Soil Vulnerability to Heavy Metal Contaminant Using Hierarchical Fuzzy Inference System and its Application in GIS

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Abstract

Soil Vulnerability to Heavy Metal Contaminant Using Hierarchical Fuzzy Inference System and its Application in GIS

Amir Amid

Municipalities all over the world are facing serious crises from all types of pollutions (air, groundwater, soil, and water). Soil contamination is a common problem worldwide. In the past decades industrial activities have caused many types of ground contamination in urban areas. The existence of these lands and their impact on human health and the environment has led the provincial administration to apply restrains in reusing of contaminated sites (Brownfield) and to revitalize the whole sectors of the urban area.

The efficiency of all investments in remediation of the contaminated sites and the living environment relies on a powerful and transparent environmental management and environmental impact assessment (EIA). A fast and applicable tool is essential for EIA or exposure analysis to identify and prioritize the contaminated sites for any management decision.

In this thesis hierarchical fuzzy inference system (HFIS) was applied, and a tool was developed to introduce the critical environmental and geo-environmental factors for decision making purpose. In this technique the most pertinent factors and parameters involved in heavy metal contamination in topsoil were used to develop a powerful tool. The developed tool permitted the making of environmental decisions regarding identification of the heavy metal vulnerability in the top soil. The validation of the result of this method was satisfactory. The developed tool was applied to GIS in a case study for the Montreal Island to identify the high sorption areas and their impact on public health.

Acknowledgment

I would like to express my deepest gratitude and respect to my beloved parents which without their love, instructions, supports and encouragements I could never achieve any success in my life. I dedicate this thesis to them.

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GLOSSARY

AHP	Analytic Hierarchy Process
CEC	Cation Exchange Capacity
CFH	Chlorinated Hydrocarbons
EIA	Environmental Impact Assessment
FIS	Fuzzy Inference System
HM	Heavy Metals
HFIS	Hierarchical Fuzzy Inference System
MTBE	Methyl Tertiary Butyl Ether
OM	Organic Matter
RS	Remote Sensing
SSA	Specific Surface Area
TNT	Trinitrotoluene
MNA	Monitored Natural Attenuation

CHAPTER 1. INTRODUCTION

After the industrial revolution the world faced with serious environmental pollution. The pollutants affect air, soil and water. There are numerous sources for pollution, such as vehicle emissions, chemical plants, coal-fired power plants, oil refineries, nuclear waste disposal activity, incinerators, large animal farms, PVC factories, metals production factories, plastics factories, pulp and paper and other types of heavy industry. Municipal landfills can also be the source of many chemical substances entering the soil environment (including groundwater), emanating from the wide variety of refuse accepted, especially substances illegally discarded there, or from pre-1970 years landfills that may have been subject to little control. Pollution can be the consequence of a natural disaster. For examples hurricanes cause often water contamination from sewage, petrochemical failures, destroyed boats and automobiles. Larger scale and environmental damage is not uncommon when coastal platforms or refineries are involved. Other sources of pollution, such as nuclear power plants or oil tankers, can produce widespread and potentially hazardous releases when accidents occur.

Chlorinated hydrocarbons (CFH), petroleum products such as MTBE (methyl tertiary butyl ether), heavy metals such as lead (which is found in lead paint and until recently in gasoline), cadmium (which is found in rechargeable batteries), chromium, zinc, arsenic and mercury are among common soil contaminants. Heavy metal contaminated soils are a common problem worldwide. Industrial activities have resulted in contamination of many lands including urban areas and urban industrial zones. Location of these lands is essential for re-development zones and this has led the governments to halt the re-use of certain sites or the revitalization of whole sectors of the city.

In response to the Love Canal disaster in the United States, U.S. Congress in December 1980 introduced the law of the Comprehensive Environmental Response, Compensation, and Liability Act (Superfund). This Act created a tax on petroleum and chemical industries and provided broad Federal authority to respond directly for releases or threatened releases of hazardous substances that may endanger public health and the environment. Following the US action toward this crisis several other countries enacted somehow similar regulations to protect the environment. The tax collected through these acts goes to a trust fund for cleaning up abandoned or uncontrolled hazardous waste sites. In spite of advancement in technology, the amount of industrial waste, and the number of contaminated areas increase much faster than the number of remediated sites (McCarty, 1994). For example, the first Superfund of 1.6$ billion was considered for remediation of 400 Brownfield (at an average cost of 3.6$ million per site); but by 1990, US EPA projected a total cost of 27$ billion (at an average cost of 26$ million per site (McCarty, 1994); therefore, the efficiency of all investments for cleaning up the contaminated environment relies on powerful and transparent environmental management. The prioritization for remediation of contaminated sites has also an enormous impact on public health and environment. In addition to planning for remediation, the pollution prevention is considered to be one of the key issues to reduce the quantitative differences between remediated and contaminated lands. The CCME (Canadian Council of Ministries of the Environment) indicates:

"Pollution prevention is needed to secure a safe and healthy environment and a sound and prosperous economy. It is a key component of environmental protection and sustainable development and part of an overall pollution management approach that is comprised of prevention, control and clean-up. Pollution prevention is not a new idea, but there is a need for a consistent shift in emphasis towards anticipating and preventing pollution, instead of reacting to it after the fact."

Canadians are increasingly worried about the public health and financial costs of a polluted environment, including the requirements for clean-up, control and enforcement, as well as the impact on economic competitiveness in national and international scales. Pollution prevention is a very important issue because it:

- accelerates the reduction and/or elimination of pollutants;
- minimizes health risks;
- promotes the development of source reduction technologies;
- uses energy, materials and resources more efficiently;
- minimizes the need for costly enforcement;
- limits future liability with greater certainty; and
- Avoids costly clean-up in the future" (CCME, n.d.)

There is a need to develop a new approach for Brownfield management. It seems that an approach containing contaminated site knowledge with more computation and mathematical techniques can be useful in decision process regarding brownfields. For example, GIS tools could help environmental mangers to either make decision for pollution prevention or to prioritize the contaminated sites based on minimizing the costly enforcement, avoiding costly cleanups and limiting future liabilities with greater certainties, especially on the area exposed to heavy metal contamination. This analysis and decision making requires processing of lots of data at the same time. Although the present system of collecting information has the advantage of a vast and complicated network for manual in situ data collection, it suffers from various limitations such as incompatible data formats, lack of procedures for updating and conventional storage methods. The demand for the storage, analysis and display of complex and huge environmental data has led, to the use of computers for data handling and of sophisticated information systems (Tomilson, 1976). The Geographical Information System (GIS), which is especially suited for handling data with large spatially distributed features, activities or events, is a valuable tool for estimating population exposure, health risk (Sengupta et al., 1996), and modeling of the environment in general.

Fuzzy knowledge is a very useful system in the process of subjective decision making. It has been widely applied in engineering applications: as controllers, decision support aids and within planning systems. These systems are generally recognized for being faster to develop for their natural language type interface, where information can be stored as a set of "easily" interpreted fuzzy rules (Brown et al., 1995).

This research focuses on decision making techniques for identification of the areas with immobilization capacity to heavy metals. Before applying any method the existing models and techniques should be studied and evaluated. There are essential parameters involved in immobilization of heavy metal, such as pH, CEC, SSA etc. which they should be studied. The reviews for heavy metal contaminant, parameters involved in their immobilization and available models for identifying the vulnerable area are presented in the next chapter.

CHAPTER 2. LITERATURE REVEIEW

2.1. Environmental Contaminants

When contaminants come into contact with people, ecosystems, crops, materials, or any other valuable object they cause harm and damage to their quality. Based on contaminant properties, they can be physical, biological or chemical. Loss of wetlands from dredging or the effect of warm water discharge of power plants into rivers is examples of physical contamination. Microorganism that causes disease in man, plants, and animals are examples of biological contamination. Chemical contaminants (Figure 2-1) are consisted of inorganics such as heavy metals and organics, such as DDT, MTBE, etc. .

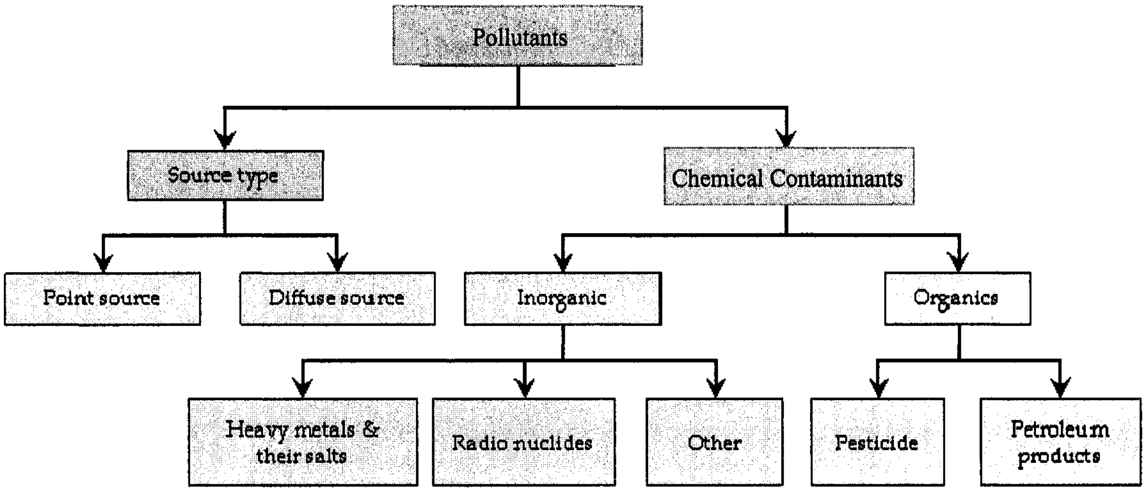

Figure 2-1 Major types of chemical pollutant in Soil (adapted from Tarradellas, 1997)

Among pollutants in soil, the organic and inorganic chemicals are the major types. Since metals change forms and are dangerous to human health, in this research inorganic chemical contaminant (heavy metals) in soil is the area of concern.

2.1.1. Organic Chemicals and Compounds

Activities associated with industrial production and use of petroleum products, solvents, pesticides and explosives (TNT, RDX, Teryl, HMX, ...) are some of the major sources of organic chemicals and compounds found in contaminated sites. Industrial intermediates using aliphatic and aromatic compounds are categorized as well into organic chemicals. Many organic chemicals are found in air and water. Some of these chemicals can cause or at least increases the risks of serious illnesses, including cancer and central nervous system damage (Nazaroff, 2001). The chemicals of concern and their compounds are listed in US EPA method 1311 for Toxicity Characteristics Leaching Procedure (TCLP), these chemicals include:

benzene, carbon tetrachloride, chlordane, chlorobenzene, o-cresol, m-cresol, p-cresol, 1,4-dicholorobenzene, 1,2-dichlororthane, 1,1 dichloroethylene, 2,4-dinititoluene, endrin, heptachlor, hexachlorobenzene, hexachloro 1,3-butadiene, hexachloroethane, lindane, methoxychlor, methyl ethyl ketone, nitrobenzene, pyridine, tetrathcloroethylene, toxaphene, trichloroethylene, 2,4,5-trichlorophenol, 2,4,6–trichlorophenol, silvex and vinyl chloride (Yong & Mulligan, 2004).

2.1.2. Inorganic - Heavy metals; Sources-Fate-Toxicity

There are 39 elements classified as heavy metals (HMs). These elements usually have densities greater than 5.0 g/cm^3 (Adriano, 2001). Heavy metals usually are being released to the environment from mining, ore refining, metal producing and electroplating industries. The common ones that had been reported in contaminated lands are cadmium (Cd), chromium (Cr), copper (Cu), Iron (Fe), Lead (Pb), mercury (Hg), nickel (Ni), tin (Sn) and zinc (Zn). The interaction mechanism leading to sorption and desorption of HMs need to be carefully identified for determining the fate of these pollutants (Yong & Mulligan, 2004). These metals contaminate the soil from different sources and show different behavior in soil. Heavy metals have specific impacts on health and environment.

Cadmium (Cd)

Cadmium is generated from industrial waste of metal plating, Ni-Cd batteries, and pesticides and as stabilizing agents in many polyvinyl chloride (PVC) products.

Cadmium is relatively rare in the nature; a normal background level of cadmium is 0.01-1.0 mg/kg (Sittig, 1994). Cadmium is usually in the form of cadmium carbonate ($CdCO_3$) and CdS (cadmium sulfide). Cadmium sulfide is used in the electronics industry for photocells and light emitting diodes (Petruzzelli, 1993). Clay minerals, carbonates or hydrous oxides of iron and manganese may absorb cadmium. In addition cadmium may precipitate as cadmium carbonate, hydroxide, and phosphate. The chemistry of Cd in soil is to a great extent, controlled by pH and Redox potential. In acidic environment, solubility of cadmium increases then amorphous colloids and organic matters can adsorb very little amount of cadmium (McLean, 1992).

Cadmium does not have a known function in the human body. The most toxic form of Cd is its ionic form. Cadmium is extremely toxic and will bioaccumulate in organisms and ecosystems. The inhalation of cadmium dust quickly creates deadly damages to the respiratory system and kidney. The normal intake of cadmium is 1-3 micrograms/day. In addition to inhalation, ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver and the kidneys. A lethal dose of cadmium for ingestion is estimated to be between 350 and 8900 milligrams. Compounds containing cadmium are also carcinogenic (Hu, 1998). Cadmium poisoning is the cause of the itai-itai disease, and where in addition to kidney damage, the bones become soft (*osteomalacia*), lose bone mass and become weaker (*osteoporosis*). This causes the pain in the joints and the back, and also increases the risk of fractures. In extreme cases of cadmium poisoning, the mere body weight causes a fracture (Lee, 1972). Based on NPI ranking, cadmium and its compounds are ranked as 6 out of 400 toxic substances The total hazard score taking into account for both human health and environmental criteria is 4.3 of 6.0 score .

Lead (Pb)

Metallic lead is used in the production of batteries, products used to shield x-rays and various metal products (pipes, solder, flashing, and ammunition/bullets, fishing weights, electronics and alloys with other metals). Some uses of lead are ; tetraethyl lead is used to make other leaded compounds, tetra-alkyl leads, and in leaded fuels (petrol). Lead compounds also are used in the manufacturing process of plastics, rubbers, and metals as well as for making pigments, dyes, paints and coats. Lead compounds are used in the manufacturing of matches, ammunition, fireworks, and explosives and in production of rodenticides and insecticides. Lead compounds are also used in pottery glazes, brake shoes, flame retardants for plastics, catalysts for industrial production and epoxy curing agents (NPI, n.d.).

Mining activities, manufacturing industries, smelting operations, Lead-containing paint, burning of fossil fuels (coal, oil, gas) are the major source of lead release to the environment.(NPI, n.d.)

Lead is mostly in its 2+ state as lead sulfide (PbS) in mining areas (Yong & Mulligan, 2004). Pb in urban soils can be found in a greater amount in top soils. Lead can be sorbed greatly into organic matter. The sorbed lead is in forms of carbonate, sulfate, halides and oxide (Davis, 1988). Soluble lead added to soil reacts with clays, phosphates, sulfates, carbonates, hydroxides and organic matters in a way that its solubility will be greatly reduced. At pH more than 6 lead will be either adsorbed on clay surfaces or form lead carbonate. (McLean, 1992)

It has been observed that Lead causes mental retardation in children and schizophrenia. This has brought about widespread reduction in its use. Paint containing lead has been withdrawn from sale in industrialized countries, though many older houses may still contain substantial lead in their old paint. It is generally recommended that old paint should not be stripped by sanding, as this generates inhalable dust. Lead salts used in pottery glazes have caused poisoning occasionally, when acid drinks, such as fruit juices, have leached lead ions out of the glaze. Lead is considered to be particularly harmful for women's fertility (lead, n.d.).

Lead and its compounds were ranked by NPI as 11 out of 400 toxic substances. The total hazard score taking into account for both human health and environmental criteria is 3.2 of 6.0 score.

Copper (Cu)

Emissions of copper to air, soil and water may result from mining and primary extraction processes such as mineral processing, smelting, electrolytic processing, leaching and solvent extraction, and from manufacturing of products using and/or containing copper (electrical goods, pipes, alloys, etc.) (NPI, n .d.) .

Copper is retained in soil by specific adsorption and exchange mechanisms. Precipitates are unstable but in case of waste-soil systems, precipitation may be also an important mechanism for retention (McLean, 1992). In calcareous soils, specific adsorption of Cu onto $CaCO_3$ may control the Cu concentration (McLean, 1992). Based on the literatures, the sorption of Cu in different soil or soil constituent in general, except Pb is higher than all other heavy metals (Forbes et al., 1976; Benjamin & Lecklie, 1981; Biddappa et al., 1981; Elliot et al., 1986; Harter, 1983).

Copper is an essential micronutrient that plays a critical role in all aerobic organisms yet it is toxic when present in excess amounts (Williams, 1999). Daily diet intake of about 1-2 milligrams is required for body. The DRI (Dietary Reference Intakes) Tolerable Upper Intake Level for adults of dietary copper from all sources is 10 mg/day. Very large single or daily intakes of copper can be harmful. High intakes of copper can cause liver and kidney damage and anemia. Thirty grams of copper sulfate are potentially lethal in humans. Drinking water that contains higher than normal levels of copper (1.3

ppm) can lead to vomiting, diarrhea, stomach cramps, and nausea. Very young children are sensitive to copper, and long-term exposure to high levels of copper in food or water may cause liver damage and death. Long-term exposure to copper dust can irritate the nose, mouth, and eyes also it causes headaches, dizziness, nausea, and diarrhea. Breathing copper fumes may cause 'metal fume fever', a flu-like illness with symptoms of metallic taste, fever and chills, aches, chest tightness and cough. The seriousness of the effects of copper can be expected to increase with both level and length of exposure (NPI, n.d.). The toxicity of copper derives from its ability to generate reactive oxygen species (ROS), such as hydroxyl radical, superoxide anion and H_2O_2 (Luna et al., 1994). An inherited condition called Wilson's disease causes the body to retain copper, since it is not excreted by the liver into the bile. This disease, if untreated, can lead to brain and liver damage. In addition, studies have found that people with mental illnesses such as schizophrenia had heightened levels of copper in their systems (Bowman, 1982).

Ranking of Copper based on NPI is 40 out of 400 toxic substances and the total hazard score for both human health and environmental criteria is 2.5 of 6.0 (NPI, n.d.).

Mercury (Hg)

Anthropogenic sources of Hg from mining, metal processing and burning fossil fuels can increase the level of concentration of Hg from its natural background.

Redox potential and pH control the distribution of elemental mercury (Hg^0), mercurous (Hg_2^{2+}) and mercuric ions (Hg^{2+}) in soils. Like other heavy metals adsorption of Hg increases with increase of pH. Both mercury's cations can be adsorbed by clay minerals, oxides, and organic matters. Formation of various precipitates can immobilize mercury's cations. In alkaline soils, mercuric cation will precipitates with carbonate and hydroxide and form a stable solid form. At lower pH, and high chloride concentration, $HgCl_2$ is formed (Kinniburgh and Jackson; 1978; McLean, 1992). The formation of the most toxic form of mercury from elemental mercury (Hg^0) happens under a mild reducing condition by degradation of both organically bound mercury and inorganic mercury compounds. The elemental mercury can be readily converted to methyl or ethyl mercury by biotic and abiotic processes and form the most toxic form of mercury (Rogers, 1976, 1977; McLean, 1992). Removal of mercury from the leachate is not due to adsorption by clays, but is due to volatilization and/or precipitation (Griffin & Shimp, 1978, McLean, 1992).

The nervous system is very sensitive to all forms of mercury. Exposure to high levels of any types of mercury can permanently damage the brain, kidneys, and developing fetus. Effects on brain functions may result in irritability, shyness, and tremors, changes in vision or hearing and memory problems. High exposures of mercury vapor may cause chest pain, shortness of breath, and a build up of fluids in the lungs (pulmonary edema) that can be fatal. Contact with mercuric chloride can cause burns to the skin and permanent damage to the eyes. Mercury also accumulates in the body. Minimata is a degenerative neurological disorder caused by poisoning with a mercury compound in seafood from waters contaminated with mercury, characterized by burning or tingling sensations, poor articulation of speech, and the loss of coordination and peripheral vision.

Mercury and its compounds were ranked as 35 out of 400 toxic substances. The total hazard score taking into account for both human health and environmental criteria is 3.7 out of 6.0 (NPI, n.d).

Nickel (Ni)

The common use of nickel is in coins, jewelry, nickel-cadmium batteries, some paints and ceramics, magnetic tapes, computer components, and goods containing stainless steel (sinks, cooking utensils, and cutlery). Combustion of coal and other fossil fuels leads to release of nickel to the atmosphere. Other sources of atmospheric nickel include emissions from mining and refining operations, steel production, nickel alloy production, electroplating, and municipal waste incineration. Sources of nickel in water and soil include wastewater from municipal sewage treatment plants. Nickel oxide has been identified in residual fuel oil and in atmospheric emissions from nickel refineries. A minor source of atmospheric nickel is windblown dust. Sources of nickel in water and soil include storm water runoff, soil contaminated with municipal sewage sludge, and landfill sites (NPI, n.d.).

The retention of Ni in soil is exclusively due to adsorption phenomena, as Ni does not form any insoluble precipitates in unpolluted soils. Nickel can be adsorbed to clays, iron, manganese oxides, and organic matters and is thus removed from the soil solution. The formation of complexes of Ni will increase the Ni mobility (McLean, 1992).

Although lack of nickel has not shown any problem for body but small amount of nickel is probably essential for humans. Exposure to nickel metal and soluble compounds should not exceed 0.05 mg/cm^3 in nickel equivalents per 40-hour work week. Nickel sulfide fume and dust is believed to be carcinogenic, and various other nickel compounds may be as well. Nickel carbonyl, (Ni $(CO)_4$), is an extremely toxic gas. The toxicity of metal carbonyls is a function of both the toxicity of a metal as well as the carbonyl's ability to give off highly toxic carbon monoxide gas. It is explosive in air. Some people may show allergy to nickel contacting their skin. The amounts of nickel being emitted by 1 and 2 Euro coins exceeds from the standards (Nestle, 2002). Lifelong exposure to nickel in the air is carcinogenic; it has been estimated that if there is 1 microgram of nickel refinery dust per cubic meter of air, in a population of 1000 people there would be 2.4 additional cases of cancer (Williams, 1999).

Nickel and its compounds were ranked as 54 out of 400 toxic substances. The total hazard score taking into account both human health and environmental criteria is 2.2 of 6.0 score (NPI, n.d.).

Arsenic (As)

Arsenic exists in the soil as either arsenate, As(V); (AsO_4^{3-}) or asrenite As(III); (AsO_2). Arsenite is the most toxic form of arsenic. Arsenates and phosphates show almost the same behavior in soil; both form insoluble precipitates with iron, aluminum, and calcium. Iron in soil is the most important element for controlling arsenate's mobility. Arsenite are 4-10 time more soluble than arsenate compounds (McLean, 1992). Both pH and the redox potential are important in assessing the fate of arsenic in soil. At high redox levels, As(V) predominates and arsenic mobility is low. With increase of pH or decrease of redox As(III) predominates. The reduced form of arsenic is more subject to leaching because of its high solubility. Formation of As(III) also may result to volatilization of arsine (AsH_3) and methyl arsines from soils (Woolsen 1977; McLean, 1992).

Arsenic or its compounds might affect the body by inhalation of contaminated air, in a workplace using or producing arsenic (or arsenic compounds). Exposure may come from ingesting water, soil, or air near areas naturally high in arsenic or contaminated with arsenic. Consumers may expose themselves to arsenic by breathing sawdust or smoke from wood containing arsenic preservatives, or using or misusing pesticides, weed killers, fungicides. Large doses of arsenic or inorganic arsenic compounds can be lethal. They are known poisons and known carcinogens. Some arsenic compounds are also considered to be teratogens (harm to fetus). Lower levels of exposure to arsenic or its compounds may cause nausea, vomiting, diarrhea, abnormal heart rhythm, damage to the blood vessels, decreased production of blood cells, and a feeling of 'pins and needles' in the hands and feet (NPI, n.d.)

Arsenic and compounds was ranked as 10 out of 400 toxic substances. The total hazard score taking into account both human health and environmental criteria is 4.0 of 6.0 total score (NPI, n.d.).

Chromium (Cr)

Sources of chromium emissions to air and water are from chemical manufacturing industry (e.g. dyes for paints), rubber and plastic products, metal finishing industry (e.g. chrome plating), Manufacturers of pharmaceuticals, wood, stone, clay and glass products, electrical and aircraft manufacturers, steam and air conditioning supply services, cement producing plants, incineration of council refuse and sewage sludge and combustion of oil and coal are major sources of chromium emission (NPI, n.d.). Iron and aluminum oxide surfaces adsorb CrO_4^{-2} at acidic and neutral pH (Davis & Leckie, 1980; Zachara et al., 1987; Ainsworth et al., 1989; McLean, 1992). The background concentration of chromium in soil is 1.5 - 40 mg/kg (Sittig, 1994).

Chromium can be found in two oxidation state situation as trivalent chromium, Cr(III), and hexavalent chromium, Cr(IV). The association of Cr(VI) with the soil surface is limited to positively charged exchange sites which with increase in pH those associations decrease. Cr(VI) is extremely mobile in soil (Griffin & Shimp, 1978). Studies on relative mobility of 11 different trace metals on various soils shows that transport of Cr(IV) can be significantly retarded on clay soils containing free iron and manganese oxides (Korte et al., 1976). Cr(VI) is the only metal studied to be highly mobile in alkaline soils. Free iron oxides, total manganese and high soil pH immobilize the Cr(VI), where the soil properties, cation exchange capacity, surface area, percent clay had no significant influence on Cr(VI), mobility (Korte et al., 1976, McLean 1992).

It was known by Griffin and Shimp (1978) that trivalent chromium is readily adsorbed by soils. Cr(III) at pH 5 was the least mobile metals in a relative mobility study. Hydroxy species of Cr(III) precipitate at pH 4.5 and the precipitation will be completed at pH 5.5 (McLean, 1992).

Chromium metal and chromium (III) compounds are not usually considered health hazards, but hexavalent chromium (chromium VI) compounds can be toxic if orally ingested or inhaled. Breathing in presence of chromium (VI) compounds can damage and irritate nose, throat, lungs, stomach and intestines; and may lead to asthma and other allergic reactions. Exposure to chromium (VI) can cause ulcers, convulsions, kidney and liver damage. A long-term exposure to airborne chromium (VI) can have adverse effects on the respiratory and the immune systems and can cause cancer (NPI, n.d.). The lethal dose of poisonous chromium (VI) compounds is about one half teaspoon of material (Chromium, n.d.).

Chromium(III) compounds were ranked as 60 out of 400 toxic substances. The total hazard score taking into account both human health and environmental criteria are 3.2. Cchromium(VI) compounds were ranked as 2 out of 400. The total hazard score taking into account both human health and environmental criteria is 5.5 (NPI, n.d.).

2.1.3. Immobilization of Heavy Metals

2.1.3.1. Natural Attenuation

Different associations have developed different definitions for natural attenuation. The U.S. Environmental Protection Agency defines monitored natural attenuation as the "reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization;

radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants" (U.S. EPA, 1997) .

The American Society for Testing and Materials (ASTM) defines natural attenuation as the "reduction in mass or concentration of a compound in groundwater over time or distance from the source of constituents of concern due to naturally occurring physical, chemical, and biological processes, such as; biodegradation, dispersion, dilution, adsorption, and volatilization" (ASTM, 2004) .

The U.S. Air Force Center for Environmental Excellence defines natural attenuation as the processes resulting "from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanism. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization." (Wiedemeier, 1999).

The U.S. Army defines natural attenuation as "the reduction of contaminant concentrations in the environment through biological processes (aerobic and anaerobic biodegradation, plant and animal uptake), physical phenomena (advection, dispersion, dilution, diffusion, volatilization, sorption/desorption), and chemical reactions (ion exchange, complexation, abiotic transformation). Terms such as intrinsic remediation or bio-transformation are included within the more general natural attenuation definition." (U.S. Army, 1995).

2.1.4. Natural Attenuation Processes

Pollutants, interact with soils in various physical, chemical, and biological processes that take place in all three (solid, gas and liquid) phases of the soil media. Natural attenuation processes as is shown in Figure 2-2.

Hydrological process as a physical process consists of advection, dispersion, infiltration and groundwater recharge. Interphase partiontioning is also another physical process which it contains sorption/desorption phenomena, volatilization and gas ex/solution. Biodegradation of contaminants is considered to be categorized in the biological processes. Chemical processes are one of the most important processes of natural attenuation which are being controlled by hydrolysis, dehydrohalogenation, precipitation and dissolution (Surampali et al., 2004).

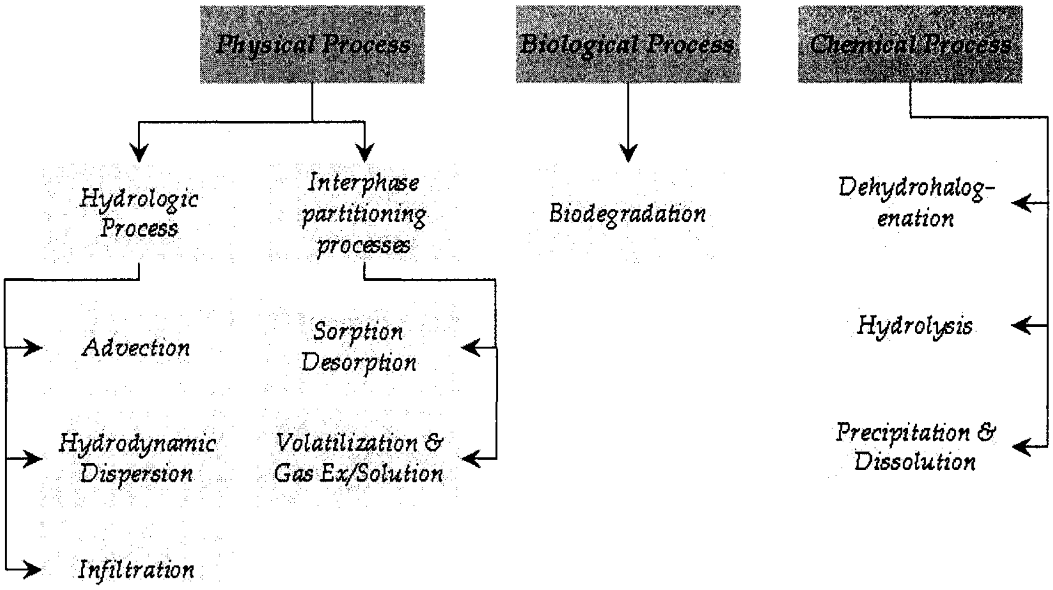

Figure 2-2 Natural Attenuation Process (adopted from Surampali et al. 2004)

Contaminants movement in soil profiles is a major environmental concern because even slow transport through the soil may finally lead to deterioration of groundwater quality. Besides, the movement of contaminants has an inverse relation to natural attenuation process; therefore, it is very important to understand the condition of pollutants in different soil types (Brady et al., 1999).

2.1.5. Parameters Involved in Natural Attenuation in Soil Environment

2.1.5.1. Soil

Soil is consisted of three phases of solid, liquid, and gas. Soils based on their constituent elements show different characteristics. Solid phase of the soil is a mixture of inorganic and organic materials. Predominant components of inorganic soils are silicon, aluminum and iron with a great number of micro and trace elements.

Soil also contains a great amount of organic materials. The Organic portion of soil consists of decomposed plant matter or humus which can be found in topsoil; therefore, organic matters in soil typically decrease with depth (Figure 2-3) (LaGrega et al., 2001).

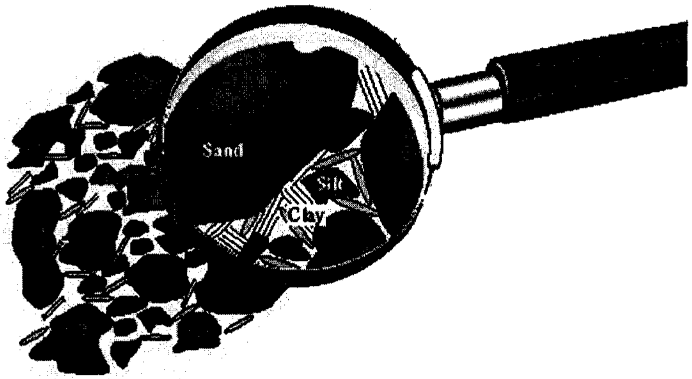

Figure 2-3 Soil aggregates in subsurface domain (Lagrega et al., 2001)

Soil Texture

Geological materials can be classified based on their size and distribution. Normally soils are named by their grain size. Soil texture, will determine the percentage of clay, sand and silt. Soil names can be chosen through standards. In Figure 2-4 Canadian and USDA soil classification system shows the ranges of each specific soil.

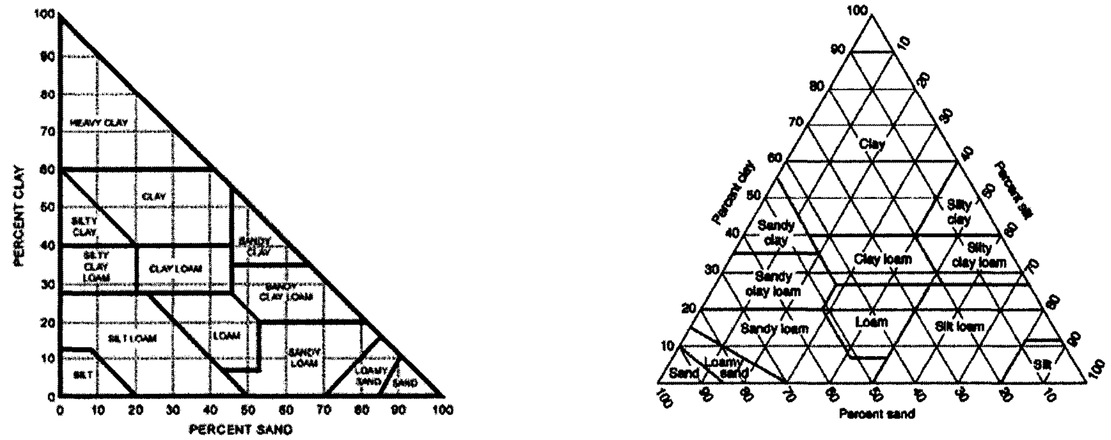

Figure 2-4 Soil textural classes in the Canadian system of soil classification (Toogood, 1958) (left), USDA soil classification (right)

Soil particle size classification based on USDA is shown in Table 2-1 and Table 2-2

Table 2-1 Soil classification based on particle Size

Material	Particle Size, mm
Clay	< 0.004
Silt	0.004-0.62
Very fine sand	0.062 – 0.125
Fine sand	0.125 – 0.25
Medium sand	0.25 – 0.5
Coarse sand	0.5-1.0
Very coarse sand	1.0 – 2.0
Very fine gravel	2.0 – 4.0
Fine gravel	4.0 – 8.0
Medium gravel	8.0 -16.0
Coarse gravel	16.0 - 32.0
Very coarse gravel	32.0 – 64.0

Source : Todd,2005

Table 2-2 -Soil particle classification based on USDA

Name of Soil	**Diameter limits (mm)**
Very coarse sand*	2.00 - 1.00
Coarse sand	1.00 - 0.50
Medium sand	0.50 - 0.25
Fine sand	0.25 - 0.10
Very fine sand	0.10 - 0.05
Silt	0.05 - 0.002
Clay	less than 0.002

Source : USDA

Generally different soils can also be categorized as:

Coarse Texture: sand and loamy sand.

Moderate coarse texture: sandy loam and fine sandy loam.

Medium texture: Very fine, sandy loam, loam, silt loam, silt.

Moderately fine texture: sandy clay loam, clay loam, silty clay loam.

Fine Texture: silty clay, clay, and sandy clay.

Till

Till is a general term for the coarsely graded and extremely heterogeneous sediments of glacial origin which it can be found in the northern part of the United States and in Canada. Till is the mixture of boulders, sand, clay and silt, but generally is sandy, with variable amounts of silt and little clay. In the regions of sedimentary bedrock in North America, glacial erosion has created a till deposit with considerable amount of silt and clay and as the result it has low permeability (Freeze & Cherry, 1979).

Clay

Clay refers to minerals which are result of chemical weathering of rocks. Secondary minerals which are result of weathering, chemical and /or biological processes of materials comprise the major fraction of clay size material in soil. These secondary minerals have effective diameter of less than 0.02mm. It has been well demonstrated in laboratory exercises and field experiences that clay soils play an important role in sorption of heavy metals. This role in addition to soil organic matters and amorphous non crystalline, is because of having high surface charge and other surface characteristic of the materials. The mineralogy of clays are different, but majority of them are consisted of silicates. Most common clays are kaolinite, illite, and montmorillonite (Yong et al., 1992).

Illites are formed on shales and clay bed (Gray & Roozitalab, 1976). Soils derived from alluvial sediment contain varying mixture of kaolinite, illite, and vermiculite (Yong & Mulligan, 2004).

Peat

Peat is soil material consisting of partially decomposed organic matter; found in swamps and bogs in various parts of the temperate zone. Peat forms when plant material, usually in marshy areas, is inhibited from decaying fully by acidic conditions. It is composed mainly of moss or sphagnum, but may also include other marshland vegetation: trees, grasses, fungi, as well as other types of organic remains, such as insects, and animal corpses. Under certain conditions the decomposition of the latter ones in the absence of oxygen is inhibited, and archaeology often takes an advantage of this (peat, n.d.).

Peat layer growth and degree of decomposition (or *humification*) depends principally on its composition and on the degree of water logging. The peat formed in very wet conditions, will grow considerably faster and be less decomposed than that in drier places. Under the right conditions, peat is the earliest stage in the formation of coal. Most modern peat bogs formed in high latitudes after the retreat of the glaciers at the end of the last ice age some 9,000 years ago. They usually grow slowly, at the rate of about a millimeter per year (peat, n.d.).

2.1.5.2. *Organic Carbon Content*

Colloidal soil organic matters can be divided in to 'non-humic' and 'humic' substances. The non-humic substances include unaltered biochemicals such as amino acids, carbohydrates, organic acids, fats and waxes that have not changed from the form they were synthesized by living organism (Alloway, 1990). Humic substances are formed by secondary synthesis reactions involving microorganism. They have wide range of functional groups, including carboxyl, phenolic hydroxyl, carbonyl, ester and possibly quinone and methoxy groups (Hayes, 1978; Stevenson, 1979).

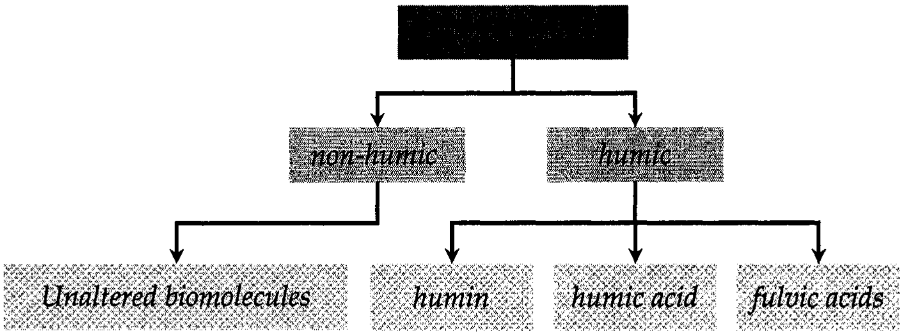

Figure 2-5 Organic matter categorization (adopted from Alloway, 1990)

Within the soil profile, the organic matter content is always highest in the surface horizon (Alloway, 1990). Organic matters in addition to participation in cation exchange reactions adsorb metals by formation of chelating agents. Low molecular weight organic ligands, not necessarily humic, can form a soluble complex with metals and prevent them from being adsorbed or precipitated (Alloway, 1990). Soil organic matter increases soil buffering capacity which result resistance to acidity changes. Organic matter also can increase the amount of soil water for instance; humus can hold the equivalent of 80 - 90% of its weight in moisture (Dragun, 1998).

Table 2-3 Typical values for the organic matter content of soils

Soil	Organic Matter content (%)
Cultivated soils	<10
Mineral soils (general)	3-5
Arable soil (SE England)	<2
Arable soil (N England /S Scotland)	2-6
Perm. grassland (S Scotland)	7.9-9.5
Prairie drained soil (USA)	5-6
Poorly drained soil	10
All soils(West Virginia, USA)	0.54-15
Tropical soils (South America)	0.5-21.7
Tundra (Russia)	73
Podzols (Russia)	10
Chernozems (Russia)	3.5-10

Source : Alloway, 1990

2.1.5.3. *Cation Exchange Capacity*

The capability of the soil to retain and exchange cations is quantifies as cation exchange capacity (CEC) (LaGrega et al., 2000). Except As, Sb, and Se and the metals Mo and V, majority of the heavy metals exist as cation in the soil solution (Alloway, 1990). Higher cation exchange capacity cause higher retention level of metals in soils. CEC is generally expressed in meq/100 g of soil. Its value depends largely on organic and clay content of the soil as well as acidity and clay mineralogy. It is possible to estimate

CEC based on soil texture, type of mineral and the OM matter of the soil as Table 2-4 and Table 2-5.

Table 2-4 Cation exchange capacity based on soil grain

Texture	Sand	LS to SL	Loam	Clay Loam	Clay
$CEC_{meq/100g}$	0-3	3-10	10-15	10-30	>30

LS: Loamy Sand, SL: Sandy Loam

Table 2-5 Cation exchange capacity of clay minerals

Clay mineral	CEC meq/100g
Kaolinite	3-15
Illite	10-40
Smectite	80-150
Plygorskite	20-30

Source: Lagrega et al., 2001
CEC: Cation Exchange Capacity

Considering % clay and % OM also is possible to approximate the CEC value. Using Equation 2-1 assume avg. CEC for percentage of OM=200 meq/100g and the average CEC for the percentage of clay=50 meq/100g; therefore,

$$CEC= (\%\ OM \times 200) + (\%\ Clay \times 50)$$

2.1.5.4. Specific Surface Area

A knowledge of the specific surface area (SSA) is necessary to assess calculating certain basic soil characteristics, such as the charge density and particle spacing, which in turn may be particularly useful in prediction and rationalization of certain engineering properties (Lutenegger & Cerato, 2001) such as sorption. Specific surface area refers to the area per unit weight of soil and is usually expressed as m^2/g. SSA is substantially different in clay minerals. The smaller the size of the particle the bigger SSA will be (Table 2-6). Clay particles and soil organic matters contain the largest specific surface area among all the soil particles. The soil surface is the part that participates in the partitioning of contaminants, thus the soil's physical and chemical properties are highly correlated with its surface area.

Table 2-6 Specific surface area for various soil type (Reddi, 2000)

	Loamy Sand	**Silty Loam**	**Clay**	**Kaolinite**	**Illites**	**Montmorilinite**
SSA m^2/g	10-40	50-100	150-250	5-39	65-200	600-800

Knowing the diameter of soil particles and number of particles per gram, the surface area of the soil for gravel and sand particles can be predicted as Table 2-7

Table 2-7 Relationship of particle size of soil to surface area (Hillel, 1998)

Size Separate	**Diameter(mm)**	**No of particles per gram**	**Surface area (cm^2/g)**
Gravel	>= 2.00	9.0 x 10	11
Very coarse sand	2.00 -1.00	9.0×10^1 - 7.2×10^2	11-23
coarse sand	1.00-0.5	7.2×10^2 - 5.8×10^3	23-45
Medium Sand	0.5-0.25	5.8×10^3 - 4.6×10^4	45-91
Fine sand	0.25-0.10	4.6×10^4 -7.2×10^5	91-227
Very fine sand	0.10-0.05	7.2×10^5 - 5.8×10^3	227-454

S_s (sphere)= $4\pi r^2$

Non-swelling clays such as kaolinite, have only external surface, whereas swelling clays like montmorillonite have a great deal on internal surface as well as external surface (Table 2-8).

Table 2-8 Specific surface area of common clay minerals

Clay Minerals	External SSA (m^2/g)	Internal SSA (m^2/g)
Halloysite	10-20	-
Kaolinite	35-70	-
Smectites	50-120	700-850
Illite	65-100	-
Montmorilonite	600-800	
Vermicullite	40-80	800-900
Chlorite	10-40	-

After Mitchell 1993 and Reddi, 2000.
SSA : Specific surface Area

2.1.5.5. pH

The interaction with the contaminants takes place in the surface of the soil. For most of the inorganic soil minerals, during the formation of crystalline structure, broken bonds (between Si and O, and between O and Al) on the edges of silica and alumina sheets would result due to disruption of the process (Wild, 1993). Thus, the positive or negative charges would result from the unsatisfied valences at these edges. Soil edge bonds would contain positive charges when the pH is low and negative ones when the pH is high (Huang, 2005). pH affects several mechanism of metal retention in soil. In a study performed by Harter (1983), the impact of soil pH on the sorption of Pb, Ni, Zn, and Cu by two soils adjusted to different pH ranging from approximately 4.3 to 8.3. Harter reported in his research (Figure 2-6) that the retention of heavy metals didn't significantly increase until the pH was greater than 7. Non-calcareous soil has pH<7 and calcareous soil has high pH (pH>7). Calcareous soils are those that have free calcium carbonate in the profile. Some soils that develop from calcareous parent materials will be calcareous throughout their profile. This will generally occur in the arid west where precipitation is less than 15 inches per year (Soil pH, 2003). Generally, heavy metal ions are most mobile under acid conditions. Increasing the pH by liming usually reduces their mobility. However molybdate anions become more available with increasing pH. Soils have pH value within the range of 4 - 9.5, owing to the buffering by Al at the lower end and $CaCO_3$ at upper end of the range (Brady, 1999).

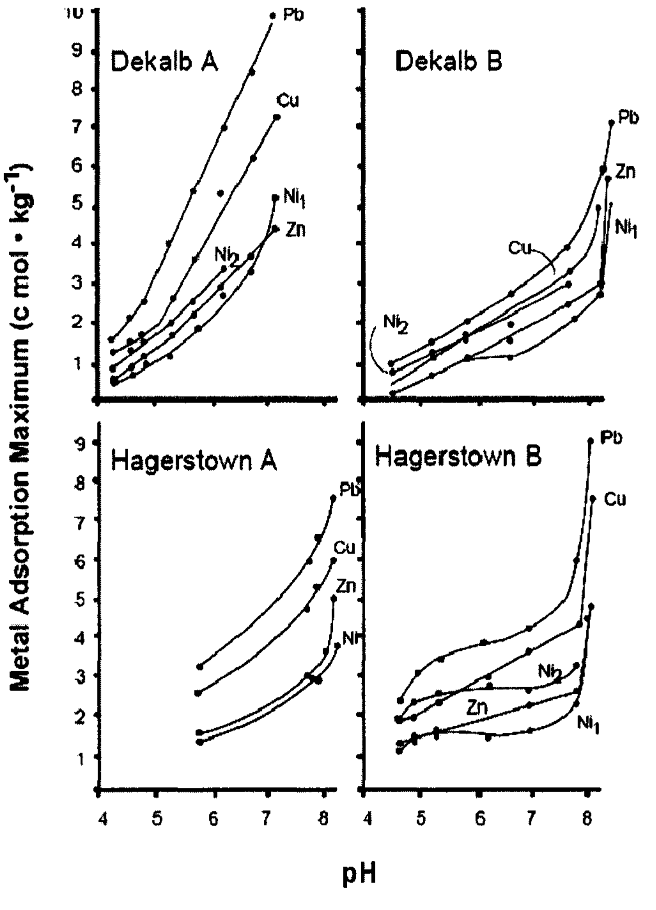

Figure 2-6 Effect of soil pH level on maximum Pb, Cu, Zn and Ni retention on two soils in A and B horizon (Harter, 1983)

Normal pH is 5 - 7 in soils for humid regions, and pH 7 - 9 in the soils of arid regions. However the maximum range of conditions found in soils is 2 - 10.5 (Alloway, 1990). Precipitation is the converse of dissolution and particularly applicable to all trace metal hydroxide, oxide, carbonate, and phosphate under alkaline conditions (Lindsay, 1979). Precipitation can occur when a chemical reaction transform a solute to a much less soluble form. Changes in oxidation state also can promote precipitation. Precipitation depends greatly on pH. Most metals precipitate at high pH levels as hydroxides (Figure 2-7).

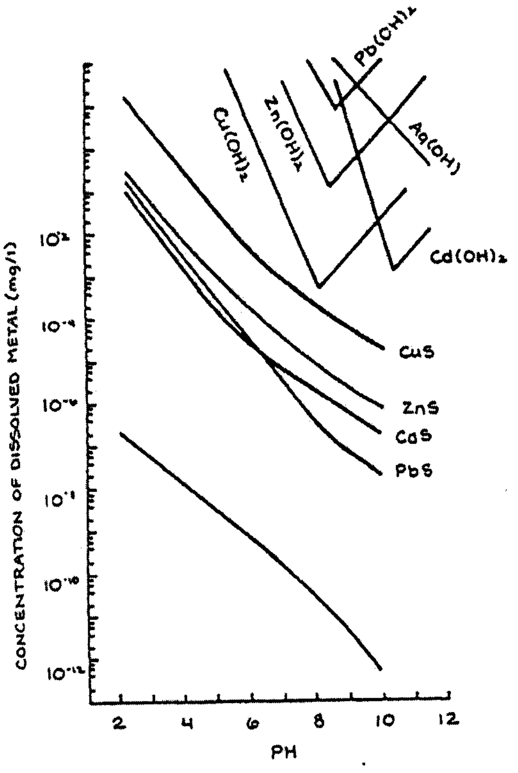

Figure 2-7 Solubility of metal hydroxides and sulphides as function of pH (Conner, 1990)

2.1.6. Partitioning Coefficient

Sorption is a term that includes both phenomena of adsorption and absorption. Adsorption is a surface phenomenon in which a chemical species adheres to an interface. Absorption is a bulk phenomenon in which a chemical species becomes distributed throughout a solid or liquid absorbent (Nazzaroff & Alvarez, 2000). Sorption slows the mobility of contaminants and decreases the concentration of contaminant in the solute. Sorption is a fundamental issue in the fate of the contaminants. The simplest and most common method of estimating contaminant retardation (*i.e.*, the inverse of the relative transport rate of a contaminant compared to that of water) is based on partition (or distribution) coefficient, K_d.

$$K_d = \frac{S_{mc}(mg/kg)}{d_{mc}(mg/L)} \tag{2-2}$$

Where, S_{mc} is sorbed metal concentration, d_{mc} is dissolved metal concentration.

Sorption and its accompanying phenomena are considered as the most important physico-chemical mechanisms of pollutants retention on the soil phase of soil matrix (Mirsal, 2004). The value of K_d varies for different contaminant. For organic matters K_d is estimated as

$$K_d = om \times K_{om} \tag{2-3}$$

Where, *om* is soil organic matter content (kg/kg) and K_{om} is the soil adsorption coefficient normalized to organic matter. Values for K_{ow} is given in tables (US EPA, 1996).

The desorption process occurs when the concentration of the sorbed elements is high (Figure 2-6). Desorption also is an extremely long time process (LaGrega et al., 2001). In general, ion exchange reactions are completely reversible over time spans. By desorption inorganics will move toward groundwater unless they be sorbed by other sorbing surfaces (Braddy, 1999).

Sorption in soil can be discussed by the following isotherms; Longmuir, Freundlich and constant linear models. Linear equation model only is used at low concentrations of contaminants where at higher concentration the two other models are being used (Rowe et al., 1995).

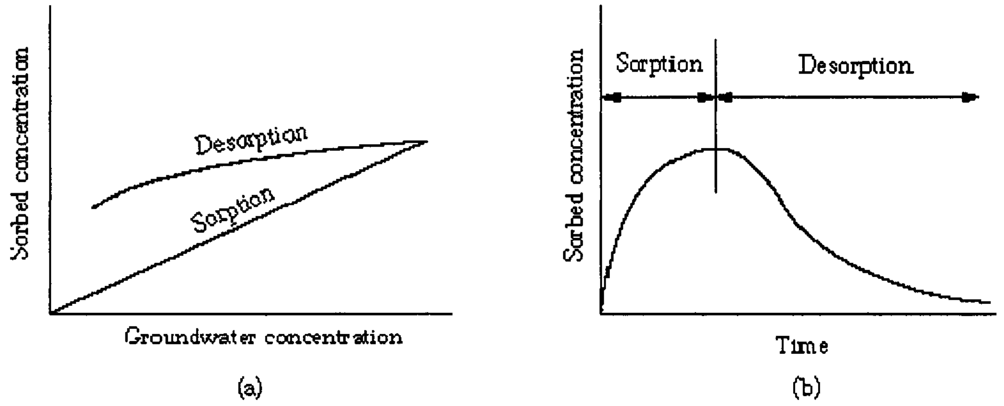

Figure 2-8 Sorption-Desorption of sorbate (LaGrega et al., 2001)

Chang et al. (1984) demonstrated that more than 90% of applied heavy metals were found in the 15cm surface of the soil. In 1996, Bright and others stated that the maximum attenuation by soils could be achieved by high clay content, organic carbon content, and carbonate content. Prior to this Anderson and Christensen (1988) had indicated that clay content, organic matter and hydrous Fe and Mn oxides provide most of the high energy binding sites for metal sorption. By conducting a series of test in to different soils, Zuhairi (2003) characterized the physical and chemical properties of a series of soil samples, and measured their adsorption capacity of heavy metals in South Wales. He used the results to highlight the best candidate for lining materials and their attenuation capacity against heavy metals, i.e. lead (Pb), copper (Cu) and zinc (Zn) (Zuhairi, 2003).

Some particles, such as clay minerals, have permanent overall negative surface charges. Compounds with a positive charge, such as metal ions, are thus more susceptible to adsorption to these particles than ions with a negative charge.

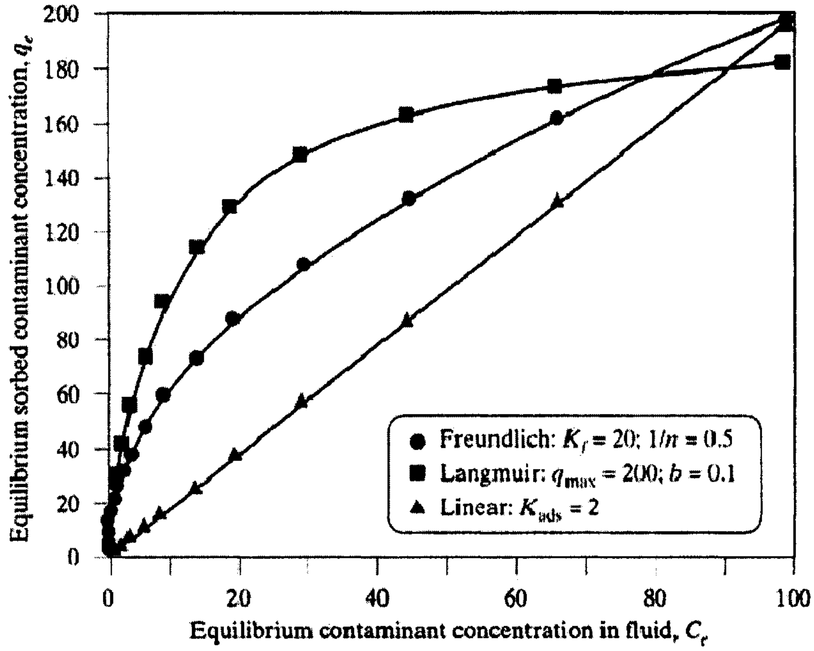

Figure 2-9 Shapes of common sorption isotherms (Nazaroff & Alvarez , 2000).

Other particles such as iron and aluminum oxides and hydroxides as well as organic macro molecules, possess functional groups that change with pH. Metal ions may become attached to these sites by chemical reaction, complexation, or electrical attraction. Not only do metal ions adsorb, but inorganic and organic metal complexes can also undergo this process. (Zachara et al., 1999)

2.1.7. Attenuation, Retardation and Transport of Heavy Metals

One model for addressing the potential for natural attenuation is presented by Brady (1999) as Equation 2-4:

$$NAF = HDF + SF + R_{irv} + BF \qquad \textbf{2-4}$$

Where NAF is Natural attenuation factor, *HDF*, is hydrologic dilution factor, R_{irv}, Irreversible uptake factor, *SF*, sorption factor and *BF* is for biodegradation/chemical transformation factor.

In the above model the hydrologic dilution and sorption terms can be obtained by US EPA soil screening procedures. Calculation of *HDF* (Equation 2-5) requires the input of several site specific hydrologic parameters such as, hydrologic conductivity, hydrologic gradient, mixing zone depth, the recharge rate and the length of the source parallel to flow.

$$HDF = \frac{K_h \cdot i \cdot d}{I \cdot L} \qquad \textbf{2-5}$$

Where;

$$d = (2\alpha_v \mathrm{L})^{0.5} + \mathrm{d_a}(1 - \exp\frac{-\mathrm{L}\cdot\mathrm{I}}{\mathrm{V_s n_e d_a}}) \qquad \textbf{2-6}$$

α_v is the vertical dispersivity (m) and is calculated from the approximation of Gelhar and Axness (1981), α_v = 0.0056 x (x is the distance (m) the contaminant travels in groundwater at velocity v (m/yr) to the nearest receptor); V_s is the horizontal seepage velocity (m/yr); n_e is the effective aquifer porosity; and d_a is the aquifer depth (m). The recharge rate, *I*, multiplied by the source area is the contaminant flux into the aquifer

The sorption factor, SF:

$$SF = \frac{\rho_b \cdot K_d}{n_e} \qquad \textbf{2-7}$$

where the n_e is the aquifer soil porosity. ρ_b is the bulk density of the soil and K_d, is the sorption coefficient in (ml/g). The application of K_d is the easiest way to represent the sorption although it is chemically least realistic approach. Langmuir adsorption isotherms are more realistic (Braddy et al., 1999) Surface complexation models also provide more realistic picture of mineral surface interactions.

The irreversibility of contaminates can be presented as Equation 2-8.

$$R_{irv} = \rho \frac{X_{irv} \cdot K_d}{n_e} \qquad \textbf{2-8}$$

Where, X_{irv} is the average fraction of sorbed contaminant that cannot be exchanged from a contaminated laboratory or field sample.

Retardation refers to processes that delay the transport of contaminants by removing or immobilizing them from a free state. Sorption, precipitation, ion exchange and filtration are the examples of these processes.

Attenuation refers to types of processes (1) irreversible removal, and (2) transformation. Removal by an attenuation process and it reduces the mass of substance. Biodegradation and hydrolysis are examples of this process (LaGrega et al., 2001).

Metals in soil solution are continuously forming precipitates, interacting with soil organic matter, being sorbed by clay minerals, and being retained by hydrous oxides. The presence of acid functional groups in soil organic matter is responsible for metal retention through both exchange and chelation mechanisms (Sposito, 1981).

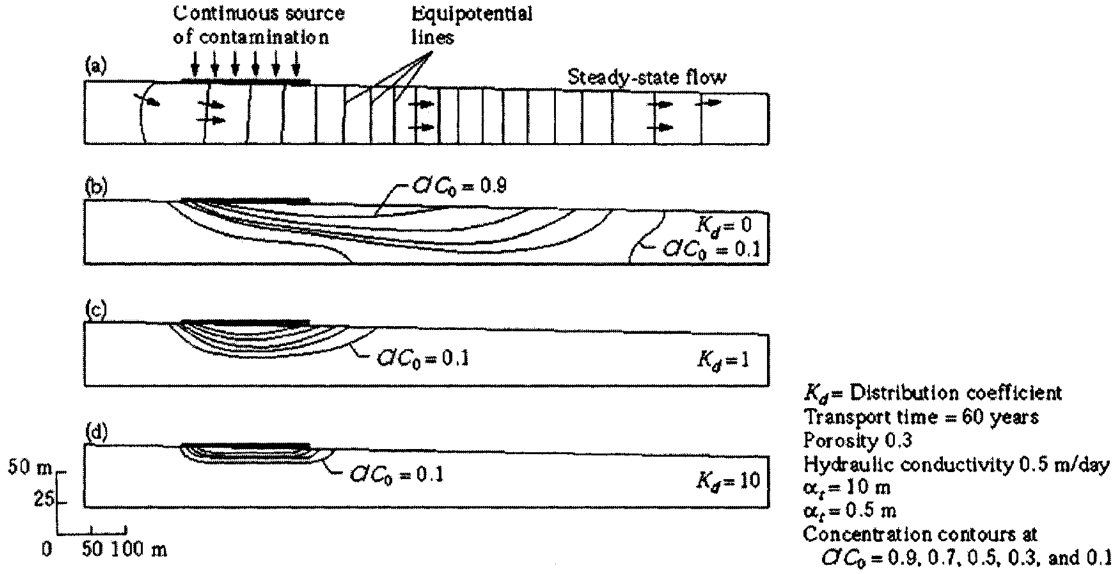

Figure 2-10 Effect of sorption (K_d) in transport of contaminant (Freeze & Cherry, 1979)

Therefore, the metals retention capacity and cation exchange capacity (CEC) tend to increase as the clay hydrous oxide, and organic matter contents increase. Because of these relations, the CEC has been used as an index of the metal retention capacity of a soil (Pierce et al., 1992). The coarse fraction of soils has very low specific surface area and as such is essentially inert from a physicochemical standpoint. Soils dominated by sands and gravel will have low attenuation capacities. In general as the proportion of clays in a soil increases, the attenuation capacity will increase (Yong et al., 1992).

Heavy Metals (HMs) Mobility

Infiltration occurs specially in areas where the permeability of the land, associated with other factors allows a rapid vertical penetration of surface waters (Perth County, 2001).

There has been so much attention to heavy metal contamination in the past decade with regard to accumulation in soils, uptake by plants, and contamination of waters and exposure to human. In soil, heavy metals may occur in ion exchange sites, be incorporated into or on the surface of crystalline or non crystalline inorganic precipitates, be incorporated into organic compound, or be in soil solution. Heavy metals are sparingly soluble and occur predominantly in a sorbed state or as part of insoluble inorganic compounds. Heavy metal movement will most likely happen with large application in a sandy, acid, low organic matter soil in a high rainfall area and irrigation. (Dowdy & Volk, 1983)

Risk of heavy metals in the environment is closely bonded to their movement in soil profiles because even slow transport throughout the soil and subsoil materials may increase the heavy metals content in the ground water. In the soils with coarse texture and low CEC, pH and organic matter content metals will have low retention capacity. In addition, metals have to be in soluble form or be associated with mobile particulates to move with water in soil. Experiments show (Figure 2-11) that concentration of metals decrease with soil depth (Lee & Shuman, 1996).

In general movement is essentially related to the physicochemical forms of the metals in soil because theses forms have different potential by inorganic or organic ligands in soil solution (McBride, 1989).

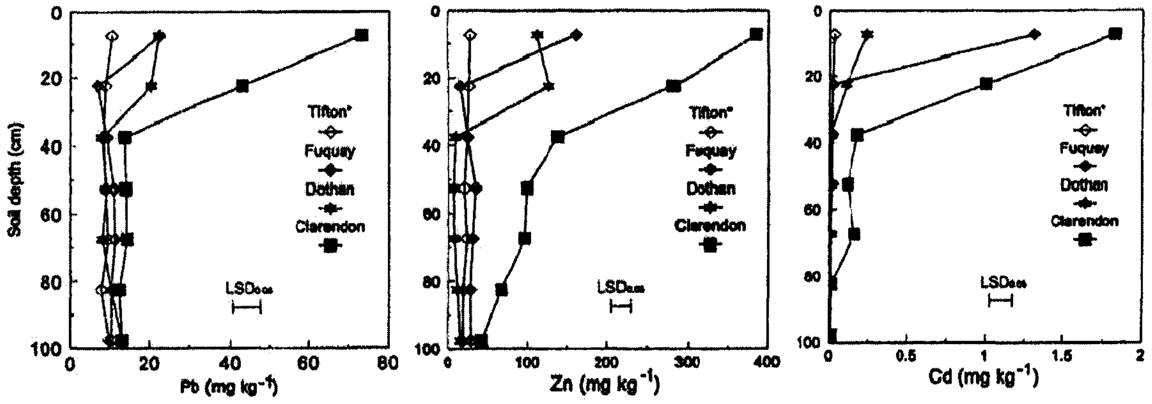

Figure 2-11 Sorption of HM reduces by depth in different soils (Lee & Shuman, 1996)

2.2. Analytic Hierarchy Process

Decision making is a complex process. It usually involves multiple objectives, alternatives, social interests and preferences. Usually the final decision on the alternative depends on the consensus of a group of decision-makers. The Analytic hierarchy process (AHP) which was developed by Thomas Saaty, allows the decision makers to model a sophisticated and multidimensional problem in a hierarchical structure. In AHP uncertainties and other influencing factors could be included in decision making process. AHP is a relatively simple technique on decision problems which represent an approach based on a pair wise comparison (Maggiora, 2003).

In AHP, a comparison matrix, A, is used to determine the relative dominance, order, importance, priority, likelihood, etc., among a set of criteria $\{C_1, C_2, \ldots, C_n\}$

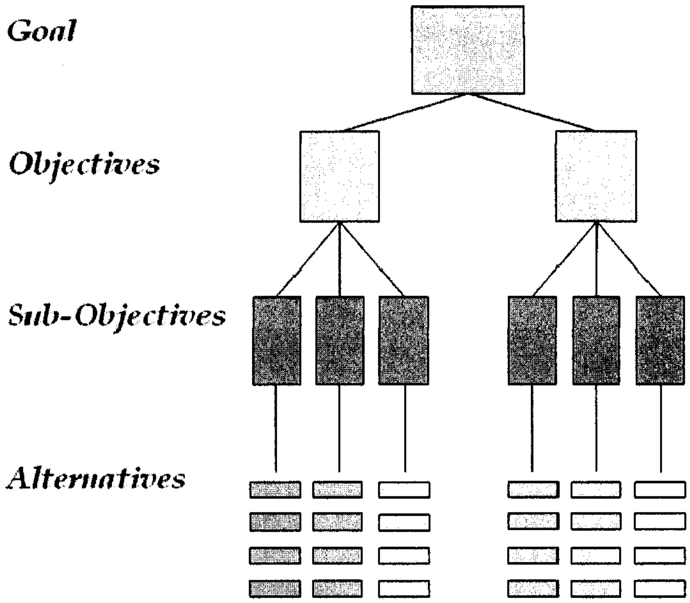

Figure 2-12 Analytic Hierarchy Process structure

Each element of matrix A, a_{ij}, is obtained by comparing criteria according to an appropriate scale: a_{ij} corresponds how much the i^{th} criterion is 'favored' over the j^{th} criterion. After creating the Matrix, it will be normalized. Then the average of each row will be calculated, in corresponding column. These averages are the weights of each criterion which will be applied in decision making.

2.3. Fuzzy Logic and Engineering Applications

Fuzzy logic refers to a large subject dealing with a set of methods to characterize and quantify uncertainty in engineering systems that arise from ambiguity, imprecision, fuzziness, and lack of knowledge. Fuzzy logic is a reasoning system based on a foundation of fuzzy set theory, itself an extension of classical set theory, where set membership can be partial as opposed to all or none, as in the binary features of classical logic (Ross, 2004).

2.3.1. Crisp Sets

Boolean logic is based on the idea of classical sets that are characterized by a crisp (non fuzzy) boundary and are represented as a collection of elements a_i:

A={ $a_1,a_2,a_3,\ldots,a_n$} where all the elements $a_1,a_2,a_3,\ldots a_n$ within the set A are listed . Alternitatively a classical set is represented as:

$$A = \{x \mid P(x)\} \qquad \textbf{2-9}$$

Where the element x belongs to the set A only and only if the proposition P(x) is true. For a crisp set the proposition P(x) can be only true or false and for x_A the same dichotomy is expressed and it indicates whether the element x belongs to the set or not (Berkan & Trubatch, 1997).

$$x_A = \begin{Bmatrix} 1 & for & x \in A \\ 0 & for & x \notin A \end{Bmatrix} \qquad \textbf{2-10}$$

Hence the characteristic function maps elements x of the Universal set X to a two-elements set {0,1} (Berkan & Trubatch, 1997).

$$x_A : X \rightarrow \{0,1\} \qquad where \qquad x \in X \qquad \textbf{2-11}$$

2.3.2. Fuzzy Sets

As described above, a crisp set is defined by the characteristic function $x_{\hat{A}}$ that takes values of one or zero. When an element x is respectively belongs or does not belong to the set Â, the characteristic function can be generalized (i.e. $\mu_{\hat{A}}$) by assigning real values within the closed interval [0, 1] (Berkan & Trubatch, 1997).

When the function takes any real value between zero and one, it indicates partial degrees of membership of the element x into the set A. This generalized characteristic function is known as membership function, μ_A defined as:

$$\mu_A : X \rightarrow [0,1] \quad where \quad x \in X \qquad \textbf{2-12}$$

The membership is defined over the closed interval [0, 1] and because it can be partial the set is known as fuzzy set and is denoted by Â. A fuzzy set Â is a set of ordered pairs represented as:

$$\hat{A} = \{(x, \mu_{\hat{A}}(x)) \mid x \in X\} \qquad \textbf{2-13}$$

Fuzzy sets are useful when the vague concepts are being described. However the representation of the concepts in terms of a membership function depends not only on the definition of the concept by itself, but also on the context of the idea (Berkan & Trubatch, 1997). As an example, definition of high pH can be different among different experts. Some people may consider 8 as very alkaline in soil where other experts may consider 9 as very alkaline soil.

Fuzzy concept will be helpful in these cases and will let us define a membership value to our sets, such as 0.56 member of high alkaline, 0.65 member of average acidity.

2.3.3. Fuzzy System Design

2.3.3.1. *Fuzzy Membership Design*

The design of fuzzy sets involves the design of membership functions that assign linguistic values to the linguistic variables. A fuzzy variable is known as linguistic variable and its universe of discourse is divided into fuzzy sets defined by the membership function. A membership function (MF) is a curve that defines how each point in the input space is mapped to a membership value (or degree of membership) between 0 and 1. For example in the Figure 2-13 the membership functions for very low, low, medium, high and very high speed is shown. For better understanding, the very low speed, if a car has a speed from 0 to 20 km/h the speed belongs to very low membership function and with increase in the speed from 20 to 35 the membership of very low set is reducing and the membership of low set will increase and so on.

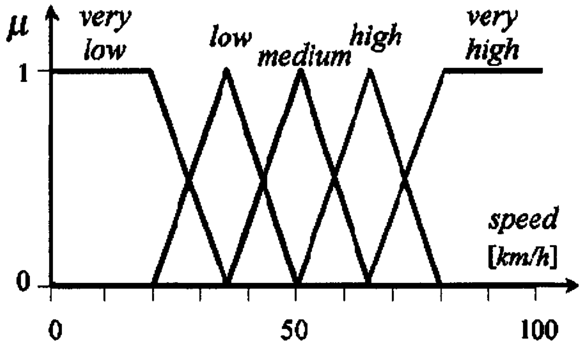

Figure 2-13 Fuzzy membership functions for very low, low, medium, high and very high speed

There are different techniques to define membership function. In the absence or not having sufficient numerical data, linguistic design will be used. The other technique (data-driven) requires a set of algorithmic approaches such as clustering and ANFIS (Adaptive-Network-based Fuzzy Inference Systems) (Berkan & Trubatch, 1997).

2.3.3.2. *Fuzzy Rule Design*

Fuzzy rules can be expressed in terms such as "If the room gets hotter, spin the fan blades faster" where the temperature of the room and speed of the fan's blades are both imprecisely (fuzzily) defined quantities, and "hotter" and "faster" are both fuzzy terms. Fuzzy logic, with fuzzy rules, has the potential to add human-like subjective reasoning capabilities to machine intelligences, which are usually based on a Boolean logic. The fuzzy rules provide an excellent means of compactly representing what the human has learned in a way that is both accurately human-like and subjective, and can be used in engineering designs. The number of rules in fuzzy system is the possible combination of the inputs. That means with higher input variables and membership functions the possible number of rules will increase as well. There are different rule composition strategies to handle the problems encounter during rule design such as Competitive rules, Cooperative rules, weighted rules Prioritized rules, Hierarchical rules and Adaptive rules (Berkan & Trubatch, 1997).

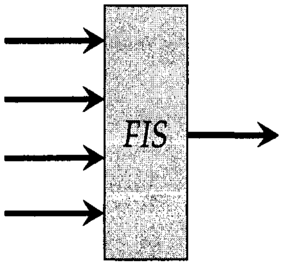

Figure 2-14 Conventional fuzzy inference system (Lee et al., 2003)

One of the most important issues in Fuzzy system design is how to reduce the number of rules. Considering a fuzzy inference system with *m* membership functions and *n* input variables will result to m^n rules. This exponential increase in rules will be problematic in most cases, where some conditions will be not easy to happen and not easy for the FIS designer to process. In order to overcome the problem of rule explosion, the hierarchical rule strategy or techniques in fuzzy systems design has been proposed (Figure 2-15).

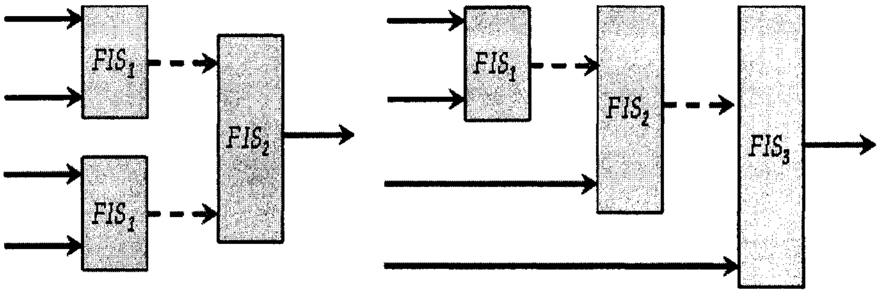

Figure 2-15 Hierarchical fuzzy inference system (Lee et al., 2003)

In this technique the number of rules will increase linearly with number of inputs (Lee, 2003).

2.3.4. Fuzzy Logic Application in Engineering

In science, engineering and many other areas of study, quantitative problems are solved using mathematical models which are cast in deterministic form, yielding closed form solutions or at least numerical solutions if this is not possible. In many real cases uncertainty may be due to the complex nature of the problem, such as the stress distribution in a component of complex geometry or the flow pattern around a bluff body in a fluid with complex rheological properties. These are not uncertainties of a statistical nature and the corresponding concept is of possibility rather than probability (Harris, 2000). In some cases the uncertainty raises because of having lack of knowledge and information. Application of Fuzzy system in generating data and dealing with vague information has been in the attention of many researchers.

Lee et al. (1995) developed a methodology to estimate human health risk from ground water contamination. They assessed nitrate-induced human health risk by applying fuzzy-set approach and characterized the uncertainty of the involved elements and their impacts on the result. Ghomshei, et al. (2000), applied fuzzy logic in an environmental risk assessment study. In their research by using fuzzy logic decision making process they provided an improved method to examine a potential problem, reducing disputes and providing additional clarity in risk analysis.

Orzen et al.(2000) developed a methodology to provide a precise and consistent evaluation tool for flood control in water resource management.

Mitra et al.(1998) applied fuzzy logic to predict soil erosion potential in watersheds. Comparison of the result with USLE (Universal Soil Loss Equation) showed a successful result for this application. Cameron and Peloso (2001) applied fuzzy logic in order to assess the aquifer pollution potential, considering values in DRASTIC model and error associated with measures and estimation. Jorde et al. (2001) applied fuzzy base models for the evaluation of fish habitat quality and in stream flow assessment. Elektorowicz et al. (2006) assessed the metal sorption capability to natural sediment by applying fuzzy logic. Amini et al. (2005) used fuzzy classification in combination of spatial prediction to assess the state of soil pollution.

2.4. GIS and Environmental Engineering

GIS (Geographical Information system) is a tool that represents a model of the real world. The results of analysis of these data are generally used for understanding environmental processes and decision making. GIS integrates various layers of data to generate new data that is required in a decision making process. Sangupta et al. (1996), applied GIS tool to assess the population exposure and risk zones due to air pollution. Bocco and Sanchez (1997) studied the potential impact of Lead contamination. They employed GIS to prepare different vulnerability map such as, demographic, economic and industrial zones. Through GIS they generated the spatial distribution of vulnerable areas to lead. In the same year another research conducted by Kohli et al., applied GIS to identify the population at risk because of radon.

The combination of GIS and Fuzzy logic has been brought into attention in recent years. Karkazi et al. (2001) presented their methodology for sitting of landfill. They integrated the fuzzy logic concept and GIS in their method. Bojorquez et al. (2002) presented an environmental impact assessment approach, integrating a fuzzy logic, geographical information systems and optimization techniques. With applying fuzzy system in assessment the complexity of impacts in addition to vagueness and imprecision of the information will be manageable. Saro Lee (2003) studied and evaluated the waste disposal sites using the DRASTIC system in southern Korea. Bien et al. (2004) developed a tool to integrate the risk assessment and spatial planning using GIS capabilities. Li et al. (2004) studied the sources of metal contaminations in urban soils of Hong Kong by application of GIS. Naoum et al. (2005) developed a GIS pre-processor to simulate the currents and pollutants transport in lakes and coastal areas. An application of Fuzzy logic with integration of GIS for phytoremediation plant selection presented by Porter et al. (2006), the combination of GIS and fuzzy logic provided a promising method for phytoremediation plant selection.

2.5. Objectives

Governmental organization has to distribute the funds and control the contaminated sites. Due to large number of contaminated sites, decision making in such organizations has become crucial. Decision making depends on personal judgment, experiments and literatures and actions based on these items are not easy and usually turns into different decision.

According to the literature 75% of Superfund sites are contaminated with toxic metals (Evankon & Dzombak, 1997). Research and publications related to site impact assessment are dedicated mostly to sites contaminated with organic compounds, because of degradation processes of organics. Metals as chemical elements have different retardation mechanism in compare with organic contaminants. Metals change forms and they don't degradate. In addition, heavy metals are dangerous to human health. Current attenuation models presented by scientists such as Brady (1999) only considers vulnerability of groundwater to environment, yet in addition to study the groundwater, the surface sorption could also be an issue for exposure of contaminant to human and environment. Existing attenuation model only considers the type of soil based on their grain size for infiltration, not chemicals and physical characteristics of the soil which are an essential elements in heavy metal behavior in soil.

Since many parameters are involved in mobility study of heavy metals, decision making through common subjective decision making techniques, such as Analytical Hierarchical Process is difficult and its result involves into huge uncertainty; therefore, a new model and method should be applied.

Major sorption of heavy metals happen in the top soil layer; therefore, considering top sorption with interaction of all different parameters in the calculation is highly remarkable effort in environmental and health impact studies.

In conclusion the major objective of this research is to introduce a methodology for designing models suitable for decision making in environmental management.

In particular objectives of this research can be summarized in the following:

- To define a methodology for soil classification to be applied in decision making, through generating sorption index of the soil.

- To introduce a practical model that deals with heavy metal contamination vulnerability in topsoil that includes the surface complexation models and surface property of the top soil.

- To develop a fast tool that processes the geological expert knowledge and environmental experience to form a platform in which the result and decision can easily be made by managers and decision makers.

- To initiate an application from the tool to assess an environment impact assessment case where independent data from various domains can be interfered.

- To consider major parameters of the sorption at once and showing the relationship among these parameter by application of fuzzy theory.

CHAPTER 3. CONCEPTUAL DESIGN

3.1. Research Approach

As discussed in the previous chapters, the emergent need to save time and money require identification of the areas which are more vulnerable to contamination. Using natural attenuation technique is highly related to priority making for remediation of contaminated sites; therefore, this leads to employ all the available tools and techniques to achieve the goal. The first major step in planning for a remediation project is to identify and assess the risk of the contamination. Based on the importance in any project the general approach can be set. For instance, considering the environmental impact and health impact caused by contaminant, the layers of information can be collected or generated. The environmental impact of all types of contamination in different media will be chosen and interpreted. The health data caused by contaminants as well can be identified. To analyze all the data and information, the information of health and environmental impact can be overlaid together in GIS and as the result , decisions can be made for any management purposes.

A general model for different cases developed remediation priority selection is presented in Figure 3-1. In this model environmental risk from different types of contaminant of i)hydrocarbons, ii) heavy metals, and iii) toxins in different media such as surface water, air, soil and groundwater are identified. This model can be applied in conjunction with other models and databases.

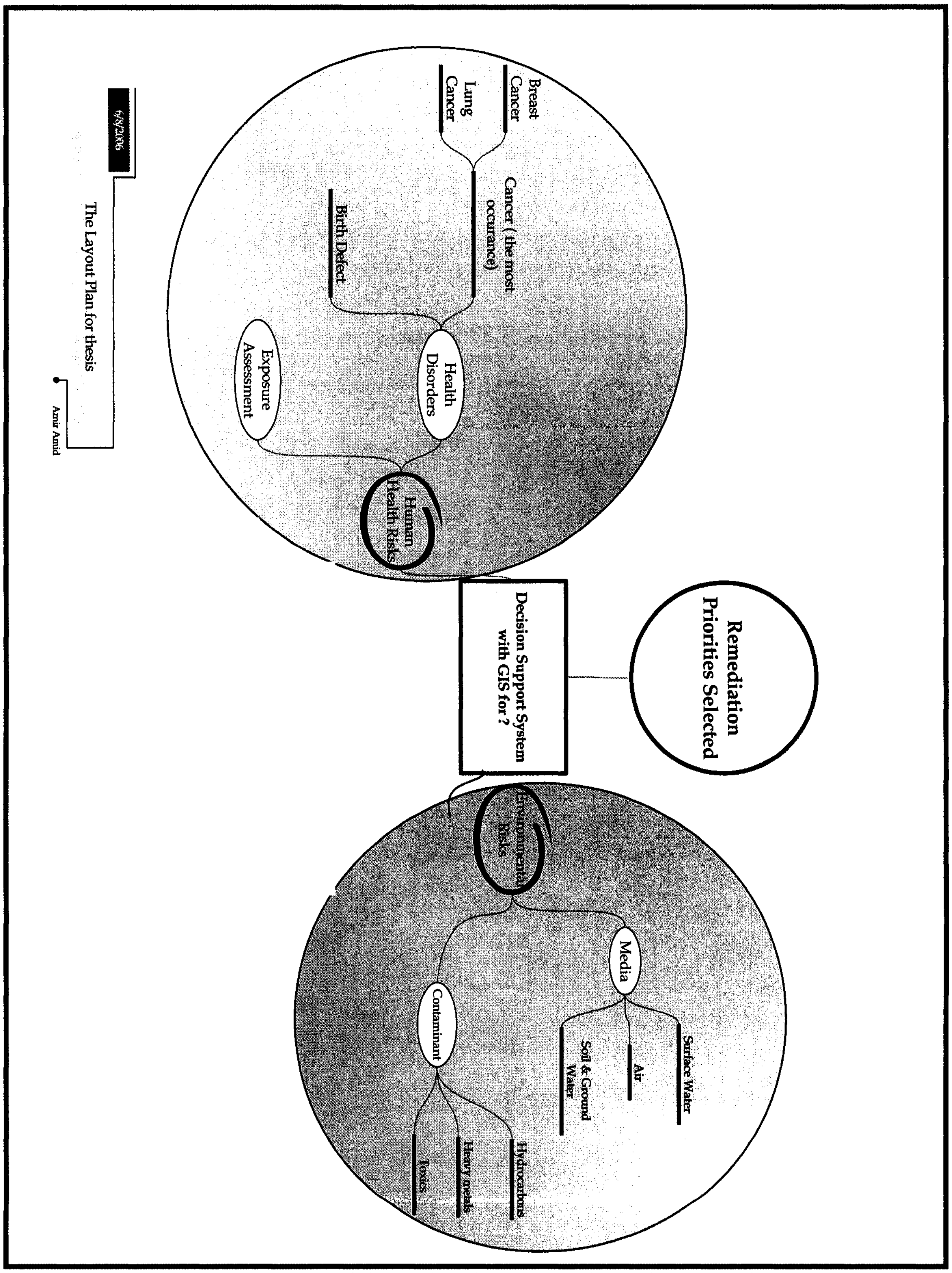

Figure 3-1 Large overview of the project for ranking hazardous sites for remediation

For example, GIS database information on health or ecosystem could be used. The result of the vulnerable environment produces the most important reference for prioritizing the contaminated lands for remediation and decision making.

In this project the assessment of vulnerable soils was selected considering the parameters that have impact on fate of heavy metal. A search for a technique and strategy was needed to facilitate the assessment of an indistinct output related to attenuation of heavy metals in topsoil.

3.2. Finding the Most Suitable Technique

Assessing the mobility of heavy metals in sites is a key constituent of prioritizing contaminant and remediation. Brady et al. (1999) presented a method to identify vulnerable soils to heavy metals. They introduced a monitored natural attenuation toolbox to screen sites for the potential implementation of MNA (Monitored Natural Attenuation). In their model the MNA functions are categorized in to dilution, sorption, irreversible uptake and decay (biodegradation or radioactive). Their model works for heavy metals, organic and radioactive contaminants and its result produces a scoreboard for MNA potential. The usage of this model and its functions are restricted to MNA in the groundwater contamination. The presented MNA toolbox needs definite available data and it can not deal with vague and imprecise data. Usually, these kinds of data are not easily accessible or stored in provincial or national scale.

For being able to estimate the attenuation potential, topsoil vulnerability should also be considered. For this reason other involved characteristics of the soil and specifically those related to sorption of heavy metals ought to be well studied; therefore, every individual function involved in the fate of heavy metals was studied. The effect of all of these parameters should be selected and aggregated together. In this study, the first attempt was to create a weight for each the individual parameters so based on that, by adding the weighted values, a final result be achieved. In order to avoid full subjective decision making, a scientific method had to be used. The AHP (Analytic Hierarchy Process) is a method that helps the decision makers to create the weight of each variable. Since for creating the AHP matrix the importance of the variables is involved with huge uncertainties and without proper valid knowledge (purely subjective) this technique could not be used. In the next attempt, in order to engage the real possible data and reduce the uncertainty to a controllable manner the fuzzy logic concept was applied. Fuzzy set theory can be applied in systems where human judgment, perceptions and emotions play a central role (Zadeh, 1977).

Because of having large number of variables, the use of a single layer fuzzy inference system could not also satisfy the needs; therefore, a multilayer fuzzy inference system (hierarchical fuzzy system) resolves this constrain and so was selected for the design. For design of the hierarchical fuzzy model, MATLAB® fuzzy toolbox was employed. The output of the model enables us to predict the sorption potential and as the consequence of that the soil Vulnerability map to heavy metal contamination can be prepared.

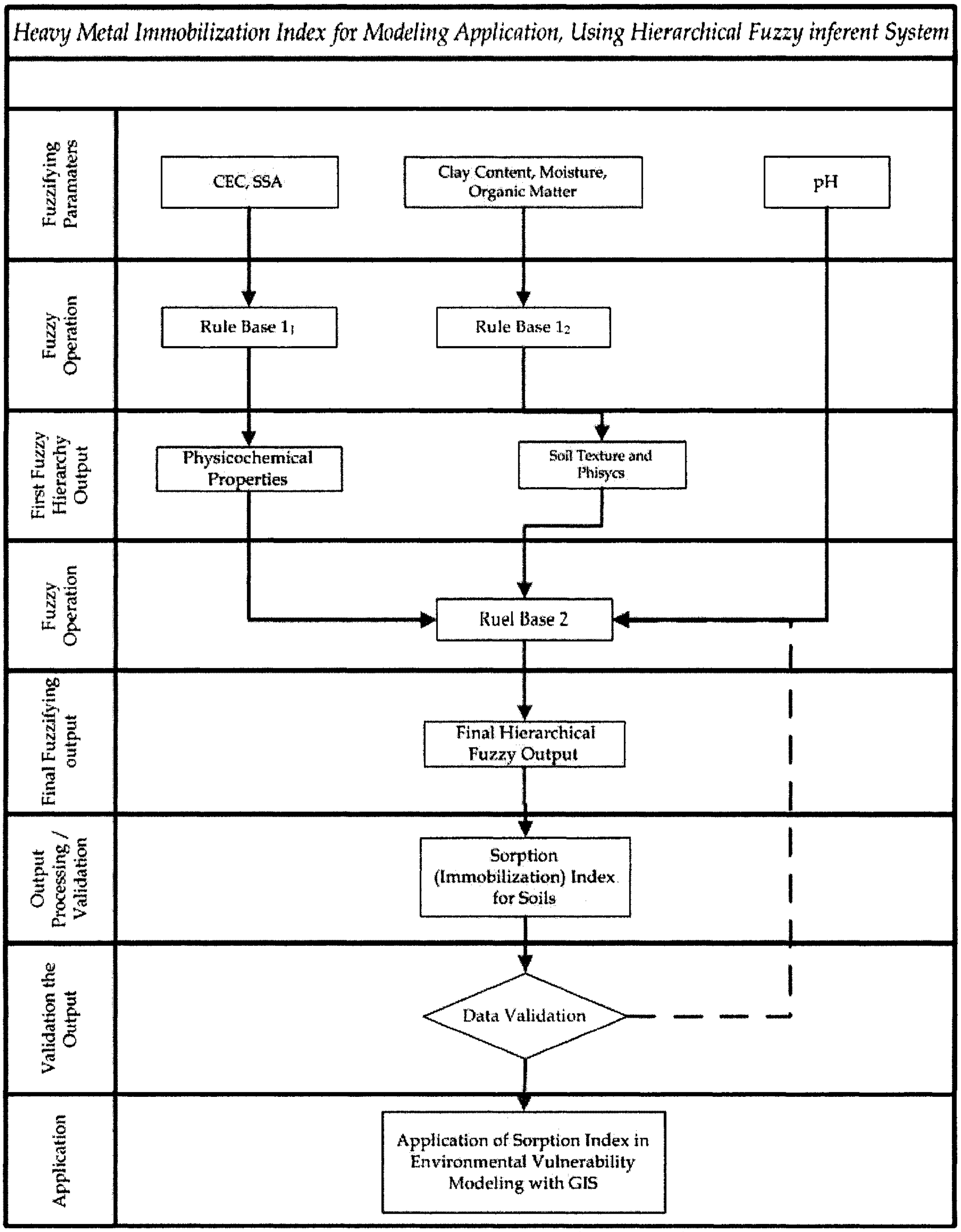

Figure 3-2 Methodology outline for identification of sorption (immobilization) index of soil to heavy metals

The detail of every step of the design of the approach and the reason of assuming the values as well as the analysis is presented in this section. The applied methodology is outlined in Figure 3-2. The important parameters in sorption are categorized in to two fuzzy inference systems which form the first layer of the design. The output of the two first layers fuzzy will act as the input of the final fuzzy inference system which also integrates the pH value. The final put of the fuzzy system will produce the sorption index which after validation it can be applied for decision making projects.

3.3. Fuzzy Membership Design

Adsorption of heavy metal in soil is related the following major soil properties as pH, redox potential, type of clay minerals, soil organic matter and calcium carbonate contenyt (McLean, 1992). Literatures also show that high moisture creates low sorption (Figure 3-3).

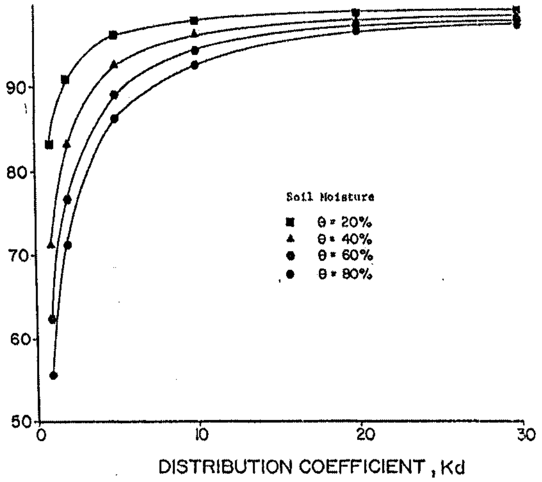

Figure 3-3 extent of sorption as a function of soil moisture θ and k_d (Elektorowicz, 2004)

Based on these, some factors that require laboratory experiment was ignored and those data which are predictable by region or soil type were selected in the study; therefore, the parameters selected for the model were limited to cation exchange capacity, specific surface area, moisture, soil organic matter, clay content and pH. All parameters were fuzzified based on expert knowledge, literature, and available tables.

3.3.1. Cation Exchange Capacity

Based on the data available from the literature (Section 2.1.5.3) and the common linguistic parameter being used for the high cation exchange capacity, the membership function for CEC was introduced. Coarse soils generally because of being primary minerals and having low exchange capacity show low CEC. According to the literature the Low CEC range for coarse sand is between 5 to 15 meq/100g. Silts are also considered to have low CEC and they have the CEC within the range of 8 to 30 meq/100g (Lines-Kelly, 1993).

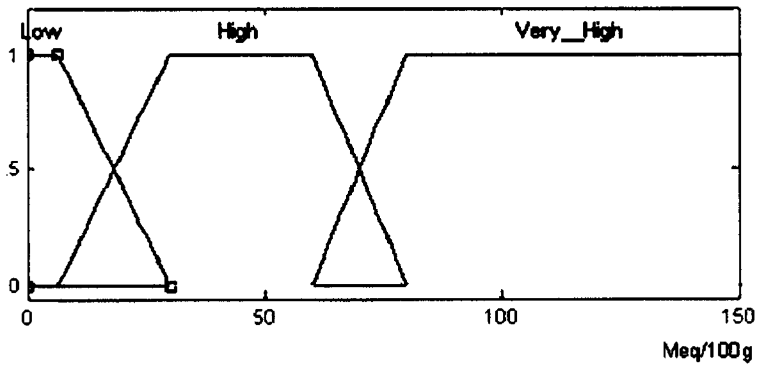

Figure 3-4 Fuzzy membership function for CEC

Clayey soils are being considered as having high to very high CEC soil. Based on structure and their formation clays show different behavior and therefore different CEC

(Table 2-4, Table 2-5) which the range is from 10 to 150 meq/100g (Lines-Kelly, 1993). Based on the above data the fuzzy membership functions for CEC were introduced as Figure 3-4.

3.3.2. Specific Surface Area

Specific surface area (SSA) as explained in the literature review (Section 2.1.5.4) is one of the influential factors on sorption. Specific surface area membership function has two roles in our design. In one hand it specifies its direct role to sorption phenomena and in the other hand covers the lack of information from texture triangle (Figure 2-4). As it can be seen in the Figure 3-6, only the ranges of clay can be extracted. Where, there are different combinations of soil with the same range of clay.

Table 3-1 Interpretation of the SSA data into linguistic value

	Loamy Sand	Silty Loam	Clay	Kaolinite	Illites	Montmorilinite
SSA m^2/g	10-40	50-100	150-250	5-39	65-200	600-800
Membeship	Low	Average	High	Low to Average	Average to High	High

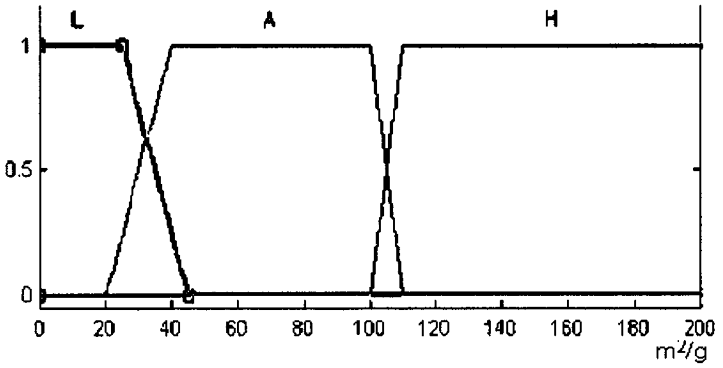

Figure 3-5 SSA fuzzy membership function (L: Low, A: Average, H: High)

For instance, sandy clay loam, clay loam and silt clay loam almost have the same range of clay. This problem can be resolved by demonstrating the difference in SSA.

Definition of the considered included ranges is preformed in the literature (Table 2-6, Figure 3-5).

3.3.3. Clay Content

Clay content of the soil is one of most important factor in heavy metal adsorption. Clay minerals increase the sorption potential of the soil. According to literature, in area with high percentage of clay accompanying with organic and carbonate content, maximum attenuation is expected (Zuhairi, 2003). Introducing the membership function for clay content was based on the percentage of clay in the triangle of soil texture (Figure 2-4, Table 3-2).

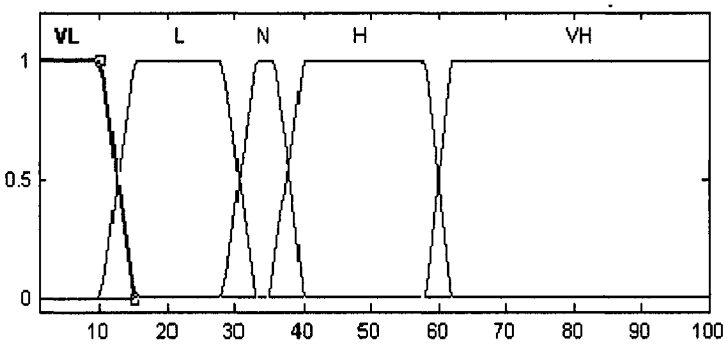

Figure 3-6 Fuzzy membership function for soil clay content, value are in % (VL=Very Low, L=Low, N=Normal, H=High, VH=Very High)

Table 3-2 Sample interpretation of soil textural classes into linguistically intorduced membership functions

Soil type	Clay content	Linguistic value
Clay	40 - 100	high to very high
Clay loam	28 - 40	Low to normal
Loam	8 – 28	Very low to low
Sandy loam	0 – 20	Very low to low
Silty clay	40 – 60	High

The reason for using these intervals was to create a link between the topsoil map legends and expert interpretation of the rules. In this case the interpretation of the texture of the topsoil maps will be more accurate.

3.3.4. Organic Matter

Organic matters are one of the key elements of sorption (Section 2.1.5.2). The existence of organic matter increases buffering capacity, soil water and cation exchange capacity which all result to more sorption of metals. However, use of literature or laboratory data that do not include the presence of complexing ligands may lead to significant overestimation or underestimation of metal mobility (McLean, 1992). Characteristic of OM and its effect was presented in the literature review.

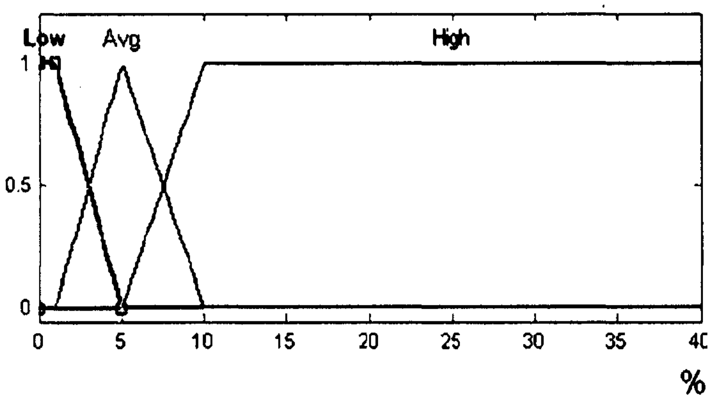

Figure 3-7 Soil organic compound membership functions

For defining the membership function to the input model, Low considered for less than 5% of organic matter, Avg. from 2-10% of organic matter, and peat and more than 10% organic matter from total percentage of soil matrix was considered to be presented by High membership function.

3.3.5. Moisture

Moisture directly affects the sorption process in soils. The high moisture, in the soil causes more movement of metal ions and contaminants in it. The real relation of moisture and sorption is not known but based on literature (Figure 3-8), it was considered to show a linear behavior.

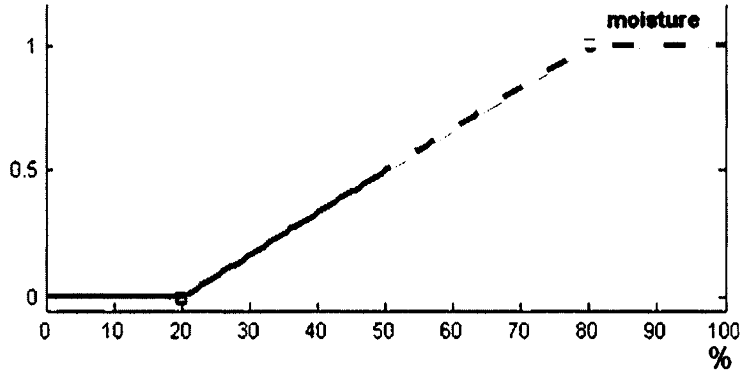

Figure 3-8 Moisture fuzzy membership function.

3.3.6. pH

pH can be considered as the most dominant parameter in sorption phenomena (Section2.1.5.5). In the low pH heavy metals can easily move through the soil layers. In general with increase of pH the mobility of heavy metals will be reduced. However, the reaction of different heavy metals in different pHs are different.

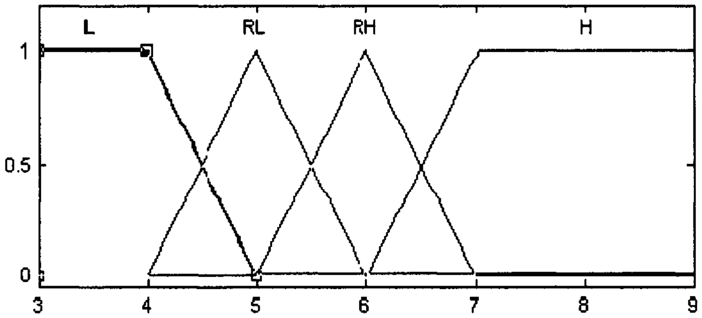

Figure 3-9 Membership functions for pH
(L=Low, RL=Relatively Low, RH=Relatively High, H=High)

Based on the literature and experiments (Young et al., 1992) the limits of the pH membership fuzzy were introduced as in Figure 3-9. The intervals for each membership function were selected based on expert knowledge and literature.

3.4. Hierarchical Selection of Membership Functions

Parameters involved in the surface sorption phenomenon as discussed are CEC (Cation Exchange Capacity), SSA (Specific Surface Area), clay content, organic matter, moisture and pH. All input variable contain from 2 to 5 membership function; therefore, the combination of the possible rules to be introduced will be 3 x 3 x 5 x 3 x 2 x 4 =1080 where introducing rules for this number of possibilities is almost impossible. In order to produce the rules there are two possible choices either reduction of the number of membership functions that will result less accuracy in output or by breaking down a single large fuzzy system to smaller fuzzy system and combining the result in another fuzzy system. The first choice (reduction of fuzzy membership functions) was not applied because there is already uncertainties in defining the membership function and more simplification will add the uncertainty. For that reason, the second choice was applied through Hierarchical Inference Fuzzy System (HIFS).

For designing the model, the parameters were categorized into two major categories; soil CEC-SSA index and Soil Texture Properties. The CEC-SSA index contains membership function of CEC and SSA and Soil Texture includes moisture, clay content and organic content. The output of these two fuzzy sets will be integrated in another fuzzy system with pH parameter; this will form the final fuzzy inference system.

3.5. Soil Texture Fuzzy Membership Function

The related parameters to Soil Texture were selected to be processed in Soil Texture Fuzzy System (STF). The result of these fuzzy systems will integrate all the parameters to perform the score for the best soil for sorption (immobilization).

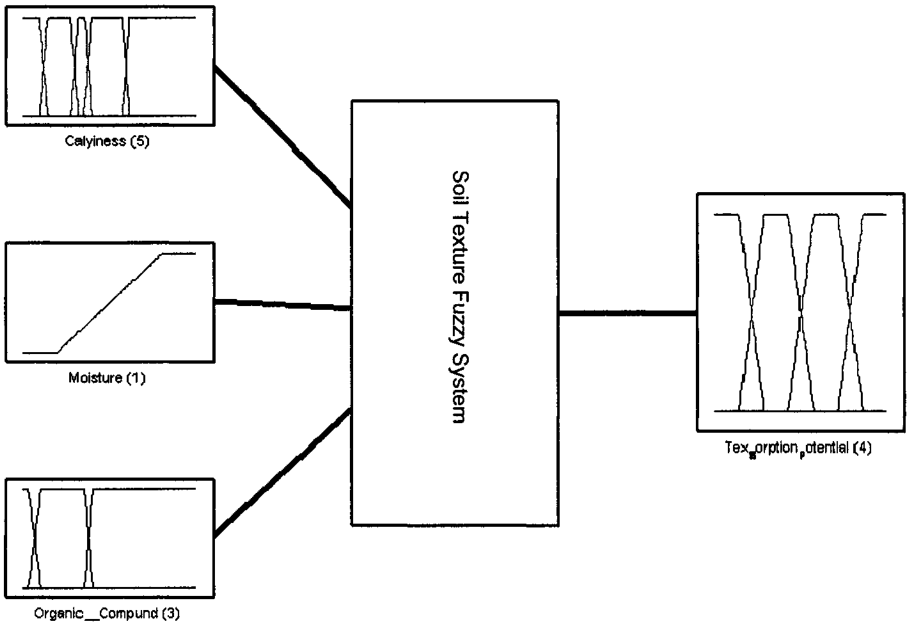

Figure 3-10 Structure of FIS (Fuzzy Inference System) for sorption potential considering texture and moisture of soil

3.5.1. Output

The output membership function will be Texture Sorption Potential (TSP). The linguistics of the output is Low, Relatively Low, Relatively High, and High properties for sorption. Considering the input membership functions introduced earlier, the rule based can be introduced.

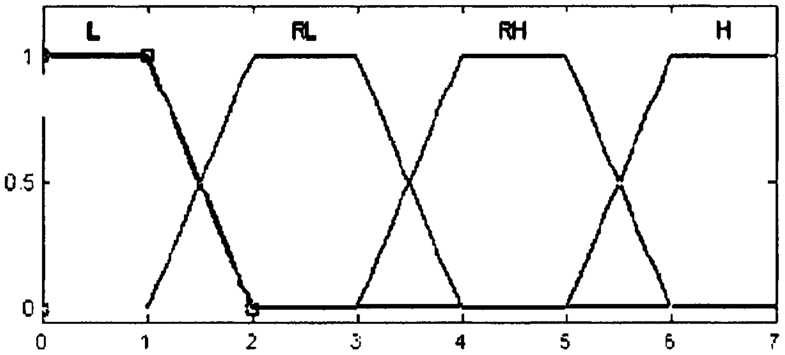

Figure 3-11 Output variable for texture
(L=Low, RL=Relatively Low, RH=Relatively High, H=High)

3.5.2. Rule based

Totally 30 rules based (Table 3-3) are possible to define for this fuzzy system developed above. Some general rules that are known from literature indicates if the clay content of the soil is very low and low (soil is categorized as sandy or silty, silty sand or sandy silt), the sorption potential would be low and in the other hand, if the organic compound and clay content of the soil be high the sorption potential of the soil will be high. Based on the literature and expert knowledge rules were introduced (Table 3-3).

Table 3-3 Fuzzy texture module rule base

	Moisture	Organic Compound	Clay	Output (O1)
1	High	Low	VL	L
2			L	L
3			N	L
4			H	RL
5			VH	RH
6		Average	VL	L
7			L	L
8			N	RL
9			H	RL
10			VH	RH
11		High	VL	RL
12			L	RH
13			N	RH
14			H	H
15			VH	H
16	Low	Low	VL	L
17			L	L

	Moisture	Organic Compound	Clay	Output (O1)
18			N	RL
19			H	RH
20			VH	H
21		Average	VL	RL
22			L	RH
23			N	RH
24			H	H
25			VH	H
26		High	VL	RH
27			L	RH
28			N	H
29			H	H
30			VH	H

L : Low VL: Very Low H: High VH: Very High N: Normal

3.6. Particle Properties Membership Function

From other remaining variables CEC and SSA are both related to soil particles. Integration of both characteristics as it has been reviewed in section 2.1.5 has a huge impact on sorption process.

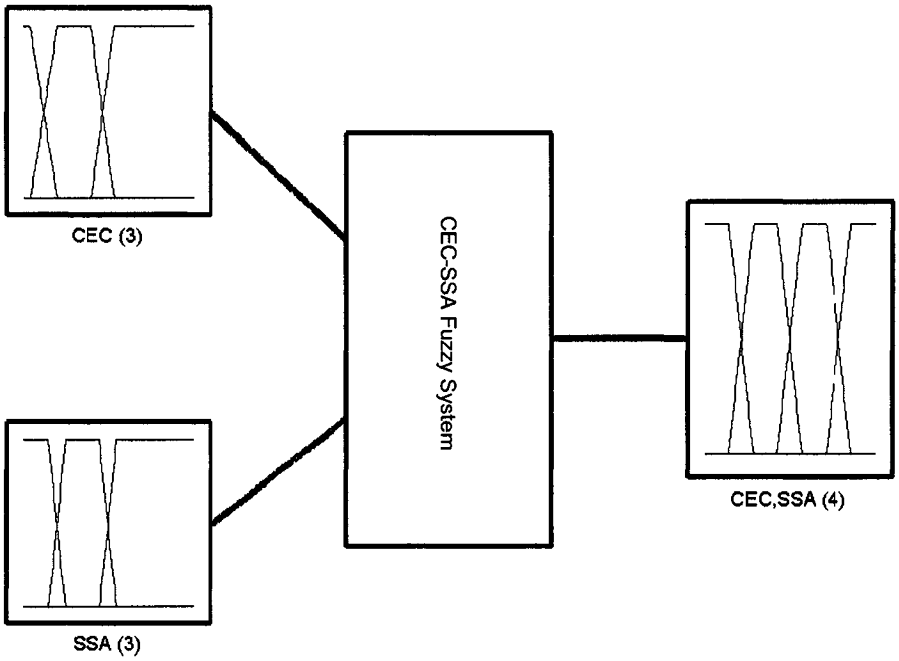

Figure 3-12 FIS model for sorption potential considering CEC and SSA. (#)=indicate the membership function of each input

Introduction of the CEC-SSA index is important because in addition to considering the effect of CEC it will distinguish the exact type of soil texture or clay mineral type (illite, montmorilonite, smectite). In this regard, they will be integrated in the FIS (Fuzzy Inference System) model for evaluation of the sorption (Figure 3-12).

3.6.1. Rule based

Each variable has three memberships function which results into 9 possible rules. Low SSA belongs to large particle size soil such as sand, gravel and sandy silt where, CEC is different in even clay mineral soils (Section 2.1.5.3).

Table 3-4 Rule based design for CEC-SSA index FIS (layer 1)

SSA	CEC	Output
Low	L	L
	High	RL
	Very High	RH
Average	L	RL
	High	RH
	Very High	H
High	L	RL
	High	RH
	Very High	H

Based on literatures and expert knowledge the rule based related to these two parameters developed as is shown in Table 3-4.

3.6.2. Output

The output is the same as the output designed for soil texture (Figure 3-13); it has four membership functions (Low, Relatively Low, Relatively High and High). The result of this function will introduce the soil with the best possible CEC-SSA index.

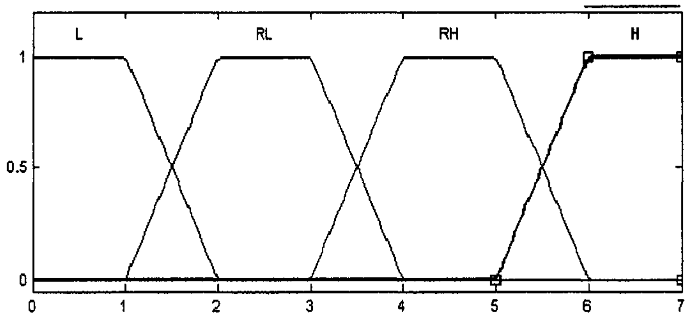

Figure 3-13 Output of the CEC-SSA index
(L=Low, RL=Relatively Low, RH=Relatively High, H=High)

3.7. Fuzzy Inference System Design for Layer 2

The second layer integrates the two output of the first layer (Figure 3-11,Figure 3-13) related to CEC-SSA and Texture properties. In addition to pH, the output of the first layer FIS after normalization will be used as the input of the second layer of FIS. In the second FIS layer, all first layer output (CEC-SSA index and Texture Index) and new parameter of pH are considered for the second layer rule base design.

3.7.1. Rule based for FIS (Layer 2)

In this step based on the expert knowledge and the literature, the rule is introduced as indicated in Table 3-5. As it can be observed from the matrix (Table 3-5), in low pH the sorption considered to be the minimum because of the dominant role of pH in sorption.

Table 3-5 Fuzzy associative matrix for final layer

Soil Text.	L				RL				RH				H			
CEC-SSA pH	L	RL	RH	H	L	RL	RH	H	L	RL	RH	H	L	RL	RH	H
H	VL	L	L	L	VL	L	H	H	H	H	VH	V	H	H	V	VH
RH	VL	L	L	L	VL	L	H	H	L	H	VH	V	H	H	V	VH
RL	VL	VL	VL	VL	VL	VL	L	L	L	L	L	L	L	L	L	L
L	VL	VL	VL	VL	VL	VL	VL	VL	VL	VL	VL	VL	VL	VL	VL	L

3.8. How to use the developed fuzzy tool

For developing the tool, MATLAB Fuzzy toolbox was used. After defining the membership function and the rules for each one of the three fuzzy systems, developed tool can be used as follows:

- For Texture index:

1-Estimate or collect the value of each of the three parameter (Moisture, Clay content and Organic compound).

2-Insert the values and collect the output

3-Normalize the output to a value between 0 and 1 to find a Texture index.

- For CEC-SSA index:

4- Estimate or collect the value of each of the two parameters; CEC and SSA

5- Insert the values and collect the output

6- Normalize the output to a value between 0 and 1 to find a CEC-SSA index.

- For Sorption index:

7- Collect the generated value of each of the two parameters of CEC-SSA index, Texture index and estimate the value of pH.

8- Insert the values and collect the output

9- Normalize the output to a value between 0 and 100.

The final results shows the sorption index of the soil, which can be used in different application.

The necessity to develop an applicable technique for predicting the immobility of heavy metals in soil resulted in to the presented fuzzy system design. With fuzzy system the integration of vague and imprecise parameter is made possible. Because of having many parameters involved in the mobility of heavy metals in soil, hierarchical fuzzy approach was chosen to develop the model with less number of rules. For development of the model and introducing its membership functions, the expert knowledge and literature data were used. Although the design of the hierarchical fuzzy system comply with the principals of the design, still the validity and reliability to the result is not obvious. Thus, in the next chapter the result acquired from some case studies will be discussed and compared to the result of the model.

CHAPTER 4. RESULTS AND DISCUSSIONS

The process of environmental decision making can be portrayed as a series of steps. In this study, the experimental approach followed four major steps. In the first major step, objectives were clarified, and for second step, the key criteria for research goal were studied. In the third step, the possible techniques and designs were analyzed. In the fourth step, technically the model was evaluated for final decision making. This procedure and all other procedures which help guide rational decision making in the real-world environmental issues, are rather simplistic. For example, it is often the case that scientific data are incomplete and sometimes their interpretations are controversial. In such case consequences of an action are very difficult to anticipate, but unintended consequences are even more difficult to predict.

In this section the evaluation of the model will be presented. For the evaluation, the available results from different experiments will be compared to the fuzzy system model and final results will be discussed.

4.1. Case I

Korte et al. (1975) studied eleven trace elements (As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, Zn) into seven represented soil order and different textural class. The objective of the experiment was to find the relative mobility of each trace metal and determining the controlling property of the soil. The analysis of the soil components in this experiment is presented in Table 4-1.

Table 4-1 Result extracted from Korte et al., 1976

Soil	order	pH	CEC $_{meq/100g}$	Surface Area $_{m2/g}$	Free Fe oxides %	Clay%	Texture
Wagram	Ultisol	4.2	2	8.0	0.6	4	Loamy sand
Ava	Alfisol	4.5	19	61.5	4	31	Silty clay loam
Kalkaska	Spodosol	4.7	10	8.9	1.8	5	Sand
Davidson	Ultisol	6.2	9	61.3	17	61	Clay
Molokai	Oxisol	6.2	14	67.3	23	52	Clay silty clay
Chalmers	Mollisol	6.2	26	125.6	3.1	35	Loam
Nicholson	Alfisol	6.7	37	120.5	5.6	49	Silty clay
Fanno	Alfosil	7	33	122.1	3.7	46	Caly
Mohave	Aridisol	7.3	10	38.3	1.7	11	Sandy loam
Mohave $_{ca}$	Aridisol	7.8	12	127.5	2.5	40	Clay loam
Anthony	Entisol	7.8	6	19.8	1.8	15	Sandy loam

The results of the experiment showed the attenuation capacity of heavy metals in different soil type as in Figure 4-1.

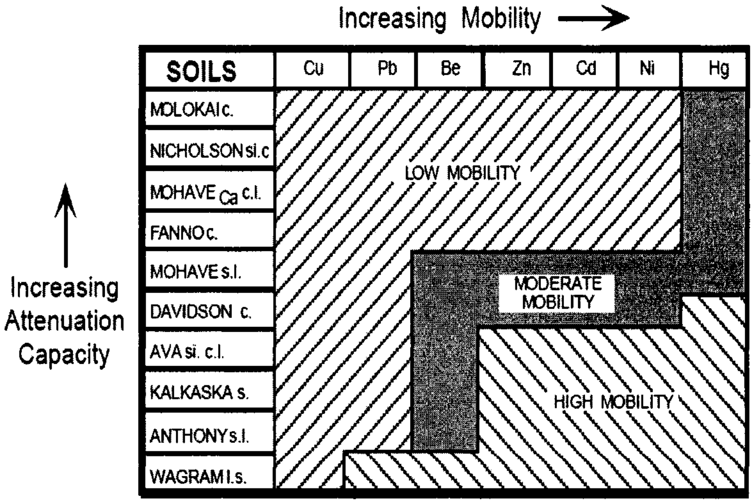

Figure 4-1 Attenuation capacity of different soil (Korte et al., 1976)

Available data of the experimental soils plugged in to the developed hierarchical fuzzy system toolbox. Among available data organic matters measurement was not available. Organic matters as discusses earlier have an effective role in sorption process, therefore the OM content based on the soil formation order and texture was only estimated.

Table 4-2 Result of the model after normalization of Indexes

Soil	Layer order	CEC meq/100g	SSA m2/g	CEC-SSA Index	Clay content %	Texture	OM %	Texture Index	pH	Sorption Index
Nicholson	Alfisol	37	120.5	1	49	Silty clay	H	1	6.7	83.4
Fanno	Alfosil	33	122.1	0.85	46	Caly	A	0.7	7	82.6
Molokai	Oxisol	14	67.3	0.55	52	Clay silty clay	A	0.8	6.2	76.1
Mohave$_{ca}$	Aridisol	12	127.5	0.52	40	Clay loam	L	0.71	7.8	74.1
Davidson	Ultisol	9	61.3	0.48	61	Clay	L	0.92	6.2	65.8
Mohave	Aridisol	10	38.3	0.43	11	Sandy loam	L	Neg.	7.3	40
Ava	Alfisol	19	61.5	0.05	31	Silty-clay loam	H	0.68	4.5	27.3
Kalkaska	Spodosol	10	8.9	Neg.	5	Sand	L	0.06	4.7	16.9
Anthony	Entisol	6	19.8	Neg.	15	Sandy loam	L	0.12	7.8	16.5
Wagram	Ultisol	2	8.0	Neg.	4	Loamy sand	L	Neg.	4.2	16.1

The CEC-SSA index and Texture index are normalized output of the first layer fuzzy inference systems.
Neg.: Negligible

Sorption index can indicate sorption capacity of the soil which it is the inverse to heavy metal mobility into ground. Higher sorption index cause lower mobility of metals in particular soil.

The comparison of the experimental and toolbox generated results indicates the same trend in the order of soil types. Mohave$_{ca}$, Fanno, Molokai, and Nicholson in both experimental and toolbox result show more sorption capacity (attenuation capacity) where Wagram, Kalkaska, and Anthony are at the bottom of the table and show low attenuation capacity. Ava, Mohave, and Davidson are showing intermediate attenuation capacity. Some difference in the order in each category can be explained as:

1- As discussed earlier, the parameters selected for design of the model are those parameters that can be estimated by regional or geological information. There are some other important soil parameters related to sorption which need experimental measurement that were not brought into model such as Mn and Fe oxides. By referring to the original literature it was found that the Molokai soil has extremely high amount of Mn (7400 ppm) and free Fe oxide (23%) which is the source of disorder this soil type.

2- Organic Metter was not measured from the original experiment and the organic matter value plugged in to model was based on definition from the order of soils and subjective. This also has caused disorder among different soil types.

These can justify the difference of attenuation capacity order among the presented soils. Based on above results and discussion, it can be concluded that presented HFIS tool and methodology can be applied to the soil sample in case study I .

4.2. Case II

Result from the experiment on different heavy metals on illite soil shows that the minimum sorption in illite soil is up to pH 4, from pH 4 to pH 6 there is generally increase in sorption in a form that at pH 7 the maximum sorption will be archived.

The results from the developed HFIS tool box indicate almost the same trend of sorption. In pH 3 - 4 sorption is at its minimum and from pH 4 it increases and the maximum sorption happens at in pH 6 and up.

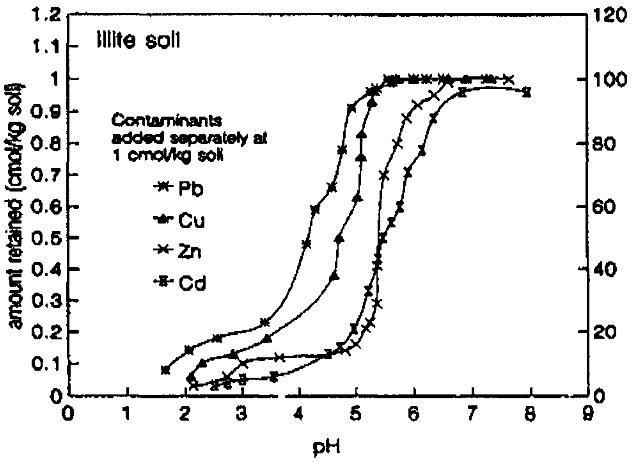

Figure 4-2 The result of attenuation by changes of pH in illite (Yong et al., 1992)

There is a shift in sorption among different heavy metals showed in Figure 4-2, which it can be covered by introducing a heavy metal type factor in to the complete model in future. Since the designed model was focusing on prediction of soil attenuation capacity score based on soil data, the shift was ignored.

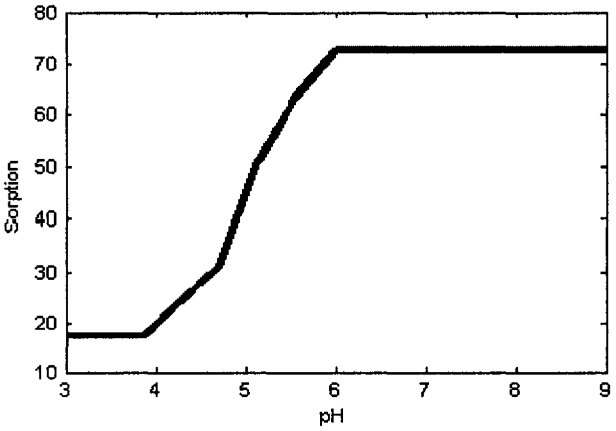

Figure 4-3 pH vs. attenuation capacity from the result model of illite showing the same trend as experiment

The above case study shows that the result of the developed HFIS is comparable to the experiments results and the model is applicable.

4.3. Case III

Zuhairi (2003) published another experiment on sorption of heavy metals in soil. In that experiment 29 soil samples collected from different landfill sites in South Wales, UK. The samples where: mudrock (MR1-MR4), glacial till (GT1-GT5), and estuarine alluvium soils from: Neath (NEA1-NEA5), New-Port (PEA1-PEA5), and Cardiff (CEA1-CEA5). Physical and chemical properties of samples based on the published paper were as presented in Table 4-3.

Table 4-3 Physical and chemical properties of five type of soil samples

Soil	CEC meq/100g	SSA $_{m2/g}$	Clay content %	Moisture %	OM %	pH
MR1	11.89	46.38	21	10	2.32	7.4
GT1	23.92	69.87	30	13	2.77	7.78
NEA4	14.84	73.34	50	30	5.11	7.93
PEA3	39.43	74.97	52	23	3.78	8.72
CEA3	38.5	66.62	57	19.2	3.63	8.62

Data are adopted from a study by Zuhairi, 2003.
CEC: Cation Exchange Capacity, SSA: Specific Surface Area,OM: Organic Matter

Using the data obtained by the experiment into model for each fuzzy inference system, and normalizing the result into the final fuzzy inference system produce the attenuation potential score. The result of the output of the model is presented in Table 4-4.

Table 4-4 Calculation of adsorption score through on the FIS model

Soil	CEC meq/100g	SSA m^2/g	CEC-SSA Index	Normal CEC - SSA	Clay content %	Moisture %	OM %	Texture Index	Normal soil texture	pH	Sorption Index
MR1	11.89	46.38	3.51	0.52	21	10	2.32	2.22	0.26	7.4	51
GT1	23.92	69.87	3.85	0.75	30	13	2.77	3.06	0.419	7.78	67
NEA4	14.84	73.34	3.59	0.57	50	30	5.11	5.5	0.865	7.93	76.4
PEA3	39.43	74.97	4.2	1	52	23	3.78	5.28	0.82	8.72	82.8
CEA3	38.5	66.62	4.2	1	57	19.2	3.63	5.54	0.87	8.62	83.1

CEC: Cation Exchange Capacity, SSA: Specific Surface Area, OM: Organic matters

Comparison of the output model and the experimental data shows high reliability to our designed fuzzy model. In both results the highest value of adsorption is for Cardiff estuarine alluvium. The Newport Estuarine alluvium soil has the second highest adsorption potential. The adsorption potential of CEA3 and PEA3 soil in both experimental results and model output (Table 4-4) are very close to the each other.

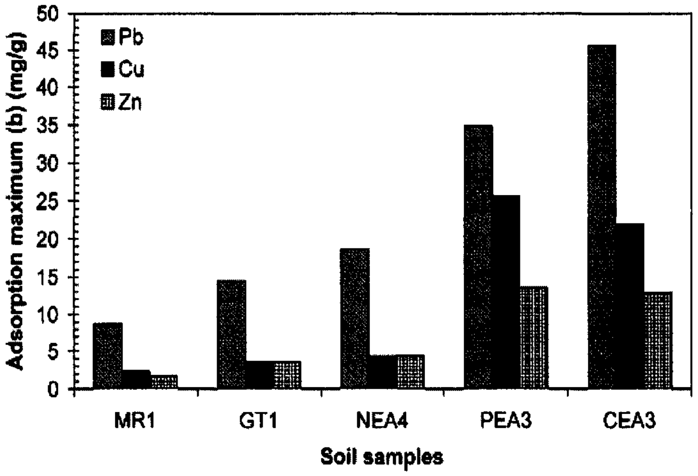

Figure 4-4 Highest adsorption maximum in soil CEA3 compared to other soils (Zuhairi, 2003)

4.4. Case IV

de Matos et al. (2001), performed a research on mobility of heavy metals in the Brazilian soils and published some soil data as in Table 4-5. The information related to moisture was not measured and therefore is not available in the table.

By applying the measured data of Table 4-5 in to the HFIS the score of fore mentioned soils will be calculated as in Table 4-6 .

Table 4-5 Chemical and physical characteristic of soil samples

Soil	CEC meq/100g	SSA m2/g	Clay content %	Moisture %	OM %	pH
U_1-A	4.67	20.1	35	n.a.	5.51	6.02
U_2-A	6.19	22	52	n.a.	5.24	6.26
O_x-A	2.32	26.2	63	n.a.	5.71	4.61

Adopted from de Matos, 2001
OM: Organic Matter, SSA: Specific Surface Area, CEC: Cation Exchange Capacity

Published results of the soil show the ranges of retardation factor (sorption) in these soils. As the outcome of the experiment the model shows relatively same range of data for soil U_1-A and U_2-A.

Table 4-6 Calculated measures of soil samples for de Matos (2001) experimental measurement

Soil	CEC meq/100g	SSA m^2/g	CEC-SSA Index	Normal CEC-SSA	Clay content %	Moisture %	OM %	Texture Index	Normal Texture	pH	Sorption Index
U_1-A	4.67	20.1	2.77	0	35	n.a.	5.51	4.64	0.70	6.02	42.7
U_2-A	6.19	22	2.84	0.05	52	n.a.	5.24	6.24	1	6.26	44
O_x-A	2.32	26.2	2.96	0.13	63	n.a.	5.71	6.24	1	4.61	29.6

The results for retardation factor can not be fully compared to model outcome score. First, there are other parameters which it was not considered in the design of the model and are effective in the real attenuation factor (Sorption Index) calculation. Second, the moisture parameter of the top soil was not available. Even with consideration of these lacks of information, still there is close relation with the order of the soil form the experiment and the toolbox output.

Table 4-7 Retardation factors (R_f) for Zn, Cd, Cu and Pb of soil samples (de Matos et al., 2001)

Soil	Horizon	R_f			
		Zn	Cd	Cu	Pb
U1	A	2.308	3.375	6.445	12.571
	B	1.566	1.841	3.393	6.691
	C	1.727	1.732	2.742	4.933
U2	A	2.398	3.151	5.676	11.264
	B	0.932	1.146	2.287	4.830
	C	1.272	1.410	2.792	5.032
Ox	A	0.902	1.226	3.238	5.901
	B	1.347	1.466	3.880	6.413
	C	1.244	1.106	1.781	3.750

As it was previously mentioned since we are looking for scoring different soil type based on their characteristics, the result are satisfactory and acceptable; therefore, the HFIS model is applicable.

4.5. Case V

By analyzing the surfaces created by the membership functions and rule bases introduced in the model, the behavior of each FIS function can be viewed. Figure 4-5 to Figure 4-7 show the some surfaces created by the membership function. No anomaly was observed neither in the analysis in the first layer FIS nor in second layer of the Fuzzy system. Figure 4-5, shows the SSA and CEC in forming of the CEC-SSA index. As it can be observed by increase in SSA and CEC the CEC-SSA index will be higher, where in low SSA and CEC the index has generated a lower value.

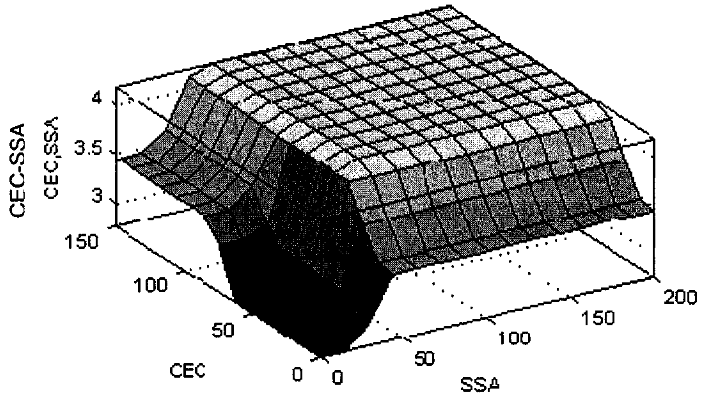

Figure 4-5 Sorption potential by physical parameters considering CEC and SSA

The texture index is consisted of three parameters of clay content, organic matters and moisture. Figure 4-6 shows how with a fixed moisture, increase of organic matter and clay content generate the higher value in texture index.

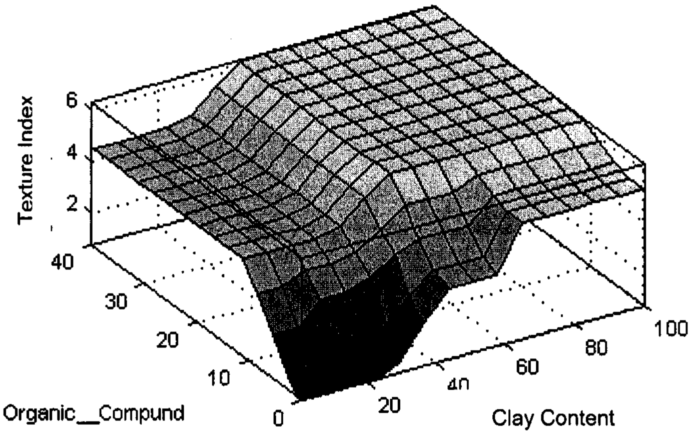

Figure 4-6 Texture suitability for sorption by clay content and organic compound

The second layer of the FIS works with the texture index, CEC-SSA index and pH. Figure 4-7 to Figure 4-9, demonstrates the relation of pH, Texture index and CEC-SSA index to the final sorption score. The red color show low sorption and more mobility to heavy metals.

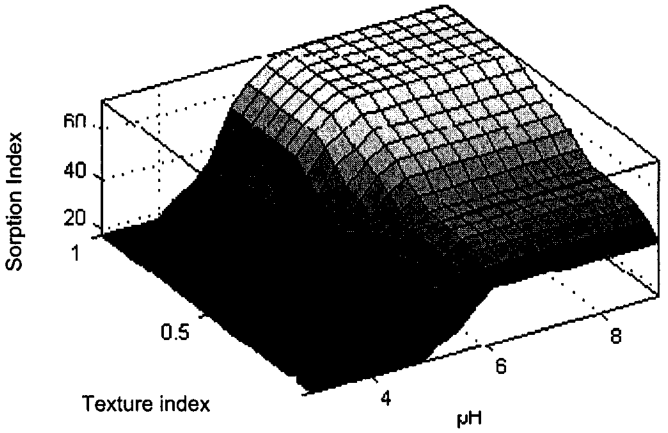

Figure 4-7 Sorption potential by pH vs. texture with CEC-SSA index of 0.5

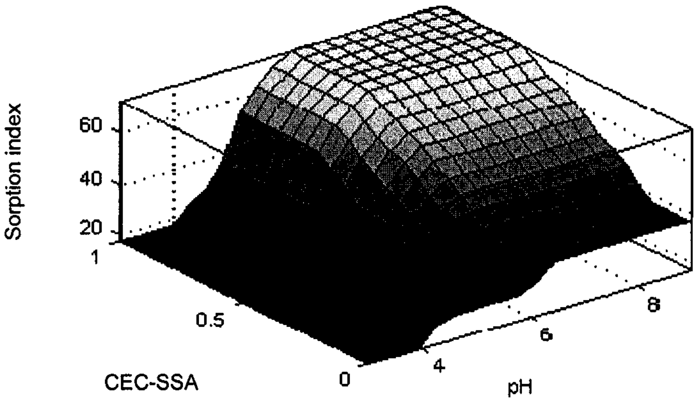

Figure 4-8 Sorption potential by pH vs. CEC-SSA index with texture index of 0.5

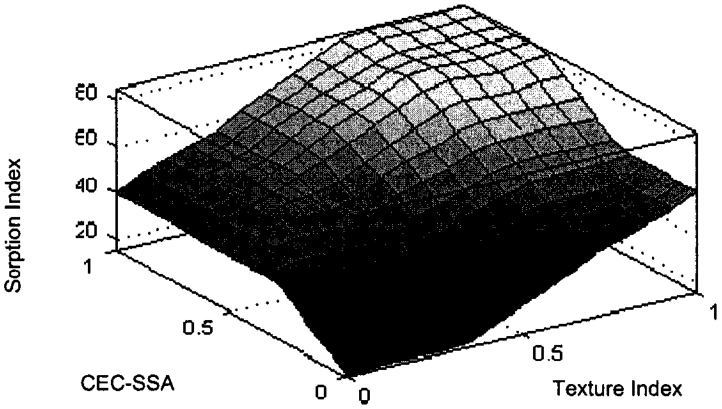

Figure 4-9 HM immobilization behavior based on texture index & CEC-SSA index at pH 6

Design of a fuzzy inference system is completely dependant on the accuracy of the design and experience of the expert designer. Based on selection of the membership function and defining the rule bases, the model will generate acceptable or unacceptable results. Thus, accessing the accuracy and reliability of the output was essential. According to the cases introduced in this chapter the designed fuzzy inference system considering all the limitations was successfully evaluated; therefore, the developed HFIS can be employed in applications. Next chapter demonstrate the application of the introduced model and HFIS toolbox with integration of GIS for soil vulnerability mapping in the Island of Montreal.

CHAPTER 5. APPLICATION OF DEVELOPED METHOD OF "HFIS" INTO GIS

Exposure assessment and analysis is not a new concept. Obtaining quantitative measures of exposure and establishing their relation to a biological effect are more complicated tasks. During the past two decades scientists and engineers in different fields have estimated exposure assessment because many cases require a multidisciplinary team to address the technical and scientific problems accurately. Correct assessment of human exposure to contaminants is a rapidly developing research area. Methodological approaches, technical skills and instruments that will aid in estimating exposure to pollutants are still being developed and if developed they are not being used widely. A large database is required to measure and analyze the population exposure and the associated risk factors. In this regard a simple application of the introduced technique considering the soil sorption and possible population exposure to heavy metals for cancer incidences in Montreal Island was studied.

5.1. Preparation of the Topsoil Map

One of the most important applications of introduced technique is its usage in heavy metal immobility mapping in soil. Since in environmental management the decision makers or legislators deal with large scale areas (national or provincial), access to experimental data and measurement is not easily possible. Hence, finding an applicable tool with low level of approximation for such data is very essential. Usually in absence of the measured data the only accessible information is linguistically interpretation of the data, such as high pH, low CEC, average SSA, etc.; therefore, finding a tool to digest, analyze and interpret the linguistic and measured variables of different areas is an important task. In this chapter a demonstration on how to employ the fuzzy system model for soil classification and soil immobility to heavy metal in GIS is demonstrated. Montreal area was selected to show this application. Based on the published topsoil map, the Montreal Island contains 12 different soil types. In order to rank the soil vulnerable area using GIS the following steps were undertaken. Firstly, the printed topsoil map was converted to a raster digital format through scanning (Figure 5-1). After scanning the digital map prepared for insertion into ARCGIS® 9.0, the image was processed with Photoshop®. The raster data, imported (Table 5-2) and geo-referenced in ARCGIS® 9.0. Since the imported raster image in to ARCGIS obtained through scanning and processing, the value of the cells was various. In the next step, the inserted raster image was classified in to 12 different categories, representing any individual soil type as mentioned in the legend of the original map. The only information was the legend of the topsoil map, and our general knowledge related to geo-environmental characteristics of the soil and sorption phenomena. Based on these two facts, a layer was created for use among other numerical layers. Three different viewpoints: of i) optimistic, ii) pessimistic, and iii) average are considered for interpretation of the topsoil map into a numerical informative map.

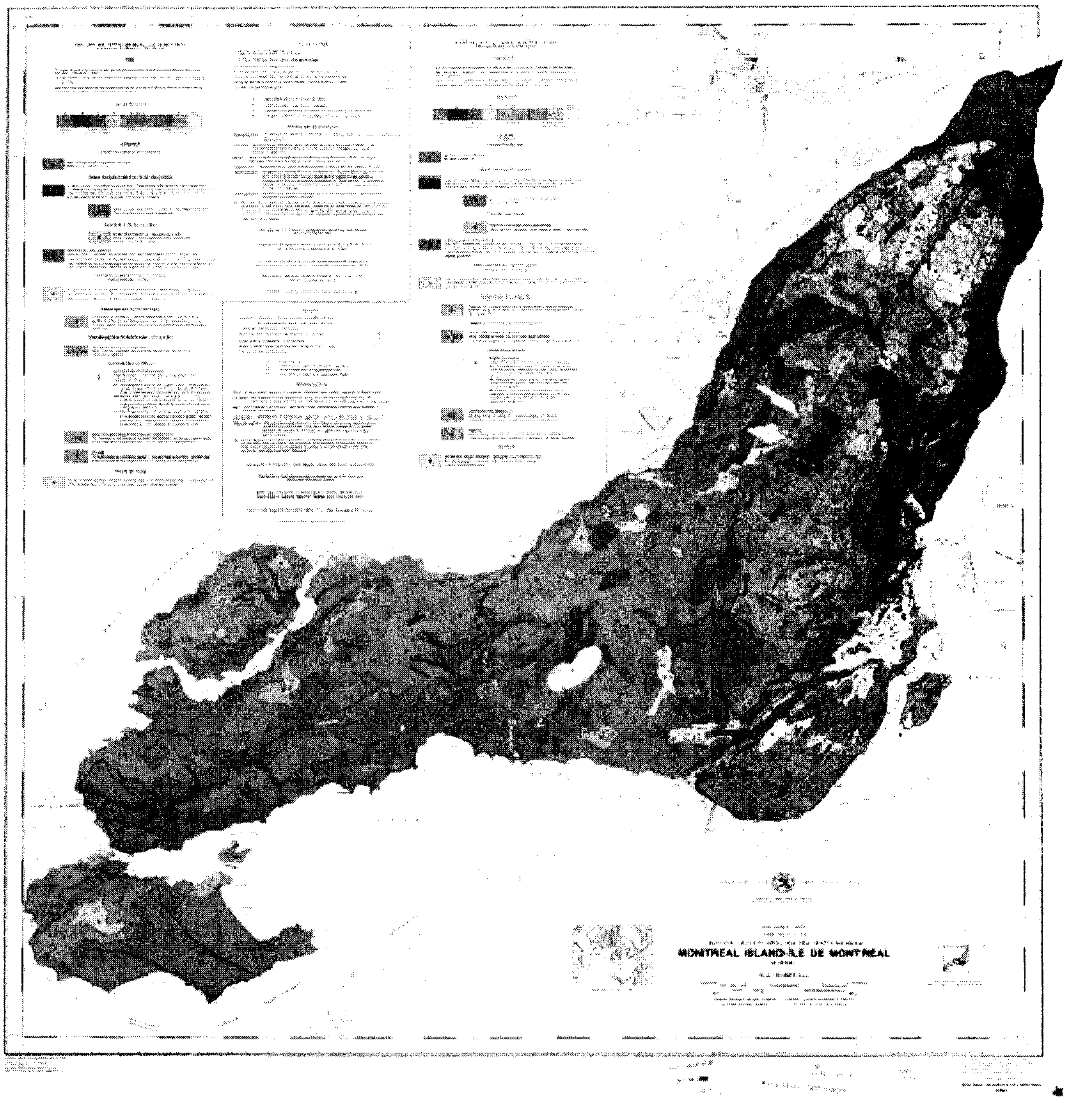

Figure 5-1 Raster image of the topsoil map of Montreal Island

This means three different data forming membership functions can be assigned to any specific area for any known characteristic. The assigned data was plugged into the designed fuzzy system. The results of fuzzy system are presented in Table 5-1 to Table 5-5.

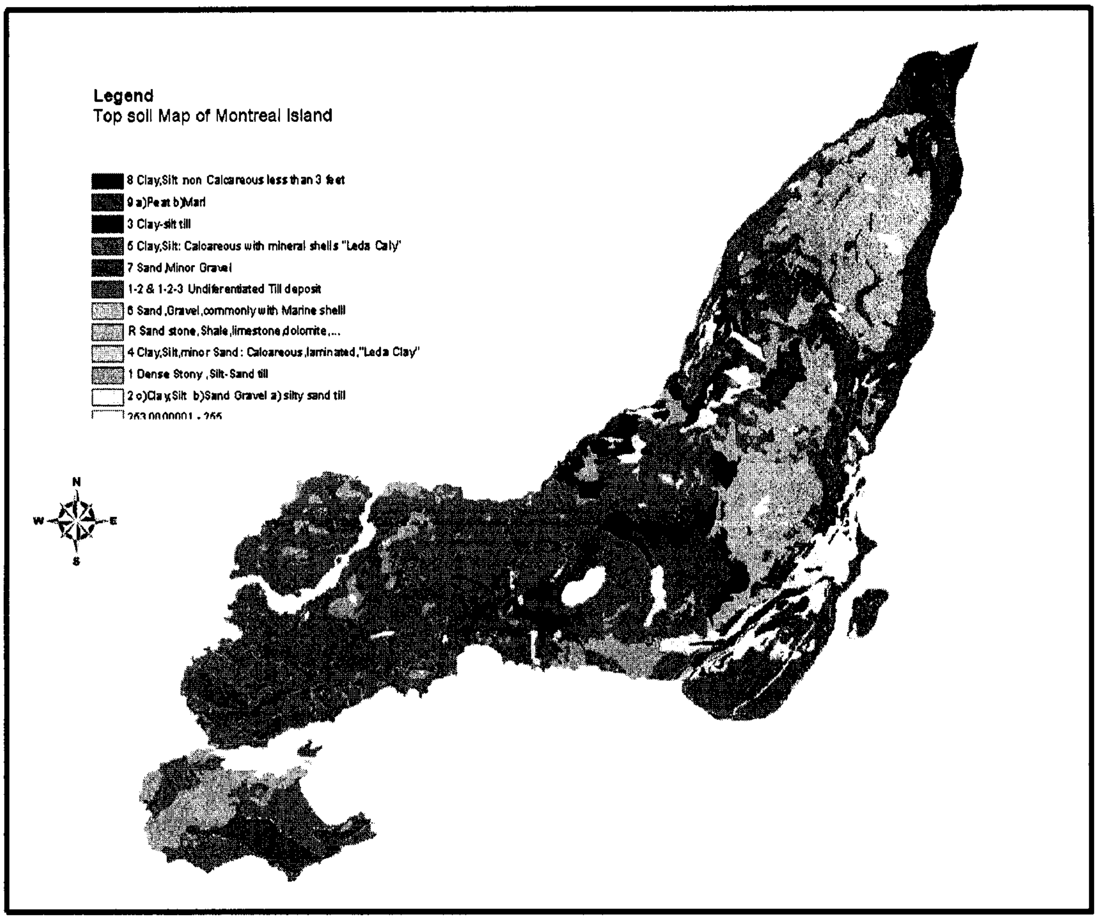

Figure 5-2 Topsoil map of Montreal island

5.2. Assigning the Parameters (Soil HM Immobility classification using HFIS)

5.2.1. Soil Texture Index (Clay Content, Organic Matter, Moisture)

The ranges of the clay content were identified from the Figure 2-4 and according to that the representative membership functions of the fuzzy inference system was identified. As in Sections 2.1.5.4 & 2.1.5.1 indicated, the distinction of different soil types having the same range of clay content is possible when SSA is introduced. The results considering clay content are presented in Table 5-1 for three different viewpoints: pessimistic, optimistic and average.

Till is an unsorted glacial sediment. Glacial drift is a general term for the coarsely graded and extremely heterogeneous sediments of glacial origin. Glacial till is that part of glacial drift, which was deposited directly by the glacier. It may vary from clays to mixtures of clay, sand, gravel and boulders (till, n.d.). According to definition, there will be very low organic matter in till. This assumption is also supported in the literature (Lin, 1999). Peat is extremely high in OM. The assumed membership functions and values are indicated in Table 5-1. In addition, for the layers that cover over peat, average OM selected for the analysis.

The value for moisture was considered 20% (minimum) except Leda Clay or Quick clay. Quick clay is a unique form of highly sensitive clay, with the tendency to change from a relatively stiff condition to a liquid mass when it is disturbed. Undisturbed quick clay resembles a water-saturated gel. When a block of quick clay is held in the hand and struck, it instantly turns into flowing ooze, a process known as spontaneous liquefaction. Quick clay behaves this way because, although it is solid, it has very high water content, up to 80%. The clay retains a solid structure despite the high water content, because surface tension holds water-coated flakes of clay together in a delicate structure. When the structure is broken by a shock, it reverts to a fluid state.

Quick clay is only found in the northern countries such as Russia, Canada, Alaska, Norway, Sweden, and Finland, which were glaciated during the Pleistocene era.

(Geoscape Ottawa - Gatineau landslides, 2005). The moisture value for the area with quick clay was considered as 40%.

5.2.2. CEC-SSA Index

CEC was selected based on the fact that, clay has high cation exchange capacity and sand and gravel has low CEC (Section 2.1.5.3). Since the exact percentage of clay silt in the area is not known, three different mindsets represent almost all possible combinations of soils. Specific surface area is also very important in sorption and illite is the major component of clay soil in Montreal Island.

5.2.3. Soil pH

Most soils in Quebec tend to be acidic (Section 2.1.5.5). However, there are alkaline soils in some parts of the Island of Montreal, Laval and nearby. Acidity of the soil is based on analysis of soil samples (Fertilizing, 2004). In addition, non-calcareous soil usually has pH<7.0 and calcareous soil has pH>7.0.

Table 5-1 Value estimation for Texture Index

Soil Type	Clay Content	Op Val.	Avg. Val.	Pes. Val.	OM	Op Val.	Av. Val.	Pes. Val.	Moist. %	Op. Score	Avg. Score	Pes. Score
R *) Sandstone, Shale, limestone, dolomite	VL	12	8	5	Low	3	2	1	20	2.31	1.29	0.76
1) Dense stony, silt, silt-till: commonly bouldery	VL	12	8	5	Low	3	2	1	20	2.31	1.29	0.76
1-2) Variability stony, silt-sand till	VL	12	8	5	Low	3	2	1	20	2.31	1.29	0.76
2) c-galciolacustrine – clay, silt : generally overlies 2b and 2a b-glaciofluvial - sand, gravel a-glacial-silt sand till: in places boulddery ;commonly substratified; occurs interbedded with and as lenses instratified sediments 2b and 2c	H	60	50	38	Low	3	2	1	20	5.71	4.85	3.59
3) Clay-silt till: locally sandy and/or stony where directly overlaying gravels, stony till or bedrock	H	60	50	38	Low	3	2	1	40	4.72	3.92	2.95
4) Clay, silt, minor sand calcareous, laminated slightly contorted, light grey; contains considerable pollen; mapped only in Cote St-Luc, where it is commonly overlain by a thin mantle of marine clay	H	60	50	38	Low	3	2	1	40	4.72	3.92	2.95
5) Clay, silt; Calcareous; locally with marine shells- “Leda Clay”	H	60	50	38	Low	3	2	1	40	4.72	3.92	2.95
6) Sand, gravel: commonly with marine shells- “ Saxicava Sand”	VL	12	8	5	Low	3	2	1	40	2.31	1.29	0.76
7) Sand,minor gravel: rare fresh-water shells,	VL	12	8	5	Low	3	2	1	20	2.31	1.29	0.76
8) Clay, silt : non calcareous; (includes sand, silt, minor clay which overlies peat	H	60	50	38	Avg.	8	5	3	40	5.53	4.76	3.45
9) a-Peat muck, sapropel b-marl, pond clay	VL	12	8	5	High	40	20	8	50	4.5	4.5	3.23

VL: Very Low Avg.: Average Pes.: pessimistic Op.: Optimistic Val.: Value H: High OM: Organic Matter Moist: Moisture

* = The number before the parenthesis was referred in the topsoil Fig. 5-1 legend.

Table 5-2 Value estimation for CEC-SSA index

Soil Type	CEC	Op Val.	Avg Val.	Pes. Val.	SSA	Op Val.	Avg. Val.	Pes. Val.	Op Score	Ave. Score	Pes. Score
R *) Sandstone, Shale, limestone, dolomite	Low	22.5	10	5	Low	25	17	10	2.95	2.76	2.76
1) Dense stony, silt, silt-till: commonly bouldery	Low	22.5	10	5	Low	25	17	10	2.95	2.76	2.76
1-2) Variability stony, silt-sand till	Low	22.5	10	5	Avg.	105	70	25	3.46	3.46	2.95
2) c-galciolacustrine – clay, silt : generally overlies 2b and 2a b-glaciofluvial - sand, gravel a-glacial-silt sand till: in places boulddery ;commonly substratified; occurs interbedded with and as lenses instratified sediments 2b and 2c	High	72.5	50	22.5	High	200	150	105	4.2	4.2	3.46
3) Clay-silt till: locally sandy and/or stony where directly overlaying gravels, stony till or bedrock	High	72.5	50	22.5	Avg.	105	70	25	4.2	4.2	2.95
4) Clay, silt, minor sand calcareous, laminated slightly contorted, light grey; contains considerable pollen; mapped only in Cote St-Luc, where it is commonly overlain by a thin mantle of marine clay	High	72.5	50	22.5	Avg.	105	70	25	4.2	4.2	2.95
5) Clay, silt; Calcareous; locally with marine shells-"Leda Clay"	High	72.5	50	22.5	High	200	150	105	4.2	4.2	3.46
6) Sand, gravel: commonly with marine shells- " Saxicava Sand"	Low	22.5	10	5	Low	25	17	10	2.95	2.76	2.76
7) Sand,minor gravel: rare fresh-water shells,	Low	22.5	10	5	Low	25	17	10	2.95	2.76	2.76
8) Clay, silt : non calcareous; (includes sand, silt, minor clay which overlies peat	High	72.5	50	22.5	Low	25	17	10	3.13	2.76	2.76
9) a-Peat muck, sapropel b-marl, pond clay	Very High	150	100	72.5	Low	25	17	10	3.46	3.46	3.13

VL: Very Low Avg.: Average Pes.: pessimistic Op.: Optimistic Val.: Value H: High OM: Organic Matter Moist: Moisture

* = The number before the parenthesis was referred in the topsoil Fig. 5-1 legend.

Table 5-3 Sorption potential score, with optimistic point of view

Soil Type	CEC-SSA Index	Text. Index	pH	Sorption Index
R*) Sandstone, Shale, limestone, dolomite	0.13	0.28	6.5	26.1
1) Dense stony, silt, silt-till: commonly bouldery	0.13	0.28	6.5	26.1
1-2) Variability stony, silt-sand till	0.48	0.28	6.5	47.5
2) c-galciolacustrine – clay, silt : generally overlies 2b and 2a b-glaciofluvial - sand, gravel a-glacial-silt sand till: in places boulddery ;commonly substratified; occurs interbedded with and as lenses instratified sediments 2b and 2c	1	0.9	6.5	82.6
3) Clay-silt till: locally sandy and/or stony where directly overlaying gravels, stony till or bedrock	1	0.72	6.5	82.6
4) Clay, silt, minor sand calcareous, laminated slightly contorted, light grey; contains considerable pollen; mapped only in Cote St-Luc, where it is commonly overlain by a thin mantle of marine clay	1	0.72	8	82.6
5) Clay, silt; Calcareous; locally with marine shells-"Leda Clay"	1	0.72	8	84.1
6) Sand, gravel: commonly with marine shells- " Saxicava Sand"	0.13	0.28	5.5	84.1
7) Sand, minor gravel: rare fresh-water shells,	0.13	0.28	5.5	26.1
8) Clay, silt : non calcareous; (includes sand, silt, minor clay which overlies peat	0.25	0.87	5.5	26.1
9) a-Peat muck, sapropel b-marl, pond clay	0.48	0.68		50

Text.: Texture * = The number before the parenthesis was referred in the topsoil Fig. 5-1 legend.

Table 5-4 Sorption potential score, with average point of view

Soil Type	CEC-SSA Index	Text. Index	pH	Sorption Index
R*) Sandstone, Shale, limestone, dolomite	0	0.09	6	17
1) Dense stony, silt, silt-till: commonly bouldery	0	0.09	6	17
1-2) Variability stony, silt-sand till	0.48	0.09	6	46.8
2) c-galciolacustrine – clay, silt : generally overlies 2b and 2a b-glaciofluvial - sand, gravel a-glacial-silt sand till: in places boulddery ;commonly substratified; occurs interbedded with and as lenses instratified sediments 2b and 2c	1	0.75	6	83.6
3) Clay-silt till: locally sandy and/or stony where directly overlaying gravels, stony till or bedrock	1	0.58	6	78.2
4) Clay, silt, minor sand calcareous, laminated slightly contorted, light grey; contains considerable pollen; mapped only in Cote St-Luc, where it is commonly overlain by a thin mantle of marine clay	1	0.58	7.5	78.2
5) Clay, silt; Calcareous; locally with marine shells-"Leda Clay"	1	0.58	7.5	78.2
6) Sand, gravel: commonly with marine shells- " Saxicava Sand"	0	0.09	5	17
7) Sand, minor gravel: rare fresh-water shells,	0	0.09	5	17
8) Clay, silt : non calcareous; (includes sand, silt, minor clay which overlies peat	0	0.72	5	40
9) a-Peat muck, sapropel b-marl, pond clay	0.48	0.68		

Text. : Texture * = The number before the parenthesis was referred in the topsoil Fig. 5-1 legend.

Table 5-5 Sorption potential score, with pessimistic point of view

Soil Type	CEC-SSA Index	Text. Index	pH	Sorption Index
R*) Sandstone, Shale, limestone, dolomite	0	0	5.5	17.4
1) Dense stony, silt, silt-till: commonly bouldery	0	0	5.5	17.4
1-2) Variability stony, silt-sand till	0.13	0	5.5	17.4
2) c-galciolacustrine – clay, silt : generally overlies 2b and 2a; b-glaciofluvial - sand, gravel; a-glacial-silt sand till: in places boulddery ;commonly substratified; occurs interbedded with and as lenses instratified sediments 2b and 2c	0.48	0.51	5.5	49.3
3) Clay-silt till: locally sandy and/or stony where directly overlaying gravels, stony till or bedrock	0.13	0.4	5.5	31.8
4) Clay, silt, minor sand calcareous, laminated slightly contorted, light grey; contains considerable pollen; mapped only in Cote St-Luc, where it is commonly overlain by a thin mantle of marine clay	0.13	0.4	6.5	31.8
5) Clay, silt; Calcareous; locally with marine shells-"Leda Clay"	0.48	0.4	7	55.8
6) Sand, gravel: commonly with marine shells- " Saxicava Sand"	0	0	4.5	17.4
7) Sand, minor gravel: rare fresh-water shells,	0	0	4.5	17.4
8) Clay, silt : non calcareous; (includes sand, silt, minor clay which overlies peat	0	0.5	4.5	27.3
9) a-Peat muck, sapropel b-marl, pond clay	0.25	0.45		

Text.: Texture * = The number before the parenthesis was referred in the topsoil Fig. 5-1 legend.

The final results for all three viewpoints were presented in Table 5-3 to Table 5-5. The value of the final result assigned to the database of soil type in the ArcGIS. In the next step by applying a simple soil classification, the whole region was classified between 5 category of Very Low, Low, Average, High and Very High. The output map for three different viewpoints is given in Figure 5-3 to Figure 5-5. As it can be observed the average and optimistic view point generate the same classification where the pessimistic viewpoint generates a very conservative map. The application of each map depends on the condition and the purpose of using the map; therefore, selecting any of these three viewpoints is totally related to the objective of any specific project. For example, the obtained results could be used for identification of HM impact on health.

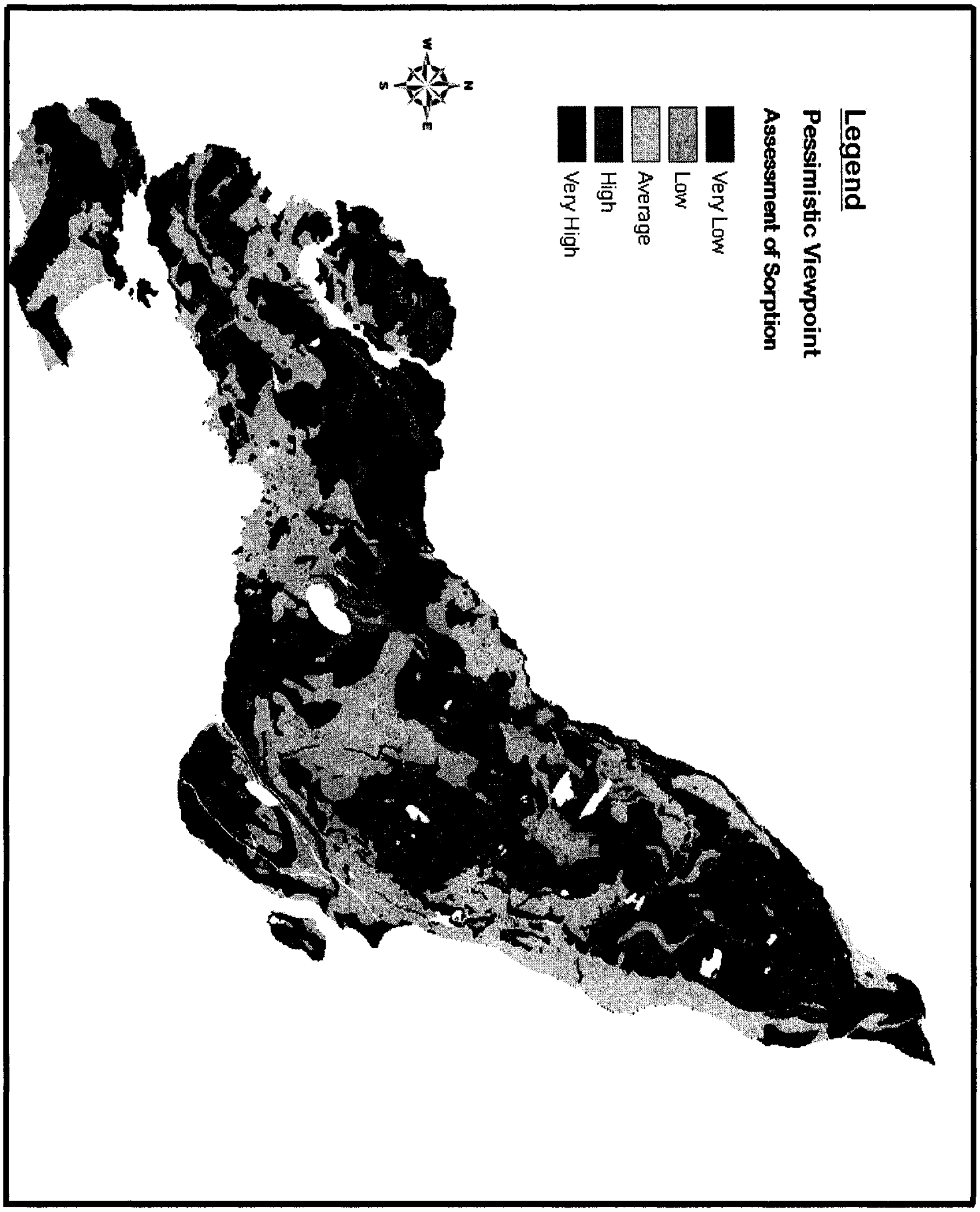

Figure 5-3 Soil classification from very low to very high sorption with pessimistic expert view point

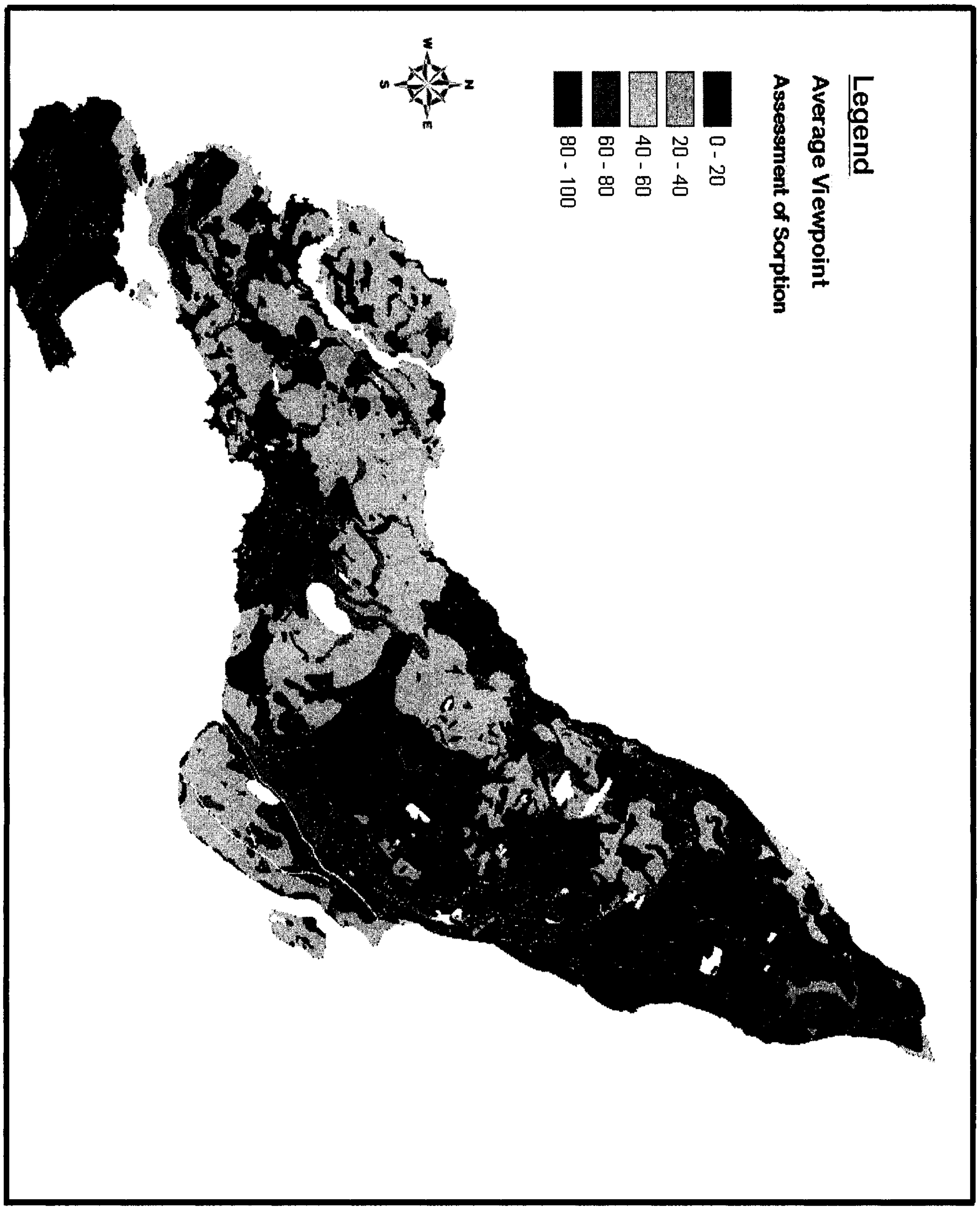

Figure 5-4 Soil classification from very low to very high sorption with average expert view point (Values show the ranges of values of the normalized FIS output for each area)

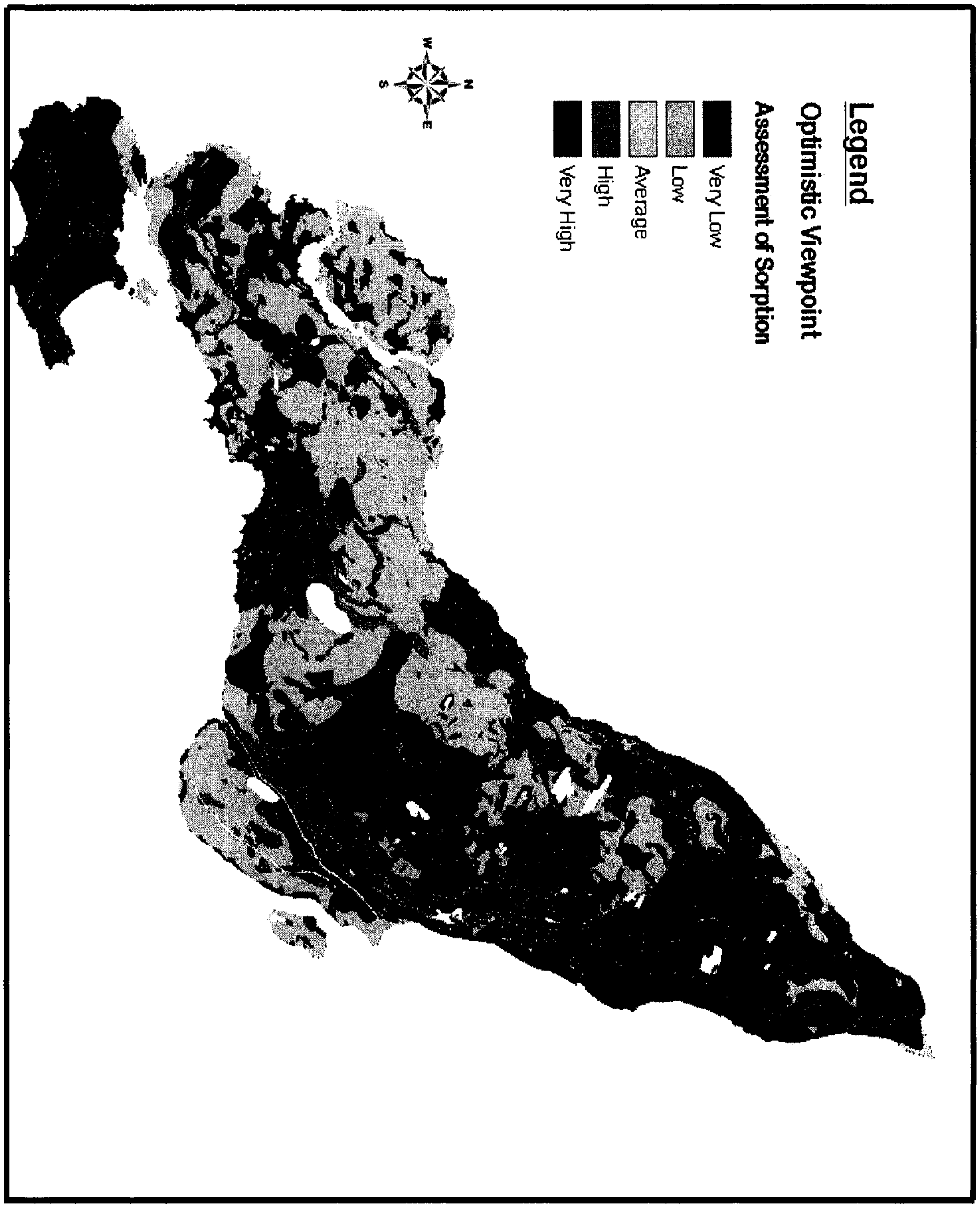

Figure 5-5 Soil classification from very low to very high sorption with optimistic expert view point

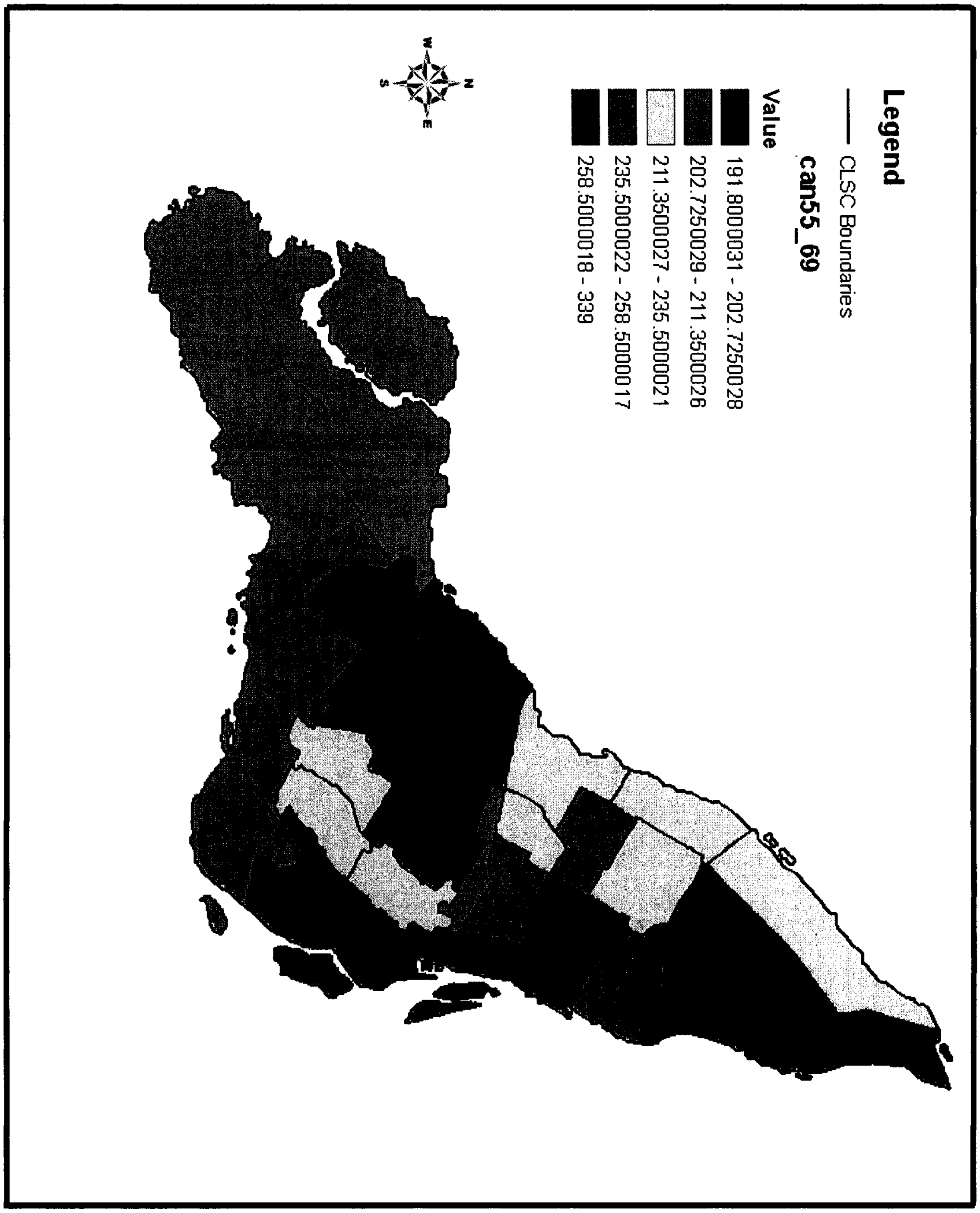

Figure 5-6 Cancer incident to population in the municipalities of Island of Montreal

By comparing Figure 5-6 and Figure 5-4 it can be observed that area with high to very high sorption shows more cases of cancer. It can be deducted that presence of metals might have impact on cancer cases appearances. In this regards, a decision can be made to create a particular health program to investigate these relations and possibilities.

The developed technique of HFIS in environmental management has a unique capability to combine several information to help the decision making process.

CHAPTER 6. CONCLUSION

Pollution concentration levels are usually determined by monitoring or sampling operations. Modeling studies generally provide an estimation of the real exposure of human beings to pollutants. However, the necessity to plan and control the exposure in large scale requires estimation of exposed distributed pollutants as a function of space and time. It is based on more accurate modeling that true indicator of risk for human health and environmental impact can be measured.

In this thesis for assessment of soil vulnerability to heavy metals, soil parameters involved in natural attenuation and sorption of heavy metals were selected. The selected parameters were introduced to a hierarchical fuzzy inference system in order to rank the highly vulnerable area or low vulnerable area in the topsoil. Generally for production of a tool through usage of fuzzy logic, there are three steps to fulfill. The first step is to find a solution to a specific problem and in the second step a fuzzy designer will design the model. The final step is to produce software or a tool by a software or hardware engineer for wide application. In this thesis, the two major steps satisfied. In the first step, a solution technique to predict the sorption potential in the soil was found and in the second step, a fuzzy inference engine was designed to be able to predict the soil vulnerability to heavy metal contamination mobility or their adsorption potential.

The validity of the developed model was proved by studying different case studies. The model in this step is useful in any specific decision making plan. In order to show the applicability of the model, the created HFIS was used to form a soil vulnerability layer in GIS. The created layer was compared to the available health data.

In conclusion, the major objective of this research was to introduce a methodology for designing models suitable for decision making in environmental management. This objective was satisfied through developing a hierarchical fuzzy inference system.

In particular achieved tasks of this research can be concluded as in the following:

1 - A practical model that deals with heavy metal contamination vulnerability in topsoil that includes the surface complexation models and surface property of the top soil was introduced.

2 - A fast tool that processes the geological expert knowledge and environmental experience to form a platform in which the result and decision can easily be made by managers and decision makers was developed.

3 - An application of the developed tool was initiated into an EIA case where independent data from various domains can be interfered.

4 - In this thesis most of the major pertinent parameter in sorption (pH, CEC, SSA, Clay content, OM, Moisture) were combined together for the first time in one engine to produce the sorption index.

CHAPTER 7. FUTURE WORKS

For the future work, it is suggested:

1 - Since the final step of the software implementation is remained, a code should be written in one of the conventional computer languages. The software will have the potential to produce a score for any soil. In addition to this software, it is highly suggested that a tool be created in ARCGIS 9.0 software to give the ability of fuzzy classification.

2 - Since in this study, only the soil map interpretable parameters were considered, an exact prediction of sorption percentage was not possible. It is suggested to consider individual heavy metals in the model and develop a model to be able to predict the partition coefficient of heavy metals in different soil types.

3 - This thesis was part of a large methodology of a project which was introduced in Chapter 3. The vulnerability in other media and different types of contaminants as well as time parameter can be studied by developing the same HFIS system.

4 - The very best application of this method and the tool developed is in Remote Sensing (RS) since in the satellite images cells have wide ranges of values, a classification method can help to process the images.

5 - One of the valuable applications of this method is to enhance the DRASTIC model which is being used for groundwater vulnerability. This tool can be easily applied to improve the soil parameter of the DRASTIC model.

REFERENCES

Adriano, D.C. (Ed.). (2001). *Trace elements in the terrestrial environment (2^{nd}ed).* Berlin Heidelberg, New York: Springer.

Ainsworth, C. C., Girvin, D. C., Zachara, J. M., & Smith, S.C. (1989). Chromate adsorption on goethite: effects of aluminum substitution. *Soil Sci. Soc. Am. J.*, 53, 411-418.

Alloway, B. J. (1990). *Heavy metals in Soils.* New York: John Wily & Sons Inc.

Amini, M., Afyuni, M., Fatahipour, N., Khademi, H., & Fluhler, H.(2005). Continuous soil pollution mapping using fuzzy logic and spatial interpolation. Geoderma. (124), 223-233.

Anderson, P. R. , & Christensen, TH. (1988). Distribution coefficients of Cd, Co, Ni and Zn in soils. *J Soil Sci.,* (39), 15–22.

ASTM, American Society for Testing Materials (2004). Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites. E1943-98

Bear, J. (1972). *Dynamics of Fluids in Porous Media.* New York: American Elsevier Publishing Company Inc., N.Y. (reprinted by Dover Publications, Inc., 1988).

Benjamin, M. M. , & Leckie, J. O. (1981). Multiple-site adsorption of Cd, Zn and Pb on amorphous iron oxhhydoxide. *J. Colloid interface Sci.,*(79),209-221.

Berkan, R.C., & Trubatch, S. L. (1997). *Fuzzy Systems Design Principles: Building Fuzzy IF-THEN Rule Base.* New York: Wiley-IEEE Press.

Biddappa, C.C. , Chino, M., & Kumazawa, K. (1981). Adsorption, desorption, potential and selective distribution of heavy metals in selected soil of Japan. *J Environ Sci. Health B.,* 16(4), 511-28.

Bien, J.D., ter Meer,J. ,Rulkens, W.H., & Rijinaarts, H.H.M. (2004). A GIS-based approach for the long term prediction of human health risks at contaminated sites. *Environmental modeling and assessment*, 9,221-226

Bocco, G., & Sanchez, R. (1997). Identifying potential impact of Lead contamination using a geographical information system. *Environmental management,* 21(1), 133-138.

Bojorquez-Tapia, L. A. , Juarez, L. , & Cruz-Bello, G. (2002). Integrating Fuzzy logic, optimization and GIS for Ecological Impact Assessment, *Environmental Management*, 30(3), 418-433.

Bowman, M. B., & Lewis, M. S. (1982). The copper hypothesis of schizophrenia: A review. *Neurosci. Biobehav. Rev.*, 6, 321–328.

Brady, P.V., Spalding, B. P., Krupka, K. M. , Waters, R. D. , et al. (1999, March). *Site Screening and Technical Guidance for Monitored Natural Attenuation at DOE Sites.* Sandia National Laboratories, SAND99-0464.

Bright, M. I. , Thornton, S. F. , Lerner, D. N. , & Tellam, J. H. (1996). *Laboratory investigations into designed high attenuation landfill liners.* Bentley S.P.(ed.) Engineering geology of waste disposal. *Geological Society Engineering Geology* Special Publications. 11, 159–164

Brown, M., Bossley, K. M., Mills, D. J., & Harris, C. J. (1995). *High dimensional neurofuzzy systems: overcoming the curse of dimensionality.* Proc. IEEE International. 2139-2146.

Cadmium (n.d.). Wikipedia. Retrieved May 03, 2006, from Answers.com Website: http://www.answers.com/topic/cadmium

Cameron E., & Peloso, G. F. (2001). An application of Fuzzy logic to the assessment of aquifers pollution potential. *Environmental Geology,* 40, 1305-1315.

CCME (n.d). Retrieved on 15july 2005, http://ccme.miupdate.com/initiatives/pollution. html.

Chang, A.C., Warneke, J. E., Page, A. L., & Lund, L. J. (1984). Accumulation of heavy metals in sewage sludge-treated soils. *Journal of Environmental Quality*, 13(1), 87-90.

Conner, J. R. (1990). Chemical fixation and solidification of hazardous wastes. New York: Van Nostrand Reinhold.

Davis, J. A., & Leckie, J. O. (1980). Surface ionization and complexing ligands at the oxide/ water interface III. adsorption of anions. *J. Colloid interface Sci.* , 74,32-43.

DEPA, Danish Environmental Protection Agency (2002).*Guidelines on Remediation of Contaminated Site*s. Retrieved May 12, 2006, from www.mst.dk/udgiv/publications /2002/87-7972-280-6/pdf/87-7972-281-4.pdf.

Domenico, P. A., & Schwartz, F. W. (1990). *Physical and Chemical Hydrogeology*. NY: John Wiley & Sons.

Dragun, J. (1988). *The soil chemistry of hazardous materials*. Massachusetts: Amherst Scientific Publishers.

Elektorowicz, M. (2004), Course handout for the Engineering aspect of site remediation, Concordia University, Montreal, Qc.

Elektorowicz, M., Qasaimeh, & A., Balazinski, M. (2003). Assessment of the Capability of Metal Sorption to Sediments of Natural Systems Using Fuzzy Knowledge. *8th Environmental and Sustainable Engineering Specially Conference of the Canadian Society for Civil Engineering.* Moncton, N.B., Canada.

Elliott, H. A., Liberati, M. R., & Huang, C. P. (1986). Competitive adsorption of heavy metals by soils. *Journal of Environmental Quality,* 15(3), 214-219.

Fertilizing your ornamental garden (2004). Retrieved July 11, 2006 from http:// www2.ville.montreal.qc.ca/jardin/en/info_verte/fertilisation/potentiel_h.htm.

Forbes, E. A., Posner A. M., & Quick, J. P. (1976). The specific adsorption of divalent Cd, Co, Pb, Zn on goethite. *J. Soil Sci.,* 27,154-166

Gelahar, L.W. & Axness, C. L. (1981). Stochastic Analysis of Macrodispersion in Three-Dimensionally Heterogeneous Aquifers Report H-8 (Socorro, U.S.A.: Geophysical Research Center, New Mexico Institute of Mining & Technology).

Geoscape Gatineau-Ottawa, Landslides (2005). Retrieved July 11, 2006 from http:// geoscape.nrcan.gc.ca/ottawa/landslides_e.php.

Gray, F., & Roozitalab , M. H. (1976). *Benchmark and key soils of Oklahoma. Oklahoma Agr. Exp. Sta.,* MP-97, 36.

Griffin, R. A., & Shimp, N. F. (1978). Attenuation of pollutants in municipal landfill leachate by clay minerals, *EPA*-600/2-78-157.

Harris, J. (2000). *An introduction to Fuzzy Logic Applications.* Netherland: Kluwer Academic Pub.

Harter, R. D. (1983). Effect of soil pH on adsorption of lead, copper, zinc, and nickel. *Soil Sci. Soc. Am. J.,* 47,47-51.

Hayes, M. H. B. , & Swift, R. S. (1978). *The Chemistry of Soil Constituents*, eds. Greenland D.J. and Hayes, M.H.B. John Wiley, Chichester, pp. 179 -320.

Hillel, D. (1980). *Fundamentals of Soil Physics*. New York: Academic Press Inc.

Hu, H. (1998). Chapter 397: Heavy metal poisoning. In: Fauci AS, Braunwald E, Isselbacher KJ, Wilson J.D. , Martin J.B. , Kasper D.L. , Hauser S.L. , Longo D.L. (eds). *Harrison's principles of Internal medicine.* 14th ed. New York: McGraw-Hill, 2564-2569.

Hunag, Y. T. (2005). *Heavy metals in Urban Soils.* Master thesis dept. Building, Civil and environmental engineering, Concordia University, Montreal, Qc.

Karkazi A., Emmanouilidi B., Mavropoulos, A., Hatzichristos, T., & Elseoud A. (2001) *Landfill sitting with GIS and Fuzzy Logic*, Proceedings Sardinia, Italy. Retrived March 2006 from http://www.epem.gr/publications.html .

Kinniburgh, D. G., & Jackson, M. L. (1978). Adsorption of mercury (II) by iron hydrous oxide gel. *Soil Sci.Soc. Am. J.*, 42, 45-47.

Kohli, S. , Sahlen, K. , Lofman, O. , Sivertun, A. , Foldevi, M., Trell, E., & Wigertz, O. (1997). Individuals living in areas with high background radon: a GIS method to identify populations at risk. *Computer methods and programs in biomedicine*, 53,105-112.

Korte, N. E., Skopp, J., Fuller W. H., Niebla E. E. & Aleshii B. A.. (1976). Trace element movement in soils: influence of soil physical and chemical properties. *Soil Sci.,* 122, 350-359.

LaGrega, M. D., & Buckingham P. L. (2001). *Hazardous Waste Management* (2nd ed.), McGraw-Hill.

Lead. (n.d.). Wikipedia. Retrieved May 04, 2006, from Answers.com Web site: http://www.answers.com/topic/lead-10

Lee, D. H. K. (Ed.) (1972). *Metallic contaminants and human health* (1st ed.). New York: Academic Press.

Lee, M. L., Chung, H. Y., & Yu, F. M. (2003). Modeling of hierarchical fuzzy systems. *Fuzzy Sets and Systems*, 138, 343-361.

Lee S. (2003).Evaluation of Waste disposal site using the DRASTIC system in southern Korea. *Environmental Geology.,* 44, 454-664.

Lee, Y. W., Dahab, M. F., & Bogardi, I.(1995). Nitrate-risk assessment using fuzzy-set approach. *J. Environ. Eng.,* 121, 245–256.

Li, Z., Shuman, L.M., (1996). Heavy Metal Movement in Metal-Contaminated soil profiles. *Soil Science,* 161(10), 656-666

Li, X., Lee S., Wong, S. Shi, W., & Thornton, I. (2004). The study of metal contamination is urban soils of Hong Kong using a GIS-based approach. *Environmental Pollution.,* 129,113-114

Lin, J. (1999). *Efficiency of Biosurfactants applied by means of Electrokinetics.* Master thesis. Faculty of Engineering of Concordia University, Montreal, QC.

Lindsay, W. L. (1979). *Chemical equilibria in soils.* New York: John Wiley and Sons.

Luna, C.M., González, C.A., & Trippi, V.S. (1994).Oxidative damage caused by an excess of copper in oat leaves. *Plant Cell Physiol.,* (35)11–15

Lutenegger, A. J., & Cerato, A. B. (2001). Surface Area and Engineering Properties of Fine-Grained Soils, Proceedings of the 15th International Conference on Soil Mechanics and Foundation Engineering, 1, 603-606.

Maggiora, G.M. (2003). Computer-Aided Decision Making in Pharmaceutical Research, Molecular Informatics: Confronting Complexity, May 13th – 16th 2002, Italy.

Mansour, M. (1993). *Fate and prediction of environmental chemicals in soils, plants and aquatic systems.* Boca Raton: Lewis Publishers.

McCarty, P. L. (1994). *Ranking Hazardous-waste Sites for remedial Action*, Commission on Geosciences, Environment and Resources, National Research council.

McLean, J. E., & Bert, E. B. (1992, October). *Behavior of metals in soils, Ground water issue*, EPA/540/S-92/018.

McWhorter, D., Sunada, B., & Daniel, K. (1977). *Ground-water hydrology and hydraulics,* Fort Collins, Colo.: Water Resources Publications.

Mirsal, I. (2004). *Soil pollution origin, Monitoring & remediation,* Heidelberg: Springer-verlag.

Mitra, B. (1998). Application of fuzzy logic to the prediction of soil erosion in a large watershed. *Geoderma*, 86, 183-209.

Morris, D. A. , & Johnson, A. I. (1967). Summary of hydrologic and physical properties of rock and soil materials, as analyzed by the Hydrologic Laboratory of the U.S. Geological Survey 1948–1960. *U.S. Geological Survey Water Supply Paper* 1839-D.

Naoum, S., Tsanis, I.K., Fullarton, M. (2002), A GIS pre-processor for pollutant transport modeling. *Environmental modeling & Software*, 20, 55-68

Nazaroff, W.W., & Alvarez-Cohen, L. (2000), *Environmental Engineering Science*, John Wiley and Sons, Inc., New York (2000).

Nestle, F. O., Speidel , H. , & Speidel, M. O. (2002). Metallurgy: high nickel release from 1- and 2-euro coins. *Nature,* 419,132.

NPI, the National Pollutant Inventory (n.d.). Retrieved May 04, 2006, Australia's national database of pollutant emissions database: http://www.npi.gov.au/cgi-bin/ npisubstance.pl.

Ozren, D., & Slobodan, S. (2000). Aggregation operators for soft decision making in water resources. *Fuzzy Sets and Systems*, 115(1) (October 2000), Special issue on soft decision analysis, 11-33, ISSN:0165-0114

Parametrix (1995). *Persistence, bioaccumulation and toxicity of metals and metal compounds*. Ottawa, Canada: ICME., p. 93.

Peat, (n.d.).Wikipedia. Retrieved May 11, 2006, from Answers.com Web site: http://www.answers.com/topic/peat.

Perth County Groundwater Study Final Report (2001), UTRC Authority, ABC Authority, MVC Authority - countyofperth.on.ca, Retrived January 10,2006, from http://www.ene.gov.on.ca/envision/water/groundwater/perth/

Petruzzelli, D., & Helfferich, F. G. (1993).*Migration and fate of pollutants in soils and subsoil,* Berlin, New York: pringer Verlag.

Pierce, F. J., Dowdey, R. H., & GIGAL, D.E. (1982). Concentrations of six trace elements in some major Minnesota soil series. *Jour. Environ. Qual.*, 11(3), 416

Reddi, L. N., & Inyang, H. I. (2000). *Geoenvironmental Engineering: Principles and Applications*. Marcel Dekker Inc., New York, 2000.

Roggers, R. D. (1976). Abiological methylation of mercury in soils. *J. Environ. Qual.*, 6, 463-467.

Roggers, R. D. (1976). Methylation of mercury in agricultural soils. *J. Environ. Qual.*, 5, 454-458.

Ross, T. J. (2004). Fuzzy Logic with Engineering Applications 3rd ed., John Wiley and Sons, 2004.

Rowe R.K., Quigley, R. M., & Booker, J. R. (1995). *Clayey barrier systems for waste disposal facilities*. London: E and FN Spon.

Sengupta, S., Patil, R. S., & Venkatachalam, P. (1996). Assessment of population exposure and risk zones due to air pollution using the geographic information system. *Computers, Environment and Urban Systems,* 20, 191–199.

Sittig, M. (1994).*World-wide Limits for Toxic and Hazardous Chemicals in Air, Water and Soil*. Park Ridge, NJ: Noyes Publications.

Soil pH (2003).Retrieved October 16, 2005, from http://www.soils.agri.umn.edu/ academics/classes/soil2125/doc/s11chap3.htm

Sposito, G., Holtzclaw, K., M., & Le Vesque-Mador, C., S. (1981). Trace metal complexation extracted by fulvic acid from sewage sludge. I. Determination of stability constants and linear correlation analysis. *SSS Am. Journal,* 45.

Stevenson, F. J. (1979). *Encyclopedia of Soil science*, eds. Fairbridge, R.,W. & Finkl, C., F., Dowden, Hutchinson & Ross, Stroudsburg Pa, 195-205.

Surampalli, R.Y. , Ong S.K., Eagren, E.,& Nuno , J. (Ed.) (2004).*Natural attenuation of hazardous wastes*.Environmental and Water Resources Institute (U.S.). Natural Attenuation Task Committee. Reston, Va. ISBN: 0784407401

Tarradellas, J., Bitton, G., & Rossel, D. (1997). *Soil ecotoxicology*. Boca Raton, FL: Lewis.

Till (n.d.). *Wikipedia*. Retrieved July 07, 2006, from Answers.com Web site: http://www.answers.com/topic/till

Toogood, J.A. (1958). A simplified textural classification diagram. *Canadian Journal of Soil Science.* 38, 54-55.

Tomilson , R.F (1976). Computer handling of geographical data , UNESCO

U.S. Environmental Protection Agency (1986), "Method 9100: Saturated Hydraulic Conductivity, Saturated Leachate Conductivity, and Intrinsic Permeability," in *Test Methods for Evaluating Solid Waste, Volume IC: Laboratory Manual Physical/Chemical Methods*, EPA SW-846, Part 3 of 4, 3rd ed., Washington, D.C.

U.S. EPA (2005). *Partition Coefficient for Metals in Surface Water, Soil and Waste* (EPA/600/R-05-074). Allison, J., D., Allison T. L.

U.S. EPA (1997). Use of monitored natural attenuation at Superfund, RCRA, corrective action, and underground storage tank sites: Office of Solid Waste and Emergency Response Directive 9200.4-17, Washington D.C.

U.S. EPA (1999). *Understanding Variation in Partition Coefficient, K_d, Values* – EPA/402-R-99-004A&B. Office of Air and Radiation, Washington.

Wiedemeier, T. H. (1999). *Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of Fuel contamination dissolved in groundwater,* vol. I, Denver, Colorado: Parsons Engineering Science Inc.

Wild, A. (1993). *Soils and the environment.* Cambridge University Press, UK.

Williams, F., Robertson, R., & Roworth, M. (1999). *Detailed profile of 25 major organic and inorganic substances.* 1st ed. Glasgow: SCEIH (Scottish Centre for Infection and Environmental Health).

Woolsen, E. A. (1977). Fate of arsenicals in different environmental substrate. *Environ. Health Perspect.,* 19, 73-81

Yong, R. N., & Mulligan, C. N. (2004). *Natural attenuation of contaminants in soils.* Boca Raton (FL): CRC Press.

Yong, R. N., Mohamed, A. M. O., & Warkentin, B. P. (1992). *Principles of Contaminant Transport in Soils, Developments in Geotechnical Engineering, Series*, No. 73. Amsterdam: Elsevier.

Yu, C., Loureiro, J. J., Cheng, L. G., Jones, Y. Y., Wang, Y. P., & Chia E. F. (1993). Data Collection Handbook to Support Modeling Impacts of Radioactive Material in Soil. Argonne National Laboratory, Argonne, IL (1993).

Zachara, J. M., & Westall, J.C. (1999).*Chemical modeling of ion adsorption in soils. Soil Physical Chemistry (2nd ed).* Boca Raton, FL: CRC Press.

Zachara, J. M., Girvin D. C., Schmidt R. L., & Resch C. T. (1987).Chromate adsorption on amorphous iron oxyhydroxide in presence of major ground water ions. *Environ. Sci. Technol.*,21, 589-594.

Zadeh, L. A. (1977). Fuzzy set theory: a perspective. In: Gupta, M., Saridis, G, Gaines, B. (Eds.), *Fuzzy Automoata and decision Processes.* New York: Elsevier North-Holland, pp. 3-4.

Zhenbin, Li, & Sauman, L. M. (1996). Heavy metal movement in metal-Contaminated soil profile. *Soil Science,* 161(10).

Zuhairi, W.Y. (2003). Sorption capacity on lead, copper and zinc by clay soils from South Wales, United Kingdom. *Environmental Geology [Environ. Geol.],* 45(2), 236-242.

APPENDIX A

MATLAB FUZZY INFERENCE SYSTEM CODES

Soil Texture Index

```
[System]
Name='Stexture'
Type='mamdani'
Version=2.0
NumInputs=3
NumOutputs=1
NumRules=30
AndMethod='min'
OrMethod='max'
ImpMethod='prod'
AggMethod='sum'
DefuzzMethod='centroid'

[Input1]
Name='Calyiness'
Range=[1 100]
NumMFs=5
MF1='VL':'trapmf',[0 0 10 15]
MF2='L':'trapmf',[10 13 29 33]
MF3='N':'trapmf',[28 33 36 40]
MF4='H':'trapmf',[35 40 58 62]
MF5='VH':'trapmf',[58 62 117 200]

[Input2]
Name='Moisture'
```

```
Range=[0 100]

NumMFs=1

MF1='moisture':'trapmf',[20 80 103 208]


[Input3]

Name='Organic__Compund'

Range=[0 40]

NumMFs=3

MF1='Low':'trapmf',[0 0 1 5]

MF2='avg':'trimf',[1 5 10]

MF3='High':'trapmf',[5 10 40 40]


[Output1]

Name='Tex_Sorption_Potential'

Range=[0 7]

NumMFs=4

MF1='L':'trapmf',[0 0 1 2]

MF2='RL':'trapmf',[1 2 3 4]

MF3='RH':'trapmf',[3 4 5 6]

MF4='H':'trapmf',[5 6 8 8]


[Rules]

1 1 1, 1 (1) : 1

2 1 1, 1 (1) : 1

3 1 1, 1 (1) : 1

4 1 1, 2 (1) : 1

5 1 1, 3 (1) : 1
```

```
1 1 2, 1 (1) : 1
2 1 2, 1 (1) : 1
3 1 2, 2 (1) : 1
4 1 2, 2 (1) : 1
5 1 2, 3 (1) : 1
1 1 3, 3 (1) : 1
2 1 3, 3 (1) : 1
3 1 3, 3 (1) : 1
4 1 3, 4 (1) : 1
5 1 3, 4 (1) : 1
1 -1 1, 1 (1) : 1
2 -1 1, 1 (1) : 1
3 -1 1, 2 (1) : 1
4 -1 1, 3 (1) : 1
5 -1 1, 4 (1) : 1
1 -1 2, 2 (1) : 1
2 -1 2, 3 (1) : 1
3 -1 2, 3 (1) : 1
4 -1 2, 4 (1) : 1
5 -1 2, 4 (1) : 1
1 -1 3, 3 (1) : 1
2 -1 3, 3 (1) : 1
3 -1 3, 4 (1) : 1
4 -1 3, 4 (1) : 1
5 -1 3, 4 (1) : 1
```

CEC-SSA Index

```
[System]
Name='Sorption(CEC,SSA)'
Type='mamdani'
Version=2.0
NumInputs=2
NumOutputs=1
NumRules=9
AndMethod='min'
OrMethod='max'
ImpMethod='prod'
AggMethod='max'
DefuzzMethod='centroid'

[Input1]
Name='CEC'
Range=[0 150]
NumMFs=3
MF1='Low':'trapmf',[0 0 10 35]
MF2='High':'trapmf',[10 35 65 80]
MF3='Very__High':'trapmf',[65 80 1000 1000]

[Input2]
Name='SSA'
Range=[0 200]
NumMFs=3
MF1='L':'trapmf',[0 0 25 45]
```

```
MF2='A':'trapmf',[20 40 100 110]
MF3='H':'trapmf',[100 110 200 200]

[Output1]
Name='CEC,SSA'
Range=[0 7]
NumMFs=4
MF1='H':'trapmf',[5 6 7 7]
MF2='RH':'trapmf',[3 4 5 6]
MF3='RL':'trapmf',[1 2 3 4]
MF4='L':'trapmf',[0 0 1 2]

[Rules]
1 1, 4 (1) : 2
2 1, 3 (1) : 2
3 1, 2 (1) : 2
1 2, 3 (1) : 2
2 2, 2 (1) : 2
3 2, 1 (1) : 2
1 3, 3 (1) : 2
2 3, 2 (1) : 2
3 3, 1 (1) : 2
```

Sorption Index

```
 [System]
Name='Final Fuzzy system'
```

```
Type='mamdani'
Version=2.0
NumInputs=3
NumOutputs=1
NumRules=64
AndMethod='min'
OrMethod='max'
ImpMethod='min'
AggMethod='max'
DefuzzMethod='centroid'

[Input1]
Name='pH'
Range=[3 9]
NumMFs=4
MF1='RL':'trimf',[4 5 6]
MF2='RH':'trimf',[5 6 7]
MF3='H':'trapmf',[6.02 7.02380952380952 15 15]
MF4='L':'trapmf',[3 3 4 5]
[Input2]
Name='Texture'
Range=[0 1]
NumMFs=4
MF1='L':'trapmf',[0 0 0 0.333]
MF2='RL':'trimf',[0 0.3333 0.667]
MF3='RH':'trimf',[0.3333 0.6667 1]
MF4='H':'trapmf',[0.66667 1 1 1]
```

```
[Input3]
Name='P-C_param'
Range=[0 1]
NumMFs=4
MF1='L':'trapmf',[0 0 0 0.3]
MF2='RL':'trimf',[0 0.3333 0.6667]
MF3='RH':'trimf',[0.3333 0.6667 1]
MF4='H':'trapmf',[0.7 1 1 1]
[Output1]
Name='Sorption'
Range=[0 100]
NumMFs=4
MF1='VL':'trapmf',[0 0 20 40]
MF2='L':'trimf',[20 40 60]
MF3='H':'trimf',[40 60 80]
MF4='VH':'trapmf',[60 80 100 100]
[Rules]
1 1 1, 1 (1) : 1
1 1 2, 1 (1) : 1
1 1 3, 1 (1) : 1
1 1 4, 1 (1) : 1
1 2 1, 1 (1) : 1
1 2 2, 1 (1) : 1
1 2 3, 2 (1) : 1
1 2 4, 2 (1) : 1
1 3 1, 2 (1) : 1
1 3 2, 2 (1) : 1
```

```
1 3 3, 2 (1) : 1
1 3 4, 2 (1) : 1
1 4 1, 2 (1) : 1
1 4 2, 2 (1) : 1
1 4 3, 2 (1) : 1
1 4 4, 2 (1) : 1
2 1 1, 1 (1) : 1
2 1 2, 2 (1) : 1
2 1 3, 2 (1) : 1
2 1 4, 2 (1) : 1
2 2 1, 1 (1) : 1
2 2 2, 2 (1) : 1
2 2 3, 3 (1) : 1
2 2 4, 3 (1) : 1
2 3 1, 2 (1) : 1
2 3 2, 3 (1) : 1
2 3 3, 4 (1) : 1
2 3 4, 4 (1) : 1
2 4 1, 3 (1) : 1
2 4 2, 3 (1) : 1
2 4 3, 4 (1) : 1
2 4 4, 4 (1) : 1
3 1 1, 1 (1) : 1
3 1 2, 2 (1) : 1
3 1 3, 2 (1) : 1
3 1 4, 2 (1) : 1
3 2 1, 1 (1) : 1
```

```
3 2 2, 2 (1) : 1
3 2 3, 3 (1) : 1
3 2 4, 3 (1) : 1
3 3 1, 3 (1) : 1
3 3 2, 3 (1) : 1
3 3 3, 4 (1) : 1
3 3 4, 4 (1) : 1
3 4 1, 3 (1) : 1
3 4 2, 3 (1) : 1
3 4 3, 4 (1) : 1
3 4 4, 4 (1) : 1
4 1 1, 1 (1) : 1
4 1 2, 1 (1) : 1
4 1 3, 1 (1) : 1
4 1 4, 1 (1) : 1
4 2 1, 1 (1) : 1
4 2 2, 1 (1) : 1
4 2 3, 1 (1) : 1
4 2 4, 1 (1) : 1
4 3 1, 1 (1) : 1
4 3 2, 1 (1) : 1
4 3 3, 1 (1) : 1
4 3 4, 1 (1) : 1
4 4 1, 1 (1) : 1
4 4 2, 1 (1) : 1
4 4 3, 1 (1) : 1
4 4 4, 2 (1) : 1
```