CHAPTER II
LITERATURE REVIEWS

Leachate from landfill is generated by a combination of decomposition of waste and infiltration of precipitation through any wastes (Fetter, 1993; 2001). Leachate migration has been implicated worldwide as a source of environmental pollution (Voegelin et al., 2003; Sparks, 2005). It contains various types of toxic chemicals (Yong, 2001). These contaminants could possibly affect any adjacent environmental receptors including local soil, water supply sources both from surface water and groundwater, vegetation and plants as well as causing a health risk to human. It is, thus, important to monitor the level of leachate contamination in the environmental receptors including soil, surface water and groundwater. However, the knowledge of landfilling practice today indicates that the landfill in most situations only postpones the pollution of the surface and subsurface from landfill leachate for a few years to a few decades (Freeze and Cherry, 1979; Lee and Sheehan, 1996).

2.1 Site Characterization

To design a new facility or investigate potential contaminant migration at an existing site, it is essential to know what lies on and beneath the site and also there is a need to understand contaminant fate, transport and exposure (Fetter, 2001; Driscoll, 1986; LaGrega et al., 2001; Sharma and Reddy, 2004). The site characterization study aims at obtaining appropriate and adequate data in order to define the type and extent of contamination as well as to assess the fate and transport of contaminants under various scenarios. The site characterization requires data related to geology, hydrogeology and contamination conditions for the site under investigation (Freeze and Cherry, 1979; Driscoll, 1986; Sharma and Reddy, 2004). The geologic data recognize the site stratigraphy and properties of the various geologic formations existing at the site. The hydrogeologic data identify the major water-bearing formations and their hydraulic properties. The contamination data provide the nature

and distribution of the chemicals encountered at the site. Moreover, it should be pointed out here that each site is *unique*. Thus, the site characterization process must be implemented to meet the site specific requirements (Sharma and Reddy, 2004)

Heavy metals in leachate from landfills have been extensively studied and monitored (Yong, 2001; Selim and Sparks, 2001). The major part of the metals is retained in the landfill. As a consequence, it must be expected that leaching of heavy metals from the landfills will continue for a long time (Freeze and Cherry, 1979; Fetter, 1993; Selim and Sparks, 2001; Yong, 2001). The major environmental problem experienced at landfills is the loss of leachate from the site and the subsequent contamination of soil, surface water and groundwater resources (Barker et al., 1988). It can take years before groundwater pollution reveals itself and chemicals in the leachate often react synergistically and often in unanticipated ways to affect the ecosystem (Lee and Sheehan, 1996). Aluko et al. (2003) studied the characterization of leachate from a municipal solid waste landfill site in Nigeria and pointed out that the quantity and composition of leachate gives an insight into appropriate, effective and sustainable treatment approaches. Corresponding to Sharma and Reddy (2004), they stated that waste containment and remediation problems require an understanding of the physical and chemical characteristics of the subsurface and the ability to engineer pollution control and remove the contaminants. Thus, it is important to characterize the site before starting other applications. In 1998, Mikac et al. studied the assessment of groundwater contamination in the vicinity of a municipal solid waste landfill. They pointed out that the horizontal distribution of the contaminants was highly dependent on the hydrogeological conditions whereas Looser et al. (1999) utilized inorganic tracers to study the detection and characterization underground pollution from landfills in order to be helpful for the detection or survey of contaminated sites. Moreover, many researches have been attempted to define the extent of leachate impact on surface and subsurface environments by integrating the various hydrogeochemical data with consideration for the site hydrogeology (Loehr et al. 1993; Al-Muzaini et al., 1995; Sterckeman et al., 2000; Abu-Rukah and Al-Kofahi, 2001; Critto et al., 2003; Mitra et al., 2003; Yaqout, 2003 and Frascari et al., 2004).

2.2 Leachate Characterization

2.2.1 Leachate Generation

Landfills have served as the ultimate disposal sites for garbage generated from residential, commercial, and industrial activities (Tchobanoglous et al., 1993). Generation and subsequent flow of leachate to groundwater is one of the main hazards from the disposal of waste by landfilling. Landfill leachate is generated by excess rainwater percolating through the waste layers. Combined physical, chemical and microbial processes in the waste transfer pollutants from the waste material to the percolating water (Christensen et al., 2001). There are two sources of water in landfill; initial water present in the waste and water added to the landfill from percolation through the top layer or groundwater flowing through the sides (Fetter; 21001). Factors that affect leachate generation are: climate (rainfall); topography (run-on/run-off); landfill cover; vegetation and type of waste (Calace et al., 2001).

2.2.2 Leachate Composition

Landfill leachate typically contains water, heavy metals, organic material in various stages of decomposition and inorganics such as ammonia, sulfate and metal cations. Leachate composition varies significantly among landfills (Sharma and Reddy, 2004). Its composition depends on several factors including; water infiltration, the state of waste decomposition, initial waste composition, codisposal practices, waste age and landfilling technology (Tchobanoglous et al., 1993; Christensen et al., 2001). Quality of leachate is a function of physical, chemical and biological processes inside the landfill. Initially inside a landfill, aerobic decomposition results in high carbon dioxide concentrations followed by rapid increase in temperature, lowering pH, and high COD, BOD and specific conductance levels in the leachate. As the landfill reaches a later stage which is the anaerobic phase, leachate is at its highest concentration levels for COD, BOD and specific conductance. The pH is at a minimum, below 6, with high concentration of carbon dioxide and towards the end of the phase, methane begins to be generated. When the landfill reaches to methanogenic phase of decomposition , the pH returns to neutral value, COD, BOD are reduced due to much of the BOD/COD material are being converted to gas, the specific

conductance is reduced due to increasing pH and methane is generated (Tchobanoglous et al., 1993).

2.2.3 Leachate Transport Mechanisms

Gravity causes leachate to move down through the landfill, to the bottom and sides, and through the underlying soil until it reaches the groundwater zone or aquifer. As leachate moves down the subsurface, it diffuses into groundwater that is held in the voids of the soil mass and this mixture moves along the groundwater flow path as a plume of contaminated groundwater. The leacahte contaminants firstly enter the unsaturated zone and eventually are transported to the potentiometric surface in the saturated zone (Fetter; 1993; 2001).

Advection and dispersion are the two major transportation processes that determine the maximum extent of the leachate plume spread and the geometric character of the concentration distribution. Neither process changes the amount of solute mass in groundwater. However, chemical processes can alter the mass of solute to another form by moving from the solute liquid (groundwater) to solid phase (aquifer material). 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 the flow domain. 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 groundwater velocity (Domenico and Schwartz, 1998). 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 as the plume size increases, the maximum concentration decreases (Domenico and Schwartz, 1998)

2.2.4 Leachate Effects

Leachate contains a host of toxic and carcinogenic chemicals, which may cause harm to both humans and the environment (Calace et al., 2001; Yong, 2001). Furthermore, 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 added financial expenditures. The use of contaminated water for irrigation can decrease soil productivity, contaminated crops, and move possibly toxic pollutants up the food chain as animals and humans consume crops grown in an area irrigated with contaminated water (Fetter, 2001).

2.2.5 Leachate Treatments

The active life of the landfill includes the period, when waste is transported to the landfill as well as the time that follows, when no more waste is dumped and the final top cover has been established, but leachate is still collected for treatment. During the active life of a sanitary landfill, the leachate created will typically be collected and undergo some kind of wastewater treatment. The leachate is typically treated on-site or is pumped out and sent to a local wastewater treatment plant. Treated leachate can be disposed of in a number of ways (e.g., discharged to surface waters or recirculated back into the landfill). By this sort of treatment, a significant amount of the heavy metals present in leachate will be retained in sewage sludge, while the rest will be emitted to the water environment causing the contamination of environmental receptors.

2.3 Behavior of Heavy Metals in Soil

Heavy metals are classified as toxic inorganic chemicals and are also considered as hazardous pollutants due to their toxicity even at low concentrations (Das and Jana, 2006). Heavy metals cannot be degraded or readily detoxified. The presence of metals among wastes can pose a long-term environmental hazard (Fetter, 1993; Yong, 2001). Metals are prevalent in the environments. They are derived from both natural and anthropogenic sources. Certain metals are essential for plant growth and for animal and human health. However, if they are in excessive concentrations they become toxic (Sparks, 2005). The fate of the metal depends on its physical and chemical properties as associated with the waste matrix and soils (Sharma and Reddy, 2004). Significantly downward transportation of metals from the soil surface occurs

when the metal retention capacity of soil is overloaded or when metals are solubilized (Sparks, 2005).

In terrestrial ecosystems, soils are the major recipient of metal contaminants, while in aquatic systems sediments are the majors sink for metals. These contaminants can then impact freshwater and groundwater systems. Freshwater systems are contaminated due to runoff and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids (Fetter, 1993; Sparks, 1995; Yong, 2001).

2.3.1 Fate of Heavy Metals in Soil

The fate of contaminants depends on the various interaction mechanisms established between contaminants and soil fractions as well as between contaminants and other dissolved solutes present in the pore water (Yong, 2001). Metals introduced into soil are distributed in the following three phases (Mclean and Bledsoe, 1991; Sharma and Reddy, 2004): aqueous, adsorbed and solids.

The *aqueous phase* represents the metals existing in soil solution as free (uncomplexed) metal ions (e.g. Cd^{2+}, Zn^{2+}), and as various soluble complexes (e.g. $CdSO_4$, $CdCl_3$). Metals can form soluble complexes with inorganic and organic ligands

The *adsorbed phase* represents the accumulation of metal ions at the interface between soil solids and the aqueous phase. This phase is associated with the surface of soil solids such as organic matter, soil minerals, iron and manganese oxides, and hydroxides, carbonates and amorphous aluminosilicates.

The *solids phase* represents metals present in precipitated form. It may consist of pure solids (e.g. $CdCO_3$, $Pb(OH)_2$) or mixed solids (e.g. $(Fe_xCr_{1-x})(OH)_3$).

2.3.2 Adsorption of Heavy Metals in Soil

The migration of heavy metals to surface and subsurface conditions is a serious environmental problem. It needs to be closely monitored to reduce the risk (Sparks, 2005). Shackelford et al. (1991) stated that *different soils* have *different sorption* characteristics. Therefore, it is important to understand the basic mechanisms of adsorption/desorption of heavy metals in the soil profile. Soils have the ability to

adsorb metal ions from aqueous solution by various mechanisms including physical and chemical adsorption, precipitation and solid state diffusion (Mclean and Bledsoe, 1991). Metal ion transfer occurs at the solid–solution interface consisting of inorganic colloids (e.g., clay), metal oxides and hydroxides, metal carbonates and phosphates, organic matter and living microorganisms (Mclean and Bledsoe, 1991; Sharma and Reddy, 2004). Another influencing parameter is the ligands in the solution responsible for the distribution of metal ions, inorganic and organic ligands such as humic and fulvic acids (Christensen et al., 1996; Christensen et al., 2001; Yong, 2001). The most significant role in heavy metal retention, mobility and bioavailability is controlled by oxides of Fe, Al, and Mn as well as soil organic matter (Silveira et al., 2003). The factors controlling exchange between heavy metal in the solution and the soil particles are soil type, solid and solution mass ratio, soil pH, metal concentration, metal speciation, multiple ions in the solution and contact time. Among them soil pH has the greatest effect of any single factor on the solubility or retention of metals. The greater retention and lower solubility of metal cations occur at high soil pH (Elzahabi and Yong, 2001).

Metals are subject to strong attenuation by sorption and precipitation in the plume (Christensen et al., 2001). The most important parameters controlling heavy metal adsorption and their distribution between soil and water are soil type, metal speciation, metal concentration, soil pH, solid to solution mass ratio, and contact time (Navrot et al., 1978; Majone et al., 1998; Alumaa et al., 2001; Morera et al., 2001; Appel et al., 2002; Yin et al., 2002; Bradl, 2004; Arias et al., 2005; Das and Jana, 2006; Sastre and Ma, 2006). Many studies have reported that nature of heavy metals in soils is different at different soil pH values and the soil's ability to retain them depends on its resistance to any change in soil pH (Cavallard and McBride, 1978; Soon, 1981; Lee and Sheehan, 1996 ; Elizahabi and Yong, 2001; Msaky and Calvet, 1990; Yu et al., 2002; Christensen, 1989). Abollino et al., 2003 also pointed out that the adsorption capability of soil varied both as a function of pH and the presence of ligands which form complexes with the metals of interest. Marosits et al., 2000 investigated the chemical bonding of copper ions on different soils and found that pH, ionic strength and changes of concentration influenced the adsorption process. It is suggested also that the presence of other divalent ions such as Ca^{2+} greatly reduces the

efficiency of heavy metals adsorption by permanent charge clays (Cavallard and McBride, 1978; Echeverria et al., 1998; Harter, 1992).

Gomes et al. (2001) demonstrated that Cr, Pb and Cu were the heavy metal cations most strongly adsorbed by all soils whereas Cd, Ni and Zn were the least adsorbed in the competitive ion situation. Many researches were carried out (Ho et al., 2004; Bellir et al., 2005;Chaturvedi et al., 2006; Foil et al., 2006) to describe the solute uptake rate which controls the residence time of sorbate uptake at the soil-solution interface. Krishnamurti et al. (1999) showed that the presence of phosphate during Cd adsorption by the soils increased the amount of Cd released in the initial 30 min. reaction period as well as the overall diffusion coefficients of Cd release. Rodriguez et al., 2003 studied the competitive retention of Pb and Cd on an agricultural soil and found that the kinetics and thermodynamics of Pb retention predominate over Cd and this sorption process can be described by the Langmuir isotherm. Erses et al., 2005 investigated sorption kinetic and adsorption potential of Fe, Cu, Zn, Ni, and Cd onto solid waste. The results showed that the time required to reach equilibrium varied from metal to metal and the relative potential for sorption of the individual metals and mixed metals on the solid waste matrix is Fe>Zn>Cu>Ni>Cd. Moreover, they also found that metal sorption depended more on metal type than soil composition.

Many isotherms have been used to express the K_d relationship in various soils studied. John (1972) reported that the conformity with the Langmuir equation provides a method for establishing the cadmium adsorption maxima of soils and bonding affinity of particular soils for cadmium. Meanwhile, Palagy and Rigas (2004) found that cadmium adsorption is rather rapid and can be well described by the Freundlich isotherm (Arias et al., 2005) and the linear isotherm. Other factors that influenced heavy metals adsorption were proposed by Anderson and Christensen (1988) by considering the distribution coefficients of Cd, Co, Ni, and Zn in soils that the metal sorption onto soils was influenced by the presence of clays and hydrous oxides of Fe and Mn. Moreover, they found that Co exhibited the highest mobility in soils whereas the mobility of Zn would increase faster with decreasing pH.

2.3.3 Processes Affecting Metals Concentrations

The pollutants may not move passively with the water. They are often retarded by adsorption on the soils or degraded by microorganisms resulting in the change of solute mass. Four processes have been reported to control heavy metal concentrations in landfill leachate: complexation,; oxidation-reduction reactions; sorption and precipitation (Christensen et al., 1994; Christensen et al., 1996; Revans et al., 1999; Flyhammar and Hakansson, 1999). These processes may be reversible if the controlling conditions change over time. A short description of each process is presented in this section.

A. Complexation: Complexation is the combination of metal ions with non-metallic ligands by covalent bonds; it is capable of increasing metal solubility (Lu et al., 1985). In general, a large fraction of the dissolved metals content is complexed with organics compared to the fraction present as the free metal ion (Jensen et al., 1999; Jensen and Christensen, 1999). For example, the humic-like substances formed from waste decomposition can serve as ligands for metal complexes (Reinhart and Grosh, 1998).

B. Oxidation-Reduction (Redox) Reactions: Oxidation-reduction reactions involve the transfer of electrons which are influenced by pH. These processes are important for metals that posses more than one oxidation state. Heavy metals such as Cr, As, Mn, Fe and Hg are referred to as redox elements or redox couples since they have more than one possible oxidation state (Kaoser, 2003). However, Ag, Cd, Cu and Zn with only one valence state, can also be influenced by redox processes. Under very low redox conditions, Pb and Cd, with one oxidation state, form insoluble sulphide minerals. Moreover, at a pH of 7 or 8 where redox conditions not moderately low, they form insoluble carbonate minerals. The changes in redox potential affect the soil pH. Reducing conditions enhance pH value while oxidation brings pH down.

C. Sorption: Sorption refers to partitioning of contaminants between the fluid and solid phases and includes processes of: adsorption; absorption; desorption; surface complexation and ion exchange. Adsorption and absorption occur when the molecules of a gas, liquid or dissolved substance and a particle "stick" together (Lu et al., 1985). This process generally decreases metals concentrations in landfill leachate. Divalent metal cations tend to favor sorption with negatively charged sites such as

colloidal particles, calcite, clay minerals, organics and oxides of Fe, Mn, Al and Si (Fetter, 2001; Sparks, 2005; Yong, 2001). However, it is difficult to differentiate between sorption and ion exchange processes. Sorption can cause the lowering of total dissolved solids and attenuate leachate whereas ion exchange simply exchanges solutes with cations, due to electrostatic forces.

.   **D. Precipitation:** Precipitation occurs when a metal species falls out of solution as a solid. Sulfides and carbonates are capable of forming precipitates with Cd, Ni, Zn, Cu and Pb. Occasionally, phosphates and hydroxides will also precipitate metals (Christensen et al., 2001). Hydroxide precipitates form at pH neutral or above which is typically the case in methanogenic leachate. Sulfide is formed from sulfate during waste decomposition in landfills. Sulfide precipitation is often cited as an explanation for low concentrations of heavy metals (Christensen et al., 1996; Christensen et al., 2001). Even small concentrations of sulfides will precipitate heavy metals except for Cr, which does not form an insoluble sulfide compound. However, Cr does tend to form insoluble precipitates with hydroxide while carbonates are abundant in landfill leachate. The solubilities of metal carbonates are generally higher than that of metal sulfides. In general, sulfide precipitation is expected to dominate heavy metal attenuation compared to other complexation agents (Christensen et al., 2001).

2.4 Sorption Isotherms

Sorption is a physical and/or chemical process in which a substance is accumulated at an interface between phases. The overall rate of sorption of metals on a solid waste matrix depends on composition (density and surface area) of the solid waste, concentration of adsorbate (metal ion) in solution, solid waste to solution ratio, contact time, history of the solute concentration with the solid waste, solution sampling procedure, pH, temperature and biodegradable characteristics of the solid waste.

Two types of reactions between anions and inorganic solids are recognized: specific adsorption and nonspecific adsorption. Specific adsorption refers to incorporation of anions as a ligand in the coordination shell of an adsorbent, while

nonspecific adsorption refers to adsorption of anions by simple coulombic (electrostatic) interactions with positive charges. Nonspecific sorption may occur at the localized positive charges that occurred on *(1)* Fe- and Al- oxide surfaces, *(2)* edges of aluminosilicate clay surfaces where the oxygen atoms are not fully coordinated by Al or Si atoms, and *(3)* on amine and amino groups of organic substances.

2.4.1 Mathematical Description of Sorption

There is a range of equations used for describing the experimental data for the interactions of a substance as liquid and solid phases.

Empirical models-sorption isotherms: Sorption isotherms are the depiction of sorptional interactions using simple empirical equations. Initially, the measurements were done at constant temperature; that is why the term isotherm was introduced.

Linear regression isotherm: The simplest form of a sorption isotherm is the linear regression equation. Linear sorption terms have the advantage of simplicity and they provide the possibility of converting them into a retardation factor, R_f, so that the general transport equation can be easily expanded by applying the correction term.

The isotherm models are discussed in more detail in Section 2.4.2.

2.4.2 Adsorption Isotherms

Heavy metal adsorption in soils can be described by many isotherms. Isotherms are graphical representations of the mass of contaminant adsorbed per unit dry mass of soil versus the concentration of the contaminant. In order to use isotherms to estimate the mass adsorbed an instantaneous equilibrium must be reached between the sorbent and the sorbate, and the isotherm must be considered reversible (Silveira et al., 2003; Bradl, 2004).

The ***Linear isotherm*** is used to predict continuous (no limit) adsorption of substance. This isotherm should be used with the knowledge with extrapolation limits, usually based on experimental information as described following equation

$$q = K_d C_e$$

2.1

where the amount of heavy metals adsorbed by soil (q, mg kg^{-1}) as a function of the equilibrium concentrations of heavy metals (C_e, mg L^{-1}). K_d constant is the distribution coefficient describing contaminant or pollutant partitioning between liquid and solid (L kg^{-1} of soil).

The *Langmuir isotherm* is proposed as the first isotherm model which assumed monolayer coverage of the adsorbent surface. This model assumes uniform energies of sorption onto a homogeneous sorbent surface and no migration of the sorbate in the plane of the surface (Sparks, 1995). Naturally, the soil is a heterogeneous material, thus, the application of Langmuir model might be precaution. However, it is widely employed to describe the relationship of metals sorption and soil (Echeverría et al., 1998; Sastre et al., 2006). The Langmuir equation for describing adsorption data for solid–liquid systems is

$$\frac{x}{m} = \frac{K_L M C_e}{1 + K_L C_e}$$ 2.2

where x is the amount or concentration of the solute adsorbed in mg, m is the mass of the adsorbent in kg, C_e is the equilibrium concentration of the solute in mg L^{-1}, K_L and M are constants. The linearized expression of this equation is

$$\frac{1}{x/m} = \frac{1}{K_L M C_e} + \frac{1}{M}$$ 2.3

An EPA report (Roy and Krapac, 1991) concluded that the Langmuir constant or affinity parameter (K_L) is related to the bonding energy between the adsorbed ion and the adsorbent (L kg^{-1}), but that the specific functional relationship is uncertain and M is depicted as the adsorption maximum (mg kg^{-1} of soil) expressing the amount of solute adsorbed per unit weight of adsorbent in forming the complete monolayer on the surface.

In addition, the K_L constant can be used to predict the isotherm shape whether a sorption system is "favorable" or "unfavorable" (Ho et al., 2002; Karthikeyan and Ilango, 2007; Ong et al., 2007). The essential features of the Langmuir isotherm can

be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, K_R which is defined by the following relationship:

$$K_R = \frac{1}{(1+K_L C_o)} \qquad 2.4$$

where K_R is a dimensionless separation factor, C_o the initial concentration (mg L^{-1}), K_L the Langmuir constant (L mg^{-1}). The parameter K_R indicates the shape of the isotherm and nature of the adsorption process as following:

Value of K_R	Type of isotherm shape
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

(Ho et al., 2002)

The *Freundlich isotherm* represents a simple situation in which no metal sorption maximum is defined because the model does not consider the saturation of the sorption sites (Sparks, 1995). However, this model has been extensively applied to describe metal adsorption in soils (Echeverría et al., 1998; Rauret et al., 2006; Yang et al., 2005; Antoniadis and Tsadilas, 2007). It has the form

$$\frac{x}{m} = K_f C_e^{1/n} \qquad 2.5$$

where x/m is unit of adsorbate added per unit of adsorbent (mg kg^{-1}), C_e is equilibrium concentration of adsorbate in solution (mg L^{-1}). K_f and n can be determined experimentally by determining the degree of adsorption x/m at different concentrations C_e. The information can then be plotted using the following equation.

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \qquad 2.6$$

In a plot of the above equation, the K_f can be determined from the intercept, which has been defined as distribution coefficient of soil while $1/n$ indicated the degree of non-linearity between the capacity of adsorbent and equilibrium solute concentration, from the slope of its linear form. K_f and n values are calculated using the least squares method.

Moreover, the Freundlich constant, n also indicates the degree of favorability of adsorption (Erses et al., 2005). Treybal (1980) has reported that n value between 1 and 10 represent *favorable* adsorption conditions (Figure 2.1). A smaller value of $1/n$ indicates a stronger bond between adsorbate and adsorbent. Moreover, it also describes the significant adsorption, *favorable* isotherm, taking place at low concentration but at high concentration, the increase of the amount of adsorbed becomes less significant. This tends to start out steep and level out. While, isotherms which started out flat are *unfavorable* isotherm, since they only work well at high concentrations of solute. Also, the higher the K_f value indicates the greater the adsorption intensity. Hence it should be noted that the Isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters.
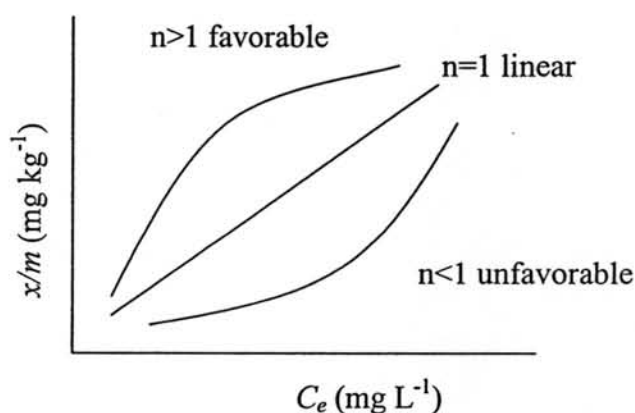

Figure 2.1 The favorable Freundlich isotherm

2.4.3 Isotherm Shape Interpretation

Shapes of Adsorption isotherms are convenient for representing the effects of adsorptive concentration on the surface excess as shown in Figure 2.2.

The *S-curve* isotherm is characterized by an initially small slope that increases with adsorptive concentration. This behavior suggests that the affinity of the soil particles for the adsorbate is less than that the aqueous solution for the adsorptive.

The *L-curve* isotherm is characterized by an initial slope that does not increase with the concentration of adsorptive in the soil solution. This type of isotherm is the resultant effect of a high relative affinity of the soil particles for the adsorbate at low surface coverage coupled with a decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increasing.

The *H-curve* isotherm is an extreme version of the L-curve isotherm. Its characteristic large initial slope (in comparison with the L-curve isotherm) suggests a very high relative affinity of the soil for an adsorbate. This condition is usually produced either by inner-sphere complexation or by significant van der Waals interactions in the adsorption process.

The *C-curve* isotherm is characterized by an initial slope that remains independent of adsorptive concentration until the maximum possible adsorption is achieved.
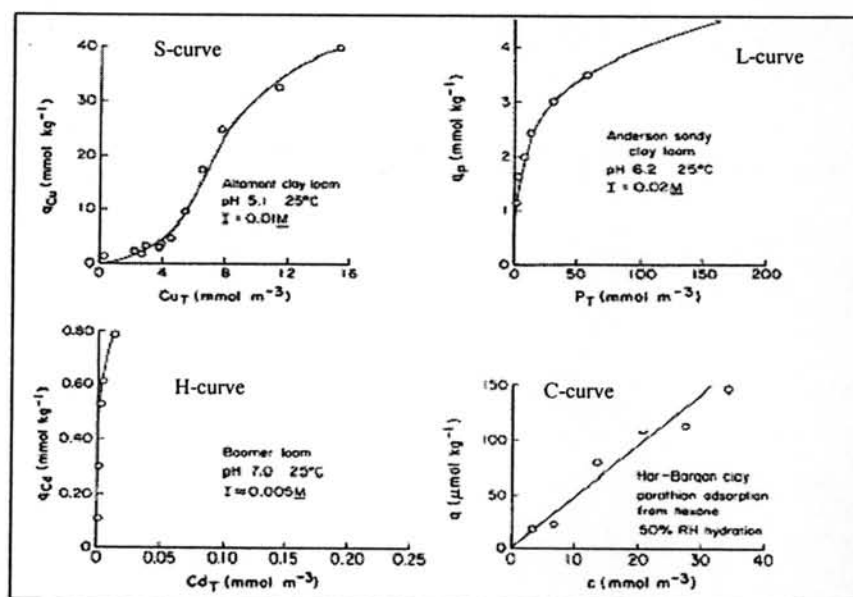

Figure 2.2 General classes of isotherm (Spoisito, 1989)

2.4.4 Partitioning Coefficient

The partitioning coefficient or distribution coefficient (K_d ; K_p ; K_f) is used to compare the behavior of contaminants in different soils. The K_d provides a measure of the ratio between the amount of a material that is adsorbed (M_{soil} ; mg kg^{-1}) and the amount that is in solution ($M_{solution}$; mg L^{-1}) when measured under the same experimental conditions (Yong, 2001), and can be represented as follows:

$$K_d = \frac{[M_{soil}]}{[M_{solution}]}$$
2.7

The adsorption of heavy metals in soils is a competitive process between metals in solution and those adsorbed to soil particles. In the solid phase, metals can be bound mainly to organic matter and onto iron and manganese oxide surfaces (Sharma and Reddy, 2004); these adsorbents have different selectivity for metals. The attributes of the surface adsorbent or the soil type and the characteristics of the metal noticeably affect the distribution coefficient. In this case, the K_d can be used to indicate the affinity of the solid phase for specific metals. Low values of K_d indicate that most of the metals presented in the system are remained in the solution and are available for transport and plant uptake. On the other hand, high values of K_d reflect a large affinity of solid soil components for the metals (Morera et al., 2001).

2.4.5 Factors Affecting Metal Adsorption

Adsorption of heavy metal ions on soils and soil constituents is influenced by a variety of parameters namely: soil pH; type and speciation of metal ion involved; heavy metal competition, and soil composition.

- ***Role of pH:*** Soil *pH* is the most important parameter influencing metal-solution and soil-surface chemistry (Harter, 1983; Soon, 1981; Msaky and Calvet, 1990). The number of negatively charged surface sites increases with pH. In general, heavy metal adsorption is small at low pH values. At high pH values, the metal ions are completely removed (Elzahabi and Yong, 2001).

- ***Role of metal ions***: The *metal selectivity* (Gomes et al., 2001; Covelo et al., 2004) depends on a number of factors such as the chemical nature of the reactive surface groups, the level of adsorption (i.e., adsorbate/adsorbent ratio), the pH at

which adsorption is measured, the *ionic strength* of the solution in which adsorption is measured, the intensity of *competition* determined by other cations for the bonding sites, and the presence of soluble *ligands* that could complex with the free metals. All these variables may change the metal adsorption isotherms. The preference or affinity is measured by a selectivity or distribution coefficient K_d (Roy and Krapac, 1991).

- Role of Soil Type: The *soil type and composition* play an important role in heavy metal retention. In general, coarse-grained soils exhibit lower tendency for heavy metal adsorption than fine grained soils. The fine-grained soil is soil particles with large surface reactivities and large surface areas such as clay minerals, iron and manganese oxyhydroxides, humic acids, and others. They display enhanced adsorption properties (Sparks, 1986). Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange as well as metal oxyhydroxides (Mclean and Bledsoe, 1992). Soil *organic matter* exhibits a large number and variety of functional groups and high cation exchange capacity, CEC, values, which results in enhanced heavy metal retention ability, mostly by surface complexation, ion exchange, and surface precipitation (Roy et al., 1991; Mclean and Bledsoe, 1992).

2.5 Transport of Heavy Metals in Soil

There are three processes controlling the transport of contaminants in subsurface conditions: physical; chemical, and biological processes. The physical processes that control the flux in and out of the system are advection and hydrodynamic dispersion. Meanwhile the loss or gain of solute mass in the system is described by the chemical and biological reactions. Parameters which influence solute transport through soil are soil water velocity, soil solute adsorption-desorption characteristics, chemical reactions and transformation by microorganism (Freeze and Cherry, 1979).

2.5.1 Physical Processes

These processes control the extent of contaminant migration in the subsurface condition.

Advection refers to the contaminant movement by flowing groundwater in response to a hydraulic gradient at a macroscale level. As a result, the rate of solute particle transport is equal to the average linear groundwater velocity. The porous media parameters that control the advective transport are: hydraulic gradient; hydraulic conductivity and transmissivity; specific yield and storativity, porosity and effective porosity.

Hydrodynamic dispersion expresses the non-uniform velocity and causes dilution of the solute. It occurs because of molecular diffusion and mechanical dispersion phenomena. *Molecular diffusion* is defined as the movement of contaminants under a chemical concentration gradient. The *mechanical fluid mixing* or *mechanical dispersion* shows the difference in microscale water velocities due to path length differences due to tortuosity, pore size differences and friction in pores.

2.5.2 Chemical and Biological processes

These processes are responsible for the change in contaminants concentration that takes place within the aqueous phase or transfer the solute to or from other phases or radioactive contaminant decayed.

Transport and reaction of the contaminant in the porous medium can be represented by the equation below (Fetter, 2001)

$$\frac{\partial C}{\partial t} = \frac{D_L \partial^2 C}{\partial x^2} - \frac{v_x \partial C}{\partial x} - \frac{\rho_b}{\theta} \frac{\partial C^*}{\partial t} + \left[\frac{\partial C}{\partial t} \right]_{rxn} \qquad 2.8$$

Where

C = Concentration of solute in liquid phase $[M\,L^{-3}]$

t = Time $[T]$

D_L = Longitudinal dispersion coefficient $[L^2 T^{-1}]$

v_x = Average linear groundwater velocity $[LT^{-1}]$

ρ_b = Bulk density of aquifer $[M\,L^{-3}]$

θ = Volumetric moisture content or porosity for saturated media

C^* = Amount of solute sorbed per unit weight of solid

rxn = Subscript indicating a biological or chemical reaction of the solute (other than sorption) $[M\,L^{-3}T^{-1}]$

The first term of the right side of Equation 2.6 represents the dispersion of the solute, the second is the advection of the solute and the third term is the transfer of the solute from the liquid phase to the solid particle by sorption (retardation process). The last term indicates that there may be a change in concentration of the solute with the time due to biological or chemical reactions or radioactive decay. The retardation factor, R_f, (under rectangular dash) is the empirical parameter commonly used in transport models to describe the chemical interaction between the contaminant and geological materials.

Values of R_f and D (dispersion coefficient) are normally derived from column experiments in the laboratory. It should be kept in mind that R_f and D values are specific to different soil types, and usually determined empirically. The transport modeling of dissolved heavy metals in this soil can be confirmed and improved by determining R_f and D values for the soil samples by column experiments and from additional field measurements of soil density, moisture and porosity.

In the transport modeling of dissolved heavy metals in soil, values of R_f and D are determined from column experiments in the laboratory. The column experiment is widely used by many scientists for various applications (Bejat et al., 2000). Yong et al. (2001) indicated that the continuous column method was used as it is better for simulating natural conditions. Korte et al. (1976) demonstrated that the transport rate of Cd, Ni, and Zn in soil was significantly affected by clay content, surface area, percentage of free iron oxides, and pH. Plassard et al. (2000) studied the retention and distribution of three heavy metals in a carbonate soil through comparison between batch and unsaturated column studies. They also reported the retention of all heavy metals was lower for columns than in batches. Thornton et al. (2000) studied fate of organic and inorganic pollutants in a laboratory column. Elzahabi and Yong (2001) evaluated the influence of pH on the sorption characteristics of heavy metals in the vadose zone.

Sun et al. (2001) conducted leaching studies of heavy metals from contaminated soil using EDTA and reported that the lability of metals in soil, the kinetics of metal desorption/dissolution, and the mode of EDTA addition were the main factors controlling the behavior of metal leaching with EDTA. Rodriguez et al. (2003) conducted column experiments and stated that HYDRUS 2D model could

explain how contaminants such as lead and cadmium were transported in the subsurface. They also reported that the fate studies would fail if competitive adsorption was not considered. In the study of Islam and Singhal (2004), they applied column test to study the relative significance of bacterial growth, metal precipitation, and anaerobic gas formation on biologically induced clogging of soils. Results from column leaching tests showed that the sorption characteristics of heavy metals were controlled by many factors which should be taken into consideration, i.e. the volumetric water contents, time of wetting, soil pH, and the influent heavy metal concentrations.

2.6 Partition of Heavy Metals in Soil

Knowledge of the chemical forms of soluble heavy metals or heavy metals associated with particulates or colloids is essential for estimating bioavailability, mobility and chemical reactivity in soils and sediments (Stumm and Morgan, 1996) Heavy metals associated with different fractions have different impacts on the environment (Yu et al., 2004). Sequential extraction or fractionation of trace metals from soils is a useful technique for determining chemical forms of metals in soil materials. Such information is potentially valuable in predicting bioavailability, metal leaching rates, and transformations between chemical forms in agricultural and polluted soils. Therefore, sequential extraction procedures have been widely used to partition heavy metals among various soil chemical fractions (Tessier et al., 1979; Shuman, 1985; Miller et al, 1986, Ramos et al., 1994). Such procedures utilize a series of selective extractants to remove metals from various component fractions.

Reviews of extraction procedures are provided by Tessier et al. (1979), Sposito et al. (1982) and Miller et al. (1983, 1986). Each step of sequential extraction is designed to extract trace elements associated with a single component of a soil based on its chemical properties. Moreover, this sequential extraction method is performed with solutions of increasing strength. To extract the *exchangeable fraction*, which are electrostatically bonded to soil and mineral surfaces, the cations can be replaced by other cations such as alkaline or alkaline earth cations, including K^+ (Sposito et al., 1982; Yong, 2001), Ca^{2+} (Miller et al., 1986), and Mg^{2+} (Tessier et

al., 1979; Shuman, 1985). The *carbonate fraction* is commonly extracted using weak acids including sodium acetate (Tessier et al., 1979; Ramos et al., 1994).This solubilizes the carbonates which then releases carbonat-entrapped metals. The trace metals bound to the *Mn and Fe oxides fraction* are extracted with reducing agents including hydroxylamine hydrochloride (Tessier et al, 1979; Shuman, 1985; Miller et al., 1986). The hydroxylamine hydrochloride [$NH_2OH.HCl$] reduces the ferrous and manganese hydroxides to soluble forms. Hot hydrogen peroxide in nitric acid is chosen to oxidize the *organic matter fraction* (Tessier et al., 1979; Ramos et al., 1994) and hypochlorite [OCl^-] (Shuman, 1985). Pyrophosphate ($K_4P_2O_7$) is also used to extract organic matter by dispersion (Miller et al, 1986).The oxidized organic matter then releases metals that are complexed, adsorbed and chelated. In the final step, extraction of the *residue fraction*, the silicates and other minerals are dissolved by strong acids such as HF, HNO_3, HCl, and $HClO_4$ at high temperatures.

Soils are usually regarded as the ultimate sink for heavy metals discharged into the environment. Therefore, the knowledge about the way that heavy metals are bonded to soils and the conditions that may caused their release are of importance (Banat et al., 2005). In natural soils, Mulligan et al. (2001) stated that the speciation of trace metals depend on the physical and chemical characteristics of the soil. Soil pH, redox potential, and the concentration of organics, carbonates, clays and oxides all influence metal speciation and mobility. There are many studies which have attempted to determine the form of heavy metals by extraction methods (Hickey and Kittrick, 1984; Li et al., 1995; Chlopecka et al., 1996; Pichtel et al., 2000; Yu et al., 2004; Chaturvedi et al., 2006). Miller et al (1986) studied the effect of sequence in the extraction of trace metals from soils by considering the most appropriate sequential methodology for extracting the different forms of Cu, Fe and Mn, whereas Ramos et al. (1994) studied sequential fractionation of Cu, Pb, Cd, and Zn in soils from or near Donana National Park, South Western Spain. They reported the mobility of soil metals is as follows: Cd > Zn > Pb > Cu. Meanwhile, Pichtel et al. (2000) studied the distribution of Pb, Cd and Ba in soils of two contaminated sites. They found that soil Pb occurred mostly in the organic and carbonate fractions, whereas Lu et al. (2003) pointed out that Cu, Zn, Pb and Cr were dominated by the residual fraction and were least present in the exchangeable fraction in Nanjing urban soil. The sequential

extraction method was applied to evaluate trace metals in other studies, for example, soil amendment with sewage sludge (Sposito et al., 1982) and inorganic pollutants in the clay liner of municipal landfills (Kugler et al., 2002). Tokalioglu et al. (2000) concluded that the method of sequential extraction can be used in the analysis of various environmental matrices such as soil, street dust, airborne particulates, biological materials and bottom sediments.

2.7 Heavy Metals Mobility

2.7.1 Heavy Metals Mobility in Leachate

During the later oxidized state where the degradation of the organic material leads to the formation of carbon dioxide, the mobility of the heavy metal will increase, resulting in the higher content of heavy metals in the leachate. During the stage of anoxic conditions and methane production which will be reached after a short time, the mobility of the heavy metals is commonly low due to the formation of relatively insoluble compounds (Christensen et al., 2001). The concentration of soluble metals will not only depend on the actual chemical conditions and speciation of the metals, but also on the degradation or disintegration of products in which the metals are embedded. A significant part of the heavy metals in the waste will be bonded on glass, plastics, slag, ceramics, steel, wood etc. Products and materials stored in a landfill should be expected to slowly disintegrate over time. Plastics will probably degrade in time due to biological and chemical processes including weathering processes. Glass is known to disintegrate over time in a humid environment. Metals should be expected to be oxidized slowlyand thereby be dissolved. Wood and organic materials will be decomposed by biological and chemical processes. Many of these processes are slow and are strongly influenced by the presence of oxygen, water and acids. Transport of heavy metals within a mature landfill can be compared to transport in soil and should be taken as a very slow process. The exact rate of transport will, however, vary with the metal in question, the composition of the materials and the chemical conditions within the landfill. The time requirement for a complete wash-out of a specific metal may be in the range of hundreds to thousands of years or even more. For all metals, the major part cannot be

expected to be washed out before a long time after any leachate collection has been discontinued (Yong, 2001).

2.7.2 Heavy Metals Mobility in Soil

The mobility of inorganic compounds, especially metals, is quite difficult to determine due to the many reactions which can occur between the various soil components. The mobility of metal compounds is strongly influenced by soil type and properties, e.g., texture, as well as the corresponding pH and cation exchange capacity (CEC) of the soil. Soil type or composition is a very important factor in heavy metal fixation reactions. Clays are extremely important in adsorption reactions because of their high CEC. In addition, soils high in humus or other organic matter also exhibit good exchange capacity. The type of clay mineral present also is an important factor. Many sorption reactions take place at the surface of iron and aluminum hydroxides and oxyhydroxides. Therefore, the iron and aluminum content of soils becomes an essential factor governing the ability of a soil for heavy metal immobilization (USEPA, 1984).

Soil texture or soil particle size is another factor that can influence the fixation of metals by soils. In general, finely textured soils immobilize trace and heavy metals to a greater extent than coarse textured soils. Also, finely textured soils usually have a greater CEC, which is an important factor in heavy metal fixation. Soil texture has been found to influence the transport of mercury, lead, nickel, and zinc (USEPA, 1984). Soil pH plays a very important role in the retention and mobility of metals in soil columns. The pH is a controlling factor in sorption-desorption reactions and precipitation-solubilization reactions. In addition, the CEC of soils generally increases with an increase in pH. Soil pH has been determined to be a major factor along with CEC for the fixation of lead by soils. Soil pH also influences the retention of zinc, molybdenum, mercury, and copper (USEPA, 1984). The oxidation-reduction or redox potential of a soil is very important in determining which species of an element is available for sorption, precipitation, or complexation. In general, the reduced forms of a metal are more soluble than the oxidized form. The redox potential of a soil system is usually altered through biological activity and a change in redox potential is many times correlated with changes in pH. Reducing conditions may be

associated with a low pH resulting in the formation of CO_2 and organic acids from the microbial degradation of organic matter.

A reducing environment typically exists in saturated soils underneath septic tank systems or injection zones. The anaerobic conditions would enhance the mobility of metals in system effluents. Iron is a good example of a metal which readily undergoes redox reactions. In the oxidized or ferric state, iron is reduced under anoxic conditions, the ferrous form, which is more soluble, predominates (USEPA, 1984). Metals added to a soil/ground water system will undergo fixation and adsorption processes, which directly affect the mobility of the metal. Changes in soil environmental conditions over time, such as degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility (McLean and Bledsoe, 1992).

2.8 Heavy Metals Attenuation

In the unsaturated zone, both air and water fill the pores between soil particles (Freeze and Cherry, 1979). The slow movement of leachate 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 adsorbs 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 (Fetter, 2001; LaGrega et al., 2001).

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 (Freeze and Cherry, 1979; Domenico and Schwartz, 1998; Fetter, 2001; LaGrega et al., 2001).

2.9 Chemistry of Metals of Interest

The properties and behavior of specific metals that are commonly found in landfill leachate (hazardous mixed wastes) are discussed in Sections 2.9.1 to 2.9.5.

2.9.1 Cadmium (Cd)

Contamination of soil with cadmium resulting from the application of landfill leachate is widespread. This has led to long term risk for soil fertility, ecosystem health, and groundwater quality. Cadmium is highly toxic to plants, animals, and humans. The adsorption of cadmium onto soils and silicon or aluminum oxides is strongly pH-dependent, as increasing the pH conditions become more alkaline. In alkali soils, the solubility of Cd is much greater and is controlled by adsorption on to clay minerals, oxides and soil organic matter. Cadmium and cadmium compounds are relatively water soluble compared to other heavy metals,. They are therefore also more mobile in soil, generally being more bioavailable and tending to bioaccumulate.

2.9.2 Chromium

Chromium (Cr) can exist in soil in three forms: the trivalent Cr(III) form, Cr^{+3}; and the hexavalent Cr(VI) forms, $(Cr_2O_7)^{-2}$ and $(CrO_4)^{-2}$. The dichromate ions present a greater health hazard than chromate ions, and both Cr(VI) ions are more toxic than Cr(III) ions. Because of its anionic nature, Cr(VI) associates only with soil surfaces at positively charged exchange sites. This association decreases with increasing soil pH. Although the Cr(III) is relatively immobile in soil it forms complexes with soluble organic ligands and its mobility may be enhanced. Chromium occurs in a number of oxidation states, but Cr(III) and Cr(VI) are of main biological relevance. Chromium is similar to lead and is typically found bound to particles. Chromium is in general not bioaccumulated and there is no increase in the concentration of the metal in food chains. Fe(II) containing minerals reduce hexavalent chromium; however, this reaction only occurs in the subsurface soil with a pH less than 5 units, decreasing to a pH of 2.5 units (McLean and Bledsoe, 1992). Trivalent chromium can be oxidized under certain conditions prevalent in some soils. The presence of oxidized manganese which serves as an electron acceptor is an important factor in this reaction. The

industrial use of chromium also includes organic complexed trivalent chromium, which when complexed with soluble organic ligands, will remain in the soil solution. In addition to decreased trivalent chromium adsorption, added organic matter also may facilitate the oxidation of trivalent chromium to hexavalent chromium (McLean and Bledsoe, 1992).

2.9.3 Copper

Soil retains copper (Cu) through exchange and specific adsorption. Copper adsorbs to most soil constituents more strongly than any other toxic metal, except lead (Pb). Copper has a high affinity for soluble organic ligands; the formation of these complexes may greatly increase its mobility in soil. Copper has high toxicity to aquatic organisms.

2.9.4 Lead

Lead is a heavy metal that exists in three oxidation states: O, +2(II), and +4(IV). Lead is generally the most widespread and concentrated contaminant present at a lead battery recycling site (i.e., battery breaker or secondary lead smelter). Lead tends to accumulate in the soil surface. The capacity of soil to adsorb lead increases with pH, cation exchange capacity, organic carbon content, soil/water Eh (redox potential), and phosphate levels. Lead exhibits a high degree of adsorption on clay-rich soil. Only a small percentage of the total lead is leachable; the major portion is usually solid or adsorbed onto soil particles. If battery breaking activities have occurred on-site, and the battery acid was disposed of on-site, elevated concentrations of lead and other metals may have migrated to ground water. Lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. Lead does not bioaccumulate and there is no increase in concentration of the metal in food chains.

2.9.5 Zinc

The greatest percentage of total zinc in polluted soil and sediment is associated with iron (Fe) and manganese (Mn) oxides. Rainfall removes zinc from soil because the zinc compounds are highly soluble. As with all cationic metals, zinc

adsorption increases with pH. Zinc hydrolyzes at a pH >7.7. These hydrolyzed species strongly adsorb to soil surfaces. Zinc forms complexes with inorganic and organic ligands, which will affect its adsorption reactions with the soil surface.

2.10 Environmental Modeling

2.10.1 Visual HELP

The presence of water in a landfill has both negative and positive consequence for the operation of landfill. It is necessary for biological and chemical processes which influence the decomposition of the waste. On the contrary, it can create problems to the sealing layer as well as surface water runoff problems. Moreover, the dispersal of pollutants in landfill leachate contaminated to the environmental receptors is also affected. The transport of water in a landfill site is primarily generated by the following sources: decomposition of waste; the moisture content of waste when it is deposited; infiltration of precipitation over landfill site; surface water runoff from surrounding terrain, and groundwater flows from surrounding land. Therefore, it is necessary to be studied in possession of hydrological information of the landfill site and its vicinity (Manandhar, 2000).

Thus, the water balance factors in a landfill site and how the transport of water through the landfill can be calculated by using the HELP (Hydrologic Evaluation of Landfill Performance) model to simulate the water balance in a landfill site in long-term basis as well as modeling of various layers in the landfill.

Visual HELP model, the hydrological modeling environment, is available for designing landfills, predicting leachate, mounding and evaluating potential leachate contamination as well as estimating seasonal groundwater recharge rate. In general, the Visual HELP model requires the following data: weather data (precipitation, solar radiation, temperature and evapotranspiration), soil data (porosity, field capacity, wilting point, and hydraulic conductivity) and engineering design data (liners, leachate and runoff collection systems, and surface slope). After completely inputting the data, the program will compute the amount of runoff, drainage, and leachate for the landfill site. Results from an analysis of landfill leachate can be integrated into saturated flow and transport models.

Landfill Formation and Water Balance Concept: The quantity of leachate generated in a landfill depends upon: climatic conditions in which the landfill is situated; type of waste; moisture content of the waste at the time of deposition, and the design and operating conditions of the fill. Basically, the difference between the net water input and the capacity of the wasted to restore it will be available to form leachate. The quantity of leachate generation can be predicted by quantifying water balance. A water balance involves the quantity of liquid flow into and out of the landfill system as well as of liquid stored within the system. In landfill system, the significant inflow is precipitation and water contained in the incoming waste, and the significant outflow is leachate. The various components of a water balance in landfill are demonstrated in Figure 2.1.
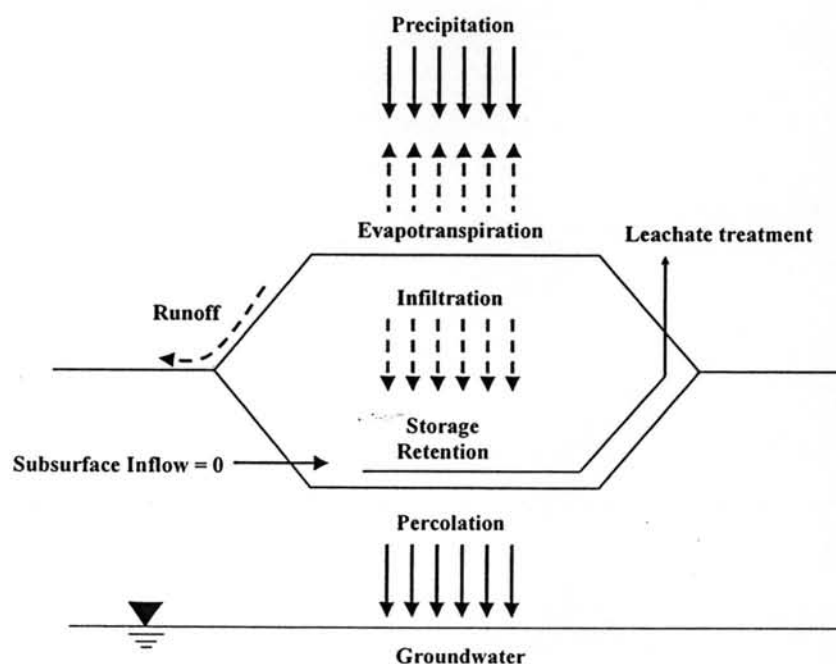

Figure 2.1 Water balance components in a sanitary landfill (Manandhar, 2000)

These components of water balance consist primarily of rainfall that precipitates to the cover. One of the important steps in the performance of water balance in a landfill is the prediction of the quantity of rainfall that actually penetrates the landfill cover. If a landfill is not covered, the major portion of the precipitation enters the fill. Flows in vertical percolation are obtained from infiltration (gravity

drainage) and evapotranspiration (remove). The conventional hydrological water balance is pursued to quantify the quantity of percolation in landfill (equation 2.7).

$$W = P - R - E_T - PER \qquad\qquad 2.9$$

Where

W =   Change in the amount of moisture stored in a unit volume of landfill (mm)

P =   Quantity of net precipitation per unit area (mm)

R =   Quantity of runoff per unit area (mm)

E_T =   Quantity of moisture lost through evapotranspiration per unit area (mm)

PER =   Quantity of water which percolates through the cover per unit area of soil cover (mm)

The amount of moisture that stored in a unit volume of soil is a function of two variables: the field capacity (FC) and the permanent wilting point (PWP). The FC refers to the maximum quantity of liquid in which remains in the pore space under gravitational force. The PWP is defined as the quantity of water that remains in a soil after plants are no longer capable of extracting anymore water. Hence, the difference between the field capacity and the permanent wilting point is called the available water content (AWC) which is the range of available water (moisture content) that can be stored in a particular type of soil and be available for growing crops. Runoff Coefficients are given as a function of rainfall for different types of soil with and without a vegetation cover. For other information requirements such as rainfall and evaporation are site specific and can be obtained from the local of meteorological station.

2.10.2 HYDRUS 2D

HYDRUS-2D is a Microsoft Windows based modeling environment for analysis of water flow and solute transport in variably saturated porous media. Moreover, the program may be used to analyze water and solute movement in unsaturated, partially saturated, or fully saturated porous media. The software package

includes the two-dimensional finite element model HYDRUS2 for simulating the movement of water, heat, and multiple solutes (nonlinear and nonequilibrium solute transport, volatile solutes) in variably saturated media. The model includes a parameter optimization algorithm for inverse estimation of a variety of soil hydraulic and/or solute transport parameters and is supported by an interactive graphics-based interface for data-preprocessing, generation of a structured mesh, and graphic presentation of the results. Some HYDRUS 2D applications are: movement of pesticides; nonpoint source pollution; seasonal risk analysis of contaminant plumes from landfills; seepage of wastewater from land treatment systems; interaction between groundwater aquifers and streams, and the environmental impact of the drawdown of shallow water tables.

Because of the great importance of aqueous speciation, adsorption, and solubility processes relative to the concentrations and mobility of contaminants that leached from waste, an understanding of the capabilities and application of chemical reaction models is essential. This understanding is additionally important because these models are used for both the scientific and legal aspects of risk and performance assessment studies of waste disposal and mitigation of environmental contaminations.