophosphate starting with step 3.
10. Calculate the total phosphate using the formulae given for orthophosphate.

## **8. BIOCHEMICAL OXYGEN DEMAND (BOD).**

Biochemical oxygen demand (BOD) is the amount of oxygen required by microorganisms to biologically degrade organic wastes. Usually the BOD test is used to measure the strength of organic pollution. One of the major factors in determining the performance of wastewater treatment plants is the BOD reduction that they achieve. Complete stabilization of a waste by microorganisms requires too long an incubation period for practical purposes; therefore, the 5-day period has been accepted as a standard. The 5-day BOD (BOD<sub>5</sub>) is the total amount of oxygen consumed by microorganisms during the first 5 days of biodegradation. Samples are incubated at 20oC in darkness. This prevents algae from adding oxygen to the air tight bottle. The typical composition of untreated domestic wastewater has a BOD<sub>5</sub> concentration of 100 - 300 mg/L.

The experimental procedure is based upon diluting the wastewater with a known amount of dilution water and measuring dissolved oxygen concentrations over the course of 5 days. One set of experiments are conducted on the dilution water only and another set is conducted on the mixture of dilution water and wastewater. The BOD of the dilution water at any time t, BOD<sub>t</sub>, is given by the following expression.

$$BOD_t = DOD_0 - DOD_t$$

Where

- ❖  $DOD_0$  is equal to the dissolved oxygen concentration (mg/L) of the dilution water at time  $t = 0$  and  $DOD_t$  is the dissolved oxygen concentration (mg/L) of the dilution water at time  $t = t$ . A similar expression can be developed for the BOD of the mixture of dilution water and wastewater at any time  $t$ ,  $BOD_{M,t}$ .

$$BOD_{M,t} = DOD_{0,t} - DOD_{t,t}$$

Mass balance considerations are then used to determine the BOD of the wastewater from the BOD of the mixture. Within the BOD bottle the “mass of BOD within the bottle” is equal to the sum of the “mass BOD from the wastewater” plus the “mass BOD from the dilution water.”

$$BOD_{w,t} = \frac{BOD_{m,t}V_m - BOD_{D,t}V_D}{V_w}$$

In many situations the data are fit to a BOD equation which provides BOD concentration of the wastewater as a function of time. This equation can be derived by assuming that the rate of oxygen utilization is linearly related to the amount of oxygen-consuming organic matter present in a sample or,

$$\frac{dL_t}{dt} = -K_c L_t$$

where:

$L_t$  = Oxygen equivalent of organic matter present at time  $t$ . (mass/volume)

$k_c$  = Reaction constant (inverse time). Please note that this constant is a function of temperature and therefore, constant temperature conditions are needed throughout the experiment.

Integrating the above expression, then

$$BOD_t = BOD_{\infty}(1 - e^{-k_c t})$$

Where:

- ❖  $BOD_t$  = ultimate BOD (mass/volume). The expression above requires the computation of  $BOD_t$  and  $k_e$  from experimental data. The results of the 5 day BOD test can be used in conjunction with one of two solution methods for computing BOD and  $k_e$ .

These methods include:

- 1). the method of least squares, and
- 2). the Thomas method.

The BOD test is one of the most common measures of organic matter in wastewater and sewage-contaminated natural waters. In the BOD test, the amount of oxygen used in the metabolism of biodegradable organics is termed the biochemical oxygen demand, or “BOD.” The principal forms of biodegradable organic matter include proteins, carbohydrates, lipids, and fats.

The BOD of a water sample is determined by placing aliquots with appropriate dilution water in glass-stoppered 300mL BOD bottles, incubating the bottles at a standard temperature (20°C), and measuring the change in oxygen concentration with time. The concentration of dissolved oxygen in the BOD bottles is determined using either a dissolved oxygen electrode or by performing the Winkler procedure.

The BOD, as a function of time, is assumed to follow a first-order rate model. Based on this model, the BOD consumed or exerted in the BOD bottle at any time is equal to the difference between the BOD existing at the initial time ( $BOD_u$  or  $L_0$ ) and the BOD remaining at any time, ( $BOD_r$  or  $L_t$ ).

$$x = L_0 - L_t = BOD_u (1 - e^{-kt}) \quad [5]$$

where

$x$  is BOD exerted at any time,  $t$ ,  $BOD_u$  is the ultimate BOD (assumed equal to the oxygen equivalent of organics at time zero,  $L_0$ ),  $k$  is a first-order rate constant, and  $t$  is time.

Because BOD changes with respect to time, it is important to report at what time a BOD measurement was made. The most common time interval for reporting BOD values is 5 days. For example, a number of national standards for BOD are based on  $BOD_5$ . The BOD is calculated as,

$$\text{BOD} = \frac{D_1 - D_2 - f(B_1 - B_2)}{P} \quad [6]$$

where

- ❖  $D_1$  and  $D_2$  are the dissolved oxygen concentrations of the mixtures in the BOD bottles before and after incubation, respectively,  $B_1$  and  $B_2$  are the dissolved oxygen concentrations in the dilution water before and after incubation, respectively,  $f$  is the fraction of dilution water in the mixture and  $P$  is the fraction of sample in the mixture.

The purpose of this section is to determine the amount of oxygen necessary for biological oxidation of wastewater, effluents, and polluted waters. To determine the amount of oxygen required by bacteria while stabilizing decomposable organic matter

### Reagent and Apparatus

- ❖ BOD bottles; 300 ml capacity
  - ❖ Air Incubator ( $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ )
  - ❖ Stir plate, stir bar, ring stand, burette, 200 ml beaker, and burette holder
  - ❖ 250 ml Graduated Cylinder
  - ❖ Containment vessel, baking soda, wash beaker, solution beaker, and pipette for handling concentrated sulfuric acid.
  - ❖ Large 40 liter carboy, with diffuser stone attached to a source of pressurized air
- a). Phosphate buffer solution: Dissolve 8.5g  $\text{KH}_2\text{PO}_4$ , 21.75 g  $\text{K}_2\text{HPO}_4$  33.4g  $\text{Na}_2\text{HPO}_4$   $7\text{H}_2\text{O}$ , and 1.7g  $\text{NH}_4\text{Cl}$  in about 500 mL distilled water and dilute to 1L. The PH should be 7.2 without further adjustment. Discard reagent (or any of the following reagent) if there is any sign of biological growth in the stock bottle.
  - b). Magnesium sulfate solution: Dissolve 22.5g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  in distilled water and dilute to 1L.
  - c). Calcium chloride solution: dissolve 27.5g  $\text{CaCl}_2$  in distilled water and dilute to 1L.
  - d). Ferric Chloride solution: dissolve 0.25g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in distilled water and dilute to 1L
  - e). Acid and alkali solutions, IN: for neutralization of caustic or acidic waste sample.
  - f). Sodium sulfite solution 0.025N: Dissolve 1.575g  $\text{Na}_2\text{SO}_3$  in 1000 mL distilled water. This solution is not stable; prepare on the day of use.
  - g). Nitrification inhibitor: 2-chloro-6- (trichloro methyl) pyridine.

h).Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103<sup>0</sup>C for 1h. Add 0.150 g glucose and 0.150g glutamic acid to distilled water, dissolve and dilute to 1 liter. Prepare fresh immediately before use.

## Procedure

1. a) Using your best engineering judgment, determine the dilution for the glucose-glutamic acid control (BOD<sub>5</sub>= 198 mg/L) and for the raw and treated wastewater samples. Suggestions: read section 22-3 in Sawyer, et al., note table 22-1.

b) Check proposed dilutions with instructor before proceeding.

2. a) Prepare four dilution water blanks by filling each bottle with the dilution water/seed mixture.

b) Prepare four raw wastewater samples. Add the appropriate volumes of raw effluent, X<sub>1</sub> ml, as determined in step 1. Add (300-X<sub>1</sub>) ml of dilution water. Make sure you shake the sample bottle thoroughly prior to pipetting sample. Samples for this lab can be pipetted directly from the sample bottle to assure that uniform samples are pipetted. Shake bottle between additions of raw wastewater to different BOD bottles.

c) Prepare four treated wastewater samples as in part b with appropriate volumes of treated wastewater, X<sub>2</sub>, and dilution water (300-X<sub>2</sub>) as determined in step 1. Make sure you shake the sample bottle thoroughly prior to pipetting sample as in part b above.

d) Prepare eight glucose-glutamic acid samples as in part b, with appropriate volumes of glucose-glutamic acid, X<sub>3</sub>, and dilution water (300-X<sub>3</sub>) as determined in step 1.

3. Add water to the reservoir at top of BOD bottle. Refill during incubation period to avoid total evaporation of water.

4. Determine the DO (day = 0) on one bottle of raw wastewater, treated wastewater, and dilution water blank, and two bottles of the glucose-glutamic acid control. (See DO determination above in section 10 ).

5. Put remaining samples in incubator (20<sup>0</sup>C).

Repeat step three for days 3, 4, and 5.

## 9. CHEMICAL OXYGEN DEMAND

The Chemical Oxygen Demand (COD) is the amount of oxygen needed to chemically oxidize wastes. In the COD test, a strong chemical oxidizing agent is used to oxidize the organics. The primary advantage of COD over BOD is that it is relatively fast, taking 2 to 3 hours, whereas BOD requires 5 days to complete. Another difference in the test methods is that BOD is a biochemical process as measured by the ability of microbes to degrade the organics, whereas COD is purely a chemical process.

To estimate the oxygen demand of organic matter when it is subjected to oxidation by a strong chemical oxidant in water. Based on the following reagents and apparatus and using standard procedures that are Open Reflux Method, Titrimetric Method COD was determined.

### Reagents and Apparatus.

- ❖ COD reactor with cover and test tube rack
  - ❖ Spectrophotometer (Milton Roy, Spec 20) with red plastic filter and phototube for reading within the 600 to 620nm range (CE-A30) .
  - ❖ Heat Resistant Gloves
  - ❖ 1.25 or 50 ml graduated cylinder
  - ❖ Pipettes (5 & 10 ml) and pipette bulbs
  - ❖ 100 ml volumetric flasks (4 per student group)
  - ❖ 50, 100, or 150 ml beakers (3 per student group)
- a). Standard potassium dichromate solution, 0.0417 M (0.25N): dissolve 12.259g  $K_2Cr_2O_7$  primary standard grade previously dried at  $103^{\circ}C$  for 2h in distilled water and dilute 100mL
- b). Sulfuric acid reagent: Add  $Ag_2SO_4$  at the rate of 5.5g  $Ag_2SO_4$  per Kg  $H_2SO_4$  Let stand 1 to 2 days to dissolve  $Ag_2SO_4$  per kg  $H_2SO_4$  let 1 to 2 days to dissolve  $Ag_2SO_4$ .
- c). Ferroin indicator solution: dissolve 1.485g 1,10-phenanthroline monohydrate and 0.695g  $FeSO_4 \cdot 7H_2O$  in distilled water and dilute to 100mL.
- d). Standard ferrous ammonium sulfate (FAS) titrant approximately 0.25M (0.25N): Dissolve 98g  $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$  in distilled water. Add 20 mL Conc.  $H_2SO_4$  Cool, and dilute to 1000 mL. Standardize daily against  $K_2Cr_2O_7$  solution as follows:-

Dilute 10.0 mL standard  $K_2Cr_2O_7$  to about 100 mL. Add 30 mL Conc  $H_2SO_4$  and cool. Titrate with FAS totrant using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicatory

e). Mercuric sulfate, crystals or powder. (extra pura )

f). Sulfamic acid

g). Potassium hydrogen phthalate (KHP) standard: Lightly crush and then dry KHP to constant weight at  $120^{\circ}C$ . Dissolve 0.425 g in distilled water and dilute to 1000 mL. KHP has a theoretical COD of 1.176 mg  $O_2$ /mg this solution has a theoretical COD of 5000g  $O_2$ /mL. This solution is stable when refrigerated for up to 3 months.

## Procedures

### Open Reflux Method, Titrimetric Method

1. Place 5 ml of sample in a 250 or 500 ml refluxing flask
2. Add about 3 glass beads to the reflux flask
3. Add approximately 1 g mercuric sulfate
4. Very slowly add 5.0 ml sulphuric acid reagent with mixing to dissolve the mercuric sulfate.
5. Cool under the tap while mixing to avoid possible loss of volatile materials
6. Add 25.0 ml of 0.0417M (0.25N) potassium dichromate solution
7. Mix until the solution is completely homogeneous
8. Attach the reflux flask to the condenser and turn on the cooling water
9. Add 75 ml of sulphuric acid reagent through the open end of the condenser continue swirling and mixing while adding the sulphuric acid reagent
10. Cover the open end of the condenser with a small beaker and reflux for exactly 2 hours.
11. Cool, and wash down the condenser with about 50 ml distilled water
12. Cool to room temperature under a tap and mix well.
13. Titrate the excess  $K_2Cr_2O_7$  with ferrous ammonium sulfate (FAS)titrant using 2 to 3 drops of ferroin indicator taking the end point of the titration the first sharp color change from blue-green to reddish brown
14. In the same manner, reflux and titrate a blank containing the reagents and 50 ml of distilled water.

**Calculation:**

$$\text{COD as mg O}_2/\text{L} = \frac{(A - B) \times M \times 8000}{Ml_{\text{sample}}}$$

Where:

A=ml FAS used for the blank

B= ml FAS used for sample

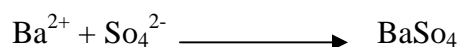
M= Molarity of FAS

**10. SULFATE**

The sulfate ion is one of the major anion occurring in natural waters. It is importance in public water supplies because of its cathartic effect up on humans when it is present in excessive amounts. For this reason, the recommended upper limit is 250 mg/L in waters intended for human consumption. Sulfates are important in both public and industrial water supplies, because of the tendency of waters containing appreciable amounts to form hard scale in boilers and heat exchangers.

Sulfates are of considerable consideration because they are indirectly responsible for two serious problems often associated with the handling and treatment of wastewater. These are odor and sewer corrosion problems resulting from the reduction of sulfates to hydrogen sulfide under anaerobic condition.

The gravimetric method is considered to yield the most accurate results and is the recommended standard procedures for sulfate concentration above 10mg/l. At noted above the quantitative aspect of this method depend up on the fact that barium ion combines with sulfate ion to form poorly soluble barium sulfate as follows.



The precipitation is normally accomplished by adding barium chloride in slight excess to samples of water acidified with HCL and kept near the boiling point. The sample is acidified to

eliminate the possibility of precipitation of  $\text{BaCO}_3$ , which might occur in highly alkaline waters maintained near to boiling temperature. Excess  $\text{BaCl}_2$  is used to produce sufficient common ion to precipitate sulfate ion as completely as possible.

Because of the great insolubility of barium sulfate ( $K_{SP}=1 \times 10^{-10}$ ), there is a considerable tendency for much of the precipitation to form in a colloidal condition that can not be removed by ordinary filtration procedures. Digestion of the samples at a temperature near boiling point for a few hours usually results in a transfer of the colloidal to crystalline forms, in accordance with the principle and filtration can then be accomplished.

The crystal of barium sulfate are usually quite small for this reason, a special grade of filter paper (suitable for sulfate determination) should be used with reasonable care to make sure that all crystals have been transferred to the filter and with sufficient washing to remove all excess barium chloride and other salts, this method is capable of measuring sulfates with a high order of accuracy. Its major limitation is time required.

The barium sulphate precipitation formed may be weight after filtration either following combustion to destroy the filter paper or by the weighing the precipitation and the filter together and then subtraction the weight of the previously tarred filter form the result to obtain the weight of the precipitation alone.

The measurement of solid matter in a wide variety of liquid and semisolid materials / ranging from potable waters through polluted waters / domestic and industrial waste and sludge produced in treatment process / is very important in environmental engineering practice.

In all other liquid materials the amount of suspended material increases the degree of pollution. Sludge represents an extreme case in which most of the solid matter is in suspended form and the dissolved fraction is in a minor consideration.

The sulfate concentration of all samples was determined using listed reagents, apparatus and standard procedures

## Reagent and Apparatus

- ❖ *Methyl red indicator solution*: dissolve 0.1 g methyl red sodium salt in distilled water and dilute to 100 ml
- ❖ *Hydrochloric acid HCl 1+1*
- ❖ *Barium chloride solution*: dissolve 100g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in 1L distilled water. Filter through a membrane filter or hard-finish filter paper prior use 1 mL is capable of precipitating approximately 40mg  $\text{SO}_4^{2-}$ .
- ❖ *Silver nitrate-nitric acid reagent*: dissolve 8.5 g  $\text{AgNO}_3$  and 0.5 mL Conc.  $\text{HNO}_3$  in 500 mL distilled water.

## Procedures

### Gravimetric method with ignition of residual

Adjust the volume of clarified sample to contain approximately 50 mg of sulfate in a 150 ml volume. Lower concentrations of sulphates may be tolerated if it is impractical to concentrate the sample to the optimum level, but in such cases limit the total volume to 150 ml

- ❖ Adjust the pH with concentrated HCl to pH 4.5-5.0 using a pH meter or the orange color of methyl red indicator. Then, add an additional 1 to 2 ml HCl.
- ❖ Heat the solution to boiling and while stirring gently, add warm barium chloride solution slowly until precipitation appears to be complete. Then add about 2 ml in excess.
- ❖ Digest the precipitate at 80-90°C for not less than 2 hours.
- ❖ Filter and wash the precipitate with small portion of warm distilled water until the washings are free of chloride as indicated by testing with  $\text{AgNO}_3/\text{HNO}_3$  reagent. Be sure that all of the precipitate is transferred to the paper.
- ❖ Place the filter paper and precipitate in ignited and weighed crucible and dry in the oven
- ❖ Ignite at 800°C for 1 hour, cool in a desiccator and weigh.

### Calculation:

$$\text{mg/L SO}_4^{2-} = \text{mg BaSO}_4 \times 411.6/\text{ml sample}$$

If the silica concentration is above 25 mg/l, it must be removed by the following method prior to sulfate determination

## **11. SOLIDS**

Particulate matter is ubiquitous in all surface water and ground water systems, and can lend to water a cloudy or hazy appearance. Due to their high specific surface area, suspended particles are efficient adsorbents and they play a major role in regulating the transport and distribution of many chemical compounds. Minute suspended particles may also indicate the presence of bacteria and non-bacterial pathogens (e.g., *Cryptosporidium*, *Giardia*, and viruses) and their presence inhibits disinfections processes.

The size spectrum of waterborne particles in both natural and polluted waters is continuous, spanning roughly 0.001  $\mu\text{m}$  to 100  $\mu\text{m}$ . The composition of these particles can be organic (e.g., bacteria, algae and viruses), inorganic (e.g., clay, sand, and iron oxides), or both. Suspended particles less than 1  $\mu\text{m}$  in diameter do not readily settle, and are considered colloids. This colloidal fraction may be highly stable, hence mobile, and can significantly enhance the transport of adsorbed contaminants in surface and ground water.

A variety of separation techniques are commonly used to gravimetrically classify solids by size and chemical characteristics. Filtration is used to separate “suspended” or “particulate” fractions from “dissolved” or “soluble” components. In this technique, glass-fiber filters are used to remove particles as they pass through the deep mat of fibers by interception and impaction. Because the average pore size and collection efficiency of commercial filters varies, it is always important to specify the type of filter used, and pore size.

Evaporation separates water from dissolved and/or suspended matter. The drying temperature has an important effect upon the results and weight losses due to volatilization of organic matter, water occluded in the interstices of crystals, water of crystallization, and gases from thermally induced decomposition may occur. In addition, weight gain due to oxidation is possible. Consequently, two drying temperatures are conventionally used: 103-105°C and/or 179-181°C. The lower temperature is used with samples containing high concentrations of organic matter, which may undergo significant weight loss due to volatilization and

decomposition at the higher temperature. There is only slight decomposition of most organic salts at 103°C. Some loss of CO<sub>2</sub> can be expected from the conversion of bicarbonate to carbonate during the dehydration process. Occluded or bound water is not completely removed at 103°C; however, its removal is virtually complete at 180°C. At 180°C, thermal decomposition of ammonium salts (especially ammonium carbonate) may occur. The type of cation in the salt greatly affects the degree of decomposition at a given temperature.

Solids are operationally characterized as either volatile or nonvolatile (in some texts the term “fixed” is used in place of nonvolatile). Volatile solids are those that volatilize when samples are heated to a temperature of 550°C. The volatile fraction is primarily composed of organics, whereas the fixed fraction is mostly inorganic. To measure these quantities, samples are placed in a “muffle” oven at 550°C for a fixed period of time. The remaining sample is weighed again and the mass loss represents the volatile fraction. Special filters, made of noncombustible glass fibers, must be used. A number of units for conductivity are in current use. The traditional unit for conductivity is 1/μohm-cm, or μmho/cm. In the SI system of units, siemens (S) is the reciprocal of ohm and conductivity is often reported in units of μS/cm. Thus, μS/cm and μmho/cm are equivalent units. The total dissolved solids (in mg/L) of a water sample can be estimated by multiplying the conductivity (in μS/cm) by an empirical constant (usually between 0.55 and 0.90). This empirical constant should be determined for a particular water sample by comparing conductivity measurements to a direct gravimetric analysis.

The purpose of this laboratory is to examine the turbidity, conductivity, and solids content of several different water samples.

### **Reagent and Apparatus.**

- a). Glassware: (250mL volumetric flask [1 per analysis team], 300mL beaker, 100 mL beaker, 25mL volumetric pipette.
- b). Check standard: (prepared by the TA by suspending 100 mg/L kaolin in a solution of 100 mg/L NaCl in deionized water)
- c). Turbidity meter and sample cells:
- d). Filtration apparatus: (vacuum flask, clamp, 2-piece membrane holder, and pump)
- e). Filter papers: (rinsed, dried at 103 – 105 °C, and stored in desiccators by TA prior to lab)

Solids including total dissolved solids and total dissolved solids in the samples were determined using standard procurers and apparatus.

## **Procedures.**

### **A. Total Dissolved solids dried at 103-105<sup>0</sup>C**

- ❖ Filter measured volume of well-mixed sample through glass-filter, wash with three successive 10-mL volumes of distilled water, allowing complete drainage between washings, and continue suction for about 3 minutes after filtration is complete.
- ❖ Transfer filtrated to a weighed evaporating dish and evaporated to dryness on a steam bath if filtrated volume exceeds dish capacity successive portions to the same dish after evaporation
- ❖ Dry for at least 1 hour in an oven at 103-105<sup>0</sup>C, cool in a desiccators to balance temperature, and weight.

### **Calculation**

$$\text{mg total dissolved solids /L} = \frac{(A-B) \times 1,000}{\text{ML sample}}$$

Where:

A= Weight of dried residue = dish, mg and

B= Weight of dish, mg

### **B. Total suspended solids (dried at 103-105<sup>0</sup>C)**

#### **Centrifugation Method**

- ❖ Clean an empty centrifuge tube thoroughly and dry at 103-105<sup>0</sup>C in an oven
- ❖ Cool in a desiccators and weigh (A gram)
- ❖ Place 10 mL of thoroughly mixed sample in the centrifuge tube by means of a pipette
- ❖ Centrifuge for 10 minutes at 2000 rpm.
- ❖ Pour off the supernatant and add distilled water. Stir the tube and centrifuge again for 10 minutes at 2000 rpm.
- ❖ Pour of the water and dry for 1 hour at 103-105<sup>0</sup>C
- ❖ Cool in a desiccators and weight (B gram)

**Calculation:**

$$\text{mg/L suspended solids} = \frac{(B-A) \times 1,000,000}{\text{mL of sample}}$$

**Sludge volume Index (SVI)**

Calculate the SVI by the following formula

$$\text{Sludge Volume Index (mL/g)} = \frac{(\text{Settled Sludge Volume (ML/L)} \times 10000)}{(\text{Suspended solids (mg/L)})}$$

**Calculation**

$$\text{Mg suspended solids/L} = (A-B) \times 1000/\text{ML sample}$$

Where:

A= Weight of filter + dried residue, mg

B= Weight of filter, mg

**12. CADMIUM**

Atomic absorption method:- For low levels of cadmium, extract the chelate with ammonium pyrrolidine dithiocarbamate into methyl ketone. This organic extract is directly fed into an air-acetylene flame of an atomic absorption spectrophotometer and its absorbance is recorded at 229 nm.

**13. CHROMIUM**

Atomic absorption method:-This method is exactly similar to that followed in case of cadmium, except that absorbance in case of chromium is measured at 358 nm.

## 14. LEAD

Atomic absorption method:- This procedure is similar to that described in case of Cadmium. Directly aspirating the sample into an air-acetylene flame and measuring the absorbance of Pb at 283.3nm can measure lead.

For lower concentration of lead follow the same procedure as that for Cd, that is, complex formation with ammonium pyrrolidine dithiocarbamate and extraction into methyl isobutyl ketone and then aspiration of the methyl isobutyl ketone complex extract into the flame (air-acetylene) of an atomic absorption spectrophotometer. Further more Copper and Nickel were determined using Atomic absorption spectrophotometer.

## ANNEX IV:-RAW DATA

Table 1:- Parameters measured in leachate and groundwater samples

Parameters	leachate mg/l	Well water mg/l	spring water mg/l
Temperature (°C)	24.4	24.3	24.7
p <sup>H</sup>	9.23	9.48	9.15
SS	29	11	Nil
TDS	5658	2154	132
Alkalinity (HCO <sub>3</sub> <sup>-</sup> )	5364	1465	173
Chloride	520	256	186
Sulfate	502	398	64
BOD	160	20	30
COD	210	54	67
DO	NA	2.6	2.8
Conductivity (µsc/cm)	2126	154	32
Ammonia	0.4	0.1	0.02
Nitrate	0.66	0.42	0.03
Phosphate	6	2	Nil
Lead	0.09	0.076	0.06
Nickel	0.07	0.04	0.01
Copper	1.40	0.04	1.40
Cadmium	0.13	0.10	Nil
Chromium	0.30	0.20	Nil

Table 2:- public health raw data

Questions	Exposed group		Non exposed group	
	Yes	No	Yes	No
1. Is there any dust nuisance in the indoor environment of the household?	305	11	3	313
2. Is there any respiratory illness in the family member of the house?	289	27	28	288
3. Was there any one who dead due to respiratory problem in one year?	2	314	1	315
4. Is there any toxic smoke from the landfill in the indoor environment?	303	13	0	316
5. Do you think there will be fire hazard from landfill?	293	23	0	316
6. Do you face any skin rash problem in your family member?	239	77	16	300
8. Do you see any children in your vicinity play with hospital waste?	303	13	0	316
9. Was there diarrhea (bloody, watery, etc) in under 5 children in the last month?	281	25	23	276
10. Was there stillbirth in you family member in the last one year?	2		2	
11. Is there any one in your family with congenital malformation?	0		0	
12. Was there an intermittent of the face, hands, and feet in the family members (etching eye)?	268	48	22	294
13. Do you have infants in you home?	15	301	12	304
14. Under weight (< 2.5 kg )	6		1	

