Novel Physical and Chemical Characterization of Stormwater Sediments

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Abstract

This work focuses on the advanced physical analysis of stormwater sediments using laser diffraction particle size analyzer and scanning electron microscope and chemical characterization using neutron activation analysis. Since previous studies of sediments from stormwater ponds in the Greater Toronto Area indicated a marginal-to-significant level of pollution by most of the regulated heavy metals, the characteristics of the stormwater sediment samples obtained in this study were compared to the sediment quality guidelines of the Ontario Ministry of the Environment. The images from optical microscope showed that the particles in the dried sediment were irregular, and the sizes of each particle vary greatly. Using scanning electron microscope, it was shown that two different structures of particles were present in the stormwater sediment. It was also observed that the main compositions (above 1000ppm) of the dried sediment included, in descending order of concentration, Ca > Al > Fe > K > Mg > Na >Ti > Mn. The trace compositions (below 1000ppm) included, also in descending order of concentration, Cl > Zn > Ba > Sr > Cr > V > La > Nd > As > Br > Co > Sc > Th > Sb > Sm > Eu. The concentrations of regulated elements such as Cr, Fe Zn, As and Mn were above the lowest effect level, suggesting that treatment of stormwater sediment may be necessary. A preliminary stormwater sediment treatment experiment using thermal plasma technology was therefore conducted. After the thermal plasma treatment, the percentage of total organic carbon decreased and eight gas compounds including CO, CO_2, NO, NO_2, NOx, SO_2,

H_2S and C_xH_y emitted during the process. Enrichments of Mg, Cl and Na were observed in the treated sludge while the concentrations of K and Ca decreased. The potential of thermal plasma technology for the treatment of contaminated stormwater sediment was demonstrated.

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Chapter 1
Introduction

1.1 Nonpoint Source Pollution

Nonpoint source pollution is the pollution caused by sediments, nutrients, organics and toxic substances originating from various land use activities or directly deposited from the atmosphere. As opposed to point sources of pollution, non-point sources of pollution, have no single, localized sources. Common origins of urban non-point source pollution include improperly sited, designed and maintained onsite wastewater treatment (septic) systems, pet wastes, lawn and garden fertilizers and pesticides, household chemicals that are improperly disposed, automobile fluids, road deicing/anti-icing chemicals, and vehicle emissions (USEPA, 2005). During rainfall events, stormwater washes off the pollutants, which have been accumulating on urban surfaces and carries them downstream. To protect downstream receiving waters, stormwater detention or retention ponds, or constructed wetlands, are designed to contain and partly treat the urban stormwater runoff (Vanloon et. al, 2000). These ponds are usually designed to trap and settle out solid materials carried by stormwater. This reduces contaminant loads discharged to rivers or lakes and improves water quality. While some contaminants will biodegrade within the pond or wetland, others are more persistent and can accumulate in the sediment, also refereed to as sludge in this thesis, at the bottoms of the stormwater ponds and wetlands.

1.2 Possible Contaminants in Stormwater Sediments

Urban land usage generates residual and waste materials from a myriad of individual and group activities. Typical urban runoff includes pollutants such as sediments, pathogens, fertilizers, nutrients, hydrocarbons and metals (USEPA, 1983; USEPA, 2005; Schroeter, 1997). Each type of land use has unique characteristics that result in the generation of different types of pollutants. Density or intensity of the land usage and percent of imperviousness also affect the quantity of pollutants (Ontario Ministry of Environment, 2001). The following factors are normally considered:

(i) Vehicular Traffic

Vehicular traffic accounts for the build-up of contaminants on road surfaces. Wear from tires, brake and clutch linings, engine oil and lubricant drippings, combustion products and corrosion affect the rate of build up of sediment particles, metals, and oils and grease. Wear on road surfaces also provides sediment and petroleum derivatives from asphalt.

(ii) Lawn and Garden Maintenance

Lawn and garden maintenance accounts for additions of organic material from grass clippings, garden litter and fallen leaves. Other potential pollutants include fertilizers, herbicides and pesticides.

(iii) Air Pollution

Air pollution fallout of suspended solid particles from traffic, industrial sources and wind erosion of soils builds up contaminants within the soil. The potential pollutants include hydrocarbons and metals.

(iv) Municipal Maintenance

Municipal maintenance activities, which include road repair and general maintenance, generate pollutants used for road surface treatment, salting and dust control.

(v) Industrial and Commercial Activities

Industrial and commercial activities can lead to the contamination of runoff from loading and unloading areas, raw material and by-product waste streams. The types of contaminants depend on the kind of activities performed. In general, mercury, chromium and zinc are the most common pollutants in industrial area (Liebens, 2001).

(vi) Illegal Connections

Illegal connections of sanitary services to storm sewers can cause contamination with organic wastes, nutrients and bacteria.

(vii) Illegal Disposal

Illegal disposal of household hazardous waste can introduce waste oil and a multitude of toxic materials to storm and sanitary sewers.

(viii) Transportation spills

Transportation spills from accidents in arterial streets and highways.

(ix)Construction Activity

Construction activity generates heavy loads of sediment and waste from direct runoff and construction vehicles.

(x) Pet Wastes and Litter

Pet fasces and litter result in organic contamination, nutrients and bacteria.

(xi)Combined Sewer Overflows

Combined sewer overflows (CSOs) contain a mixture of sanitary, commercial and often industrial wastes. CSOs can contain high levels of nutrients, suspended solids, metals, organic contaminants, oxygen demanding substances, bacteria and viruses.

(xii) Runoff from Driveways and Parking Areas

Runoff from residential driveways and parking areas can contain driveway sealants, oil, salt and car care products.

1.3 Study Objective

The objective of this study is to better characterize stormwater sediments accumulating in detention/retention ponds using a laser diffraction particle size analyzer, an optical microscope and a scanning electron microscope (SEM), and by neutron activation analysis (NAA). The concentrations of regulated elements are compared to the sediment quality guidelines of the Ontario Ministry of the Environment. If this comparison indicates a need for further treatment of

stormwater sediment, a preliminary advanced treatment method (plasma technology) will be tested out and evaluated.

Chapter 2
Literature Review

2.1 Regulations for Toxic Elements

Contaminated sediments have been singled out as a major environmental problem. The Sediment Quality Guidelines established by the Ontario Ministry of the Environment and other jurisdictions are to protect the aquatic environment by setting safe levels for metals, nutrients (substances which promote the growth of algae) and organic compounds. These guidelines are designed to protect the quality of the sediment (MOEE, 1993). The Ontario guidelines establish the following three levels of effect.

(i) The No Effect Level (NEL): This is the level at which the chemicals in the sediment do not affect fish or sediment-dwelling organisms. At this level, no transfer of chemicals through the food chain would occur and no effect is expected. Sediment that has a NEL rating is considered clean and no management decisions are required;

(ii) The Lowest Effect Level (LEL): This indicates a level of contamination, which has no effect on the majority of the sediment-dwelling organisms. The sediment is clean to marginally- polluted. Contamination in sediment that exceeds the LEL may require further testing and a management plan. The exceeded concentrations of metal and organic contaminants could endanger the organisms that live or feed in the sediment; and

(iii) The Severe Effect Level (SEL): At this level, the sediment is considered heavily polluted and likely to affect the health of sediment-dwelling organisms. If the level of contamination exceeds the SEL, testing is required to determine whether or not the sediment is acutely toxic. At the SEL, a management plan may be required. The plan may include control of the source of the contamination and removal of the sediment.

The Provincial Sediment Quality Guidelines for Metals and Nutrients in Ontario, Canada are shown in Table 2.1.

Table 2.1: Provincial Guidelines for metals element and total organic carbon (MOEE, 1993)
(values in µg/g dry weight unless otherwise noted)

Elements	**LEL µg/g**	**SEL µg/g**
Chromium	26	110
Iron	20000	40000
Zinc	120	820
Arsenic	6	32
Cadmium	0.6	10
Copper	16	110
Lead	31	250
Nickel	16	75
Mercury	0.2	2
Iron (%)	2	4
Manganese	460	1100
Total Organic Carbon		
TOC (%)	1	10

There are also provincial Sediment Quality Guidelines for nutrients, Polychlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAH) and Organochlorine Pesticides. The scope of this work, however, mainly focuses on heavy metal contamination and total organic carbon. Thus, the guidelines for other organics are not included here.

2.2 Reviews of Stormwater Ponds in Ontario

In 1997 and 1998, Environment Canada had conducted a study to evaluate the level of contaminants captured in storm water ponds and the effects of contaminants in the pond on the health of wildlife using these ponds (Great Lakes Fact Sheet, 1999). Six stormwater ponds in the Greater Toronto Area (GTA) and nine in Guelph were studied.

The catchment areas draining to these storm water ponds neighborhoods are divided into four groups: residential, commercial, commercial/light industrial and residential/commercial. Twelve ponds are located in residential areas. One is located in a commercial area, one in a commercial/light industrial area and one in a residential/commercial area. GTA ponds were sampled in July and Guelph ponds were sampled in September. Sediments from 14 of 15 ponds contained concentrations of contaminants that exceeded the "Lowest Effect Level" (LEL) of the Guidelines for the Protection and Management of Aquatic Sediments in Ontario (Persaud et al., 1992). Most pond sediments showed contaminant concentrations exceeding provincial sediment quality guidelines at the LEL for chromium, zinc and copper. For PAHs and lead, concentrations in sediments

exceeded the provincial LEL in six and seven ponds respectively. It was found that sediments in one site (commercial/light industrial) exceeded the provincial guideline at the "Severe Effect Level" (SEL) for chromium.

Another study tested the sediment toxicity and chemistry of two stormwater ponds in Toronto (Rochfort, et.al, 2000). The particle size ranged between 12μm to 3138μm. The sediments were sampled at one location in the Richmond Hill stormwater pond, while sediments were sampled at four locations in the Scarborough stormwater pond. Arsenic, copper, iron, mercury, manganese, nickel, lead and zinc were observed to exceed the LEL in a stormwater pond located in the residential area of Richmond Hill, Ontario. TOC, Arsenic, chromium, copper, manganese, nickel and zinc were observed to exceed the LEL in a stormwater pond located beside highway 401 in Scarborough, Ontario. The concentrations of five heavy metals, i.e., arsenic, copper, manganese, nickel and zinc, exceeded the LEL in both ponds though the magnitude of the contamination were different. The concentrations of total organic carbon (TOC) and heavy metals in the stormwater ponds are shown in Table 2.2.

Table 2.2: Concentrations of TOC and heavy metals (values in ug/g (ppm) dry weight unless otherwise noted) for 4 sample sites in Scarborough (S.1, S.2, S.3, S.4) and 1 sample site in Toronto area (Rh1) (Rochfort, et.al, 2000).

Element	LEL µg/g	SEL µg/g	S.1	S.2	S.3	S.4	Rh1
TOC %	1	10	2.64	1.67	2.4	0.42	0.36
Al %			1.02	1.3	0.33	0.2	1.04
As	6	33	2.5	1.3	7	2.5	15
Cd	0.6	10	<1	<1	2	<1	<1
Co			1	5	0.5	0.5	5
Cr	26	110	25	24	16	7	35
Cu	16	110	55	37	66	18	75
Fe %	2	4	1.52	2.05	1.13	0.74	2
Hg	0.2	2	0.165	0.064	0.054	0.032	0.056
Mn	460	1100	481	484	232	238	766
Ni	16	75	22	24	12	14	21
Pb	31	250	42	24	30	29	24
Ti			356	527	194	107	167
V			25	34	15	9	27
Zn	120	820	219	117	124	64	180

Table 2.3: Concentrations of ten regulated heavy metals (values in ug/g (ppm) dry weight unless otherwise noted) for 5 samples obtained from different locations in the Kingston pond. K1, K2, K3 and K4 indicate different sampling locations in the Kingston pond (Marsalek el.al, 1997).

Element	LEL µg/g	SEL µg/g	K1	K2	K3	K4
As	6	33	2	2	2	2
Cd	0.6	10	0.7	1.3	1.2	1.4
Cr	26	110	66	113	128	122
Cu	16	110	20	58	78	80
Fe %	2	4	2.62	3.15	3.06	3.02
Pb	31	250	39	123	158	149
Mn	460	1100	568	474	482	485
Hg	0.2	2	0.019	0.052	0.067	0.066
Ni	16	75	24	33	35	34
Zn	120	820	113	290	391	406

Physical and chemical properties of bottom sediment and suspended particulates were studied at a Kingston stormwater pond (Marsalek el.al, 1997). The pond is an on-stream stormwater storage facility, used to remediate the impact of runoff from a newly built shopping plaza. Five samples were taken from different locations of the pond. The size of the particles ranged from 0.24μm to 8mm. The assessment of total metals in the pond sediment against the Ontario Ministry of the Environment (MOEE) sediment quality guidelines indicated a gross pollution by Cr, and a marginal-to-significant pollution by seven regulated heavy metals (Cd, Cu, Fe, Pb, Mn, Ni and Zn).

The concentrations of ten heavy metals in the Kingston pond are shown in Table 2.3.

2.3. Treatment of Contaminated Sediment

The suitable method for the treatment of contaminated sediment depends on the nature of the contaminants and severity of the contamination. Stormwater sediments are observed to be marginal to significantly polluted, further treatment of the sediment is highly recommended before ultimate disposal. Treatment of the contaminated sediments involves the application of the primary decontamination processes to reduce, destroy or immobilize the targeted contaminants. These processes can be physical, chemical, biological or thermal. A brief review of common remediation techniques for contaminated sediments is presented below;

2.3.1 Physical Treatment

The following physical treatment methods are available:

Soil Washing

Soil washing is a process that uses water to physically separate the sediments by particle size into a reusable bulk fraction and a smaller fraction containing concentrated contaminants (Ontario Ministry of the Environment,1996). Organic contaminants are often absorbed to the finer silt and clay particles, thus the separation of the fine particles reduces the volume of total contaminated sediments and reuse the non-contaminated larger particles such as sand. This technique is suitable for treating sediments containing high concentrations of PAHs, PCBs, fuel oil, heavy metals and pesticides.

2.3.2 Chemical Treatment

The following chemical treatment techniques are available:

(i) Chelation

Chelation is a process of forming a stable bond or complex between a metal cation and a ligand (Ontario Ministry of the Environment,1996). The bond helps to stabilize the resulting complex containing the metal contaminant. Edetic acid is a commonly used polydenate-chelating agent. Chelation is one of the options to treat contaminants with high concentrations of heavy metals.

(ii) Chemical Reduction/Oxidation

Chemical reduction/oxidation technology uses chemical additives to detoxify contaminants to less toxic or immobile forms (Ontario Ministry of the Environment,1996). This process transfers electrons from the contaminant to the

oxidizing agent. Typical oxidizing agents include various forms of chlorine, potassium permanganate, hydrogen peroxide, persulfate and ozone.

(iii) EDTA Extraction

Ethylene diamine tetra acetic acid (EDTA) is a complexing agent that dissolves heavy metals. The removal efficiency for toxic heavy metals including cadmium, zinc, lead and copper is found to be 60%-90%. EDTA can also be recycled or reused the complexing agent in the process (Rienks, 1998).

(iv) Solvent Extraction

An organic solvent is used to dissolve organic pollutants in the sediment (Ontario Ministry of the Environment,1996). Extraction efficiency of this method is highly dependent on the solubility of the pollutant, the binding mechanisms of the pollutant to sediment particles and the contact between solvent and sediment particles. One commonly used organic solvent is acetone.

2.3.3 Biological Treatment

The following biological treatment techniques are avalible:

(i) Thioleaching

Thioleaching uses microorganisms of the genus Thiobacilli to produce sulphuric acid by oxidation of sulphides or added sulphur (Ontario Ministry of the Environment,1996). The change of redox potential and the souring of sulphuric acid can dissolve heavy metals. A mixture of Thiobacilli and acidophulic microorganisms can degrade organic compounds such as mineral oil and PAHs.

(ii) In-situ Bioremediation

In-situ bioremediation is a process that uses indigenous microorganisms to degrade organic contaminants (Ontario Ministry of the Environment,1996). In the presence of sufficient oxygen, microorganisms convert many organic contaminants to carbon dioxide, water and microbial cell mass. In the absence of oxygen, the contaminants may be ultimately reduced to methane, carbon dioxide and trace amounts of hydrogen gas. However, contaminants may be degraded to undesirable intermediate products.

(iii) Slurry Bioreactor

Slurry bioreactor can treat a variety of organic contaminants including chlorinated and non-chlorinated volatile organics, PAHs, PCBs and pesticides (Ontario Ministry of the Environment,1996). The sediment is mixed with water and is controlled by a biological treatment vessel.

2.3.4 Thermal Treatment

The following thermal treatment techniques are available:

(i) Incineration

Incineration destroys contaminants using high temperatures in the presence of oxygen and is effective in destroying a wide range of organic contaminants. However, waste from incineration may cause potential air quality impacts (Ontario Ministry of the Environment,1996).

(ii) Pyrolysis

Pyrolysis involves the destruction of organic material in the absence of oxygen under high temperature (Ontario Ministry of the Environment,1996). The absence of oxygen separates contaminants into organic fraction and inorganic fraction. The organic fraction includes gas and the inorganic fraction includes salts, metals and particulates. It is normally used to treat high concentration of organics that are not conductive to incineration. Air emissions contain carbon monoxide, hydrogen and methane.

(iii) Thermal Desorption

Thermal desorption is a process which removes contaminants by means of evaporation. 99% removal of organic contaminants can be achieved at an operating temperature between 500 °C and 600°C (Rienks, 1998). Beside mercury, heavy metals which have a much higher boiling temperature than organic, cannot be removed. The high temperature process that uses temperatures between 600°F and 1000°F can volatilize a greater range of contaminants. Potential pollutions of water and air by the sidestream wastes are the main concerns for this process.

As stormwater sediment contains a high concentrations of heavy metals and a fairly high amount of organics, the potentially effective treatment methods for stormwater sediments should enable the treatment of both heavy metals and organics. Soil washing can only reduce the volume of contaminated sediments, further treatment of the contaminated portion is still necessary. A combination of two treatment methods, for example, using pyrolysis followed by chelating, may

be a possible way to treat both organic and heavy metals. However, the cost and the considerable volume of work make this option not very promising either. Therefore, it is essential to develop a new, innovative method to treat the contaminated stormwater sediments.

2.4 Scope of the thesis

This thesis focuses on the advanced physical analysis of stormwater sludge using a laser diffraction particle size analyzer, an optical microscope and a scanning electron microscope (SEM); and elementary characterization by neutron activation analysis (NAA). The effects of different weather conditions and land-uses on stormwater sediment characteristics are investigated. The concentrations of the regulated elements are compared to the sediment quality guidelines of the Ontario Ministry of Environment. If this comparison indicates a need for further treatment of stormwater sediments, a preliminary advanced treatment method, i.e., plasma technology, will be tested out and evaluated.

The first two chapters have identified the sources of possible pollution of sediments accumulating in stormwater ponds and indicated a potential contamination of the sediments. For this research, samples of stormwater sediments were obtained from four stormwater detention ponds first. Details of the stormwater pond sampling sites and the associated land-use categories are presented in chapter 3. Chapter 4 describes the methodology of the physical and chemical analyses, introducing the fundamentals and principles of laser

diffraction technology, scanning electron microscope and neutron activation analysis. In chapter 5, the results of analysis are reported and compared. The effect of summer and winter conditions and different land-uses are investigated. The results from the preliminary treatment of stormwater sediments by thermal plasma are reported in Chapter 6, where the physical and elementary characteristics of the stormwater sludge after treatment are compared to the original sludge. Chapters 7 and 8 present the conclusions of the study and recommend directions for further research.

Chapter 3

Stormwater Pond Locations and Upstream Land Uses

Four different stormwater ponds around the city of Hamilton, Ontario, Canada were sampled in the summer of 2005. The city of Hamilton is situated in the west end of Lake Ontario, with Hamilton Harbour forming a major part of its waterfront. The city includes the commuities of Hamilton and Stoney Creek, Towns of Ancaster, Dundas and Flamborough, and Township of Glanbrook. It has a population of 460,000 and an area of 1,120km^2. The Ontario Ministry of Environment states that the water and sediment quality degradation occurs in local streams and Hamilton harbour, and concerns of toxic contaminants in water, air and soils have been raised (Ontario Ministry of Environemnt, 2001; Poulton, 1996; Charlton, 1996).

Two of the stormwater ponds are located in the town of Flamborough, Ontario, Canada. The remaining two ponds are located beside Dartnall Road and Ancaster soccer field in Hamilton. The first two ponds are located in residential areas and the last two ponds are located in commercial areas. For the one stormwater pond located at Waterdown Road in Flamborough, sediment samples were taken on January and July in 2005 for the purpose of winter and summer comparison.

3.1 Parkside Road Site

The Parkside Road site pond in Flamborough is bounded by Highway No.5 (Dundas Street) to the south and Parkside Drive to the north. It is on the east

side of the newly developed Waterdown settlement area. The drainage area of the pond is 31.6 hectares, it is located in Lots 4 and 5, Concession 3 in the Town of Flamborough. The stormwater detention pond was designed and constructed to control run-off quality from the residential area. The outflow from the pond drains to the Grindstone Creek via three separate outlets, hence the quality of the water will affect the natural environment.

3.2 Waterdown Road Site

This site is located in the Rockview summit subdivision, which is located in a section of Lot 11, Concession 3, former Geographic Township of east Flamborough, now in the Town of Flamborough. It is bounded by a residential subdivision to the east, Highway No.5 (Dundas street) and Belmont residential subdivision to the north; proposed industrial business parks to the west and conservation lands and the Niagara Escarpment to the south.

The site is located within the Grindstone Creek drainage basin, the upstream drainage areas include one block for street townhouses and two blocks of multiple family dwellings, the total drainage area is approximately fourteen hectares. The northern portion of the site consists of abandoned farmland while the southern portion is forested. The upstream area is well drained and generally slopes to the south towards the Niagara Escarpment. Municipal water and sanitary sewers service the upstream area of the pond.

3.3 Dartnell Road Site

The Dartnell Road stormwater detention pond is located between Dartnall Road Interchange and Lincoin Alexander Parkway in Hamilton. There are three concrete box culverts, located in Darnall Road, E-W expressway and Dartnall road south Ramp. The areas of the 3 concrete box culverts in this storwmwater pond are 1050 m^2, 1180 m^2 and 632.5 m^2 respectively. This stormwater pond is also used as part of the plan for water quality and quantity management for the Red Hill Creek. It is used to form an overall solution to mitigate potential impacts on water quality and fisheries habitat.

3.4 Ancaster Soccer Field Site

The Ancaster Soccer field Site is located in Ancaster, Ontario, Canada. The stormwater pond is bounded by Golf Links Road and Meadowlands Blvd, beside a shopping mall and a soccer field. The total area of the Facility is 3.15 ha. It is mainly used for flood control. Table 3.1 lists the location and drainage area type of the four sampling sites.

Table 3.1: Location and drainage area type for the four sampling sites

Location	Parkside Road	Waterdown Road	Dartnell Road	Ancaster Soccer field
Area Type	Residential	Residential	Highway/commercial	Commercial/light Industrial

Chapter 4
Methodology

4.1 Sampling Method

Sediment samples from the four sites were obtained by a steel scope and tray. The equipment were first washed with hexane in order to remoe any possible contaminants. The sludge was collected from the top five centimetres of sediment in the pond. The sludge was well mixed and placed into eight 250ml sealed bottles. The sludge samples were kept in a freezer at 4 ^{o}C before analysis.

4.2 Particle Characteristics

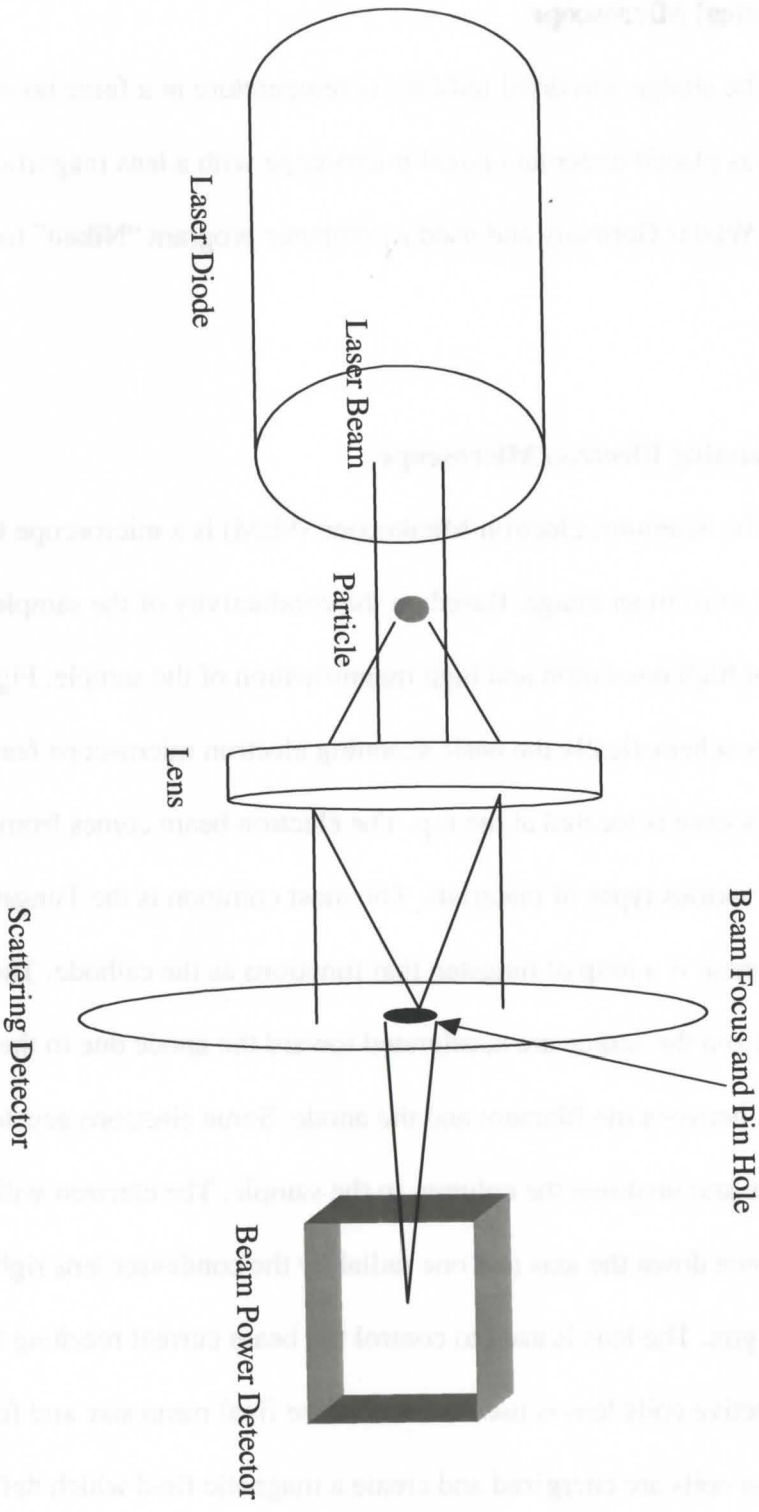
The physical properties of the sludge include the particle size distribution, image and shape of the particles. Particle size distribution is measured by the laser diffraction method. Image and shape of the particles are shown by optical microscope and scanning electron microscope.

4.2.1 Laser Diffraction Method

Wet sample was added into the laser diffraction particle size analyzer (Malvern Mastersizer 2000, HydroS) in small portions. Fifteen measurements of different parts of the sludge were taken. The bottom part of the container of the sludge may contain heavier particles while the upper part of the container might contain lighter particles due to gravity. Thus, well stirring before analyzing any sample out of the container was essential. Particles in the solution scatter the broadened beam of the laser light onto a Fourier lens, and the lens focuses the

scattered light onto a detector array. Using an inversion algorithm, a particle size distribution can be inferred from the collected diffracted light data. Laser diffraction instruments use Mie Theory as the basis of their size calculations (Malvern, 2001). This theory was developed to predict the way light is scattered by spherical particles and deals with the way light passes through, or is absorbed by the particle. Using this theory, all particles are assumed to be spherical. Accuracy of ± 1% was proved in of Malvern Quality Audit Standard. Figure 4.1 illustrates schematically the basics of laser diffraction particle size measurement.

Figure 4.1: Schematic of laser diffraction particle size measurement.



4.2.2 Optical Microscope

The sludge was dried until room temperature in a fume hood. Then the sludge was placed under an optical microscope with a lens magnification of 320 by Leitz Wtzlar Germany and used a computer program "Nikon" to view the image.

4.2.3 Scanning Electron Microscope

The Scanning Electron Microscope (SEM) is a microscope that uses electrons to form an image. Based on the conductivity of the sample, it produces images of high resolution and high magnification of the sample. Figure 4.2 illustrates schematically the basic scanning electron microscope features. The electron source is located at the top. The electron beam comes from a filament, made of various types of materials. The most common is the Tungsten hairpin gun. This filament is a loop of tungsten that functions as the cathode. The electrons emitted from the source are accelerated toward the anode due to the large potential between the filament and the anode. Some electrons accelerate right by the anode and on down the column, to the sample. The electron will experience both a force down the axis and one radial by the condenser lens right after the electron gun. The lens is used to control the beam current reaching the sample. The objective coils lens is used to resolve the final mean size and focus. The deflection coils are energized and create a magnetic field which deflects the beam

back and forth in a controlled pattern. The distance from the bottom pole piece of the objective lens can be carried and allow the electron beams to scan the samples outside the magnetic field range of the lens. When the electron beam hits the sample, it produces secondary electrons. These electrons are collected by a backscatter detector, then converted to a voltage and amplified.

For standard SEM imaging, the back-scattered electrons (BSE) and secondary electrons are detected, and the resulting signal is processed to yield a pixel in an image. Progressively, as the entire sample is scanned, an image of the sample is formed. The resulting image can be saved and reprocessed in the same way that a greyscale image can be modified by image analysis. The amplified voltage is applied to the grid of the CRT and causes the intensity of the spot with light to change. The image consists of thousands of spots of varying intensities on the face of a CRT that correspond to the topography of the sample. It is crucial to optimize the image to obtain all detailed information of the particles.

The two important issues for SEM analysis are clarity and contrast. After taking the image, the image recognition software take the approach of selecting or separating one region from another by the different image qualities of clarity and contrast. It is essential that the contrast between one region and the next be as uniform as possible over the entire image.

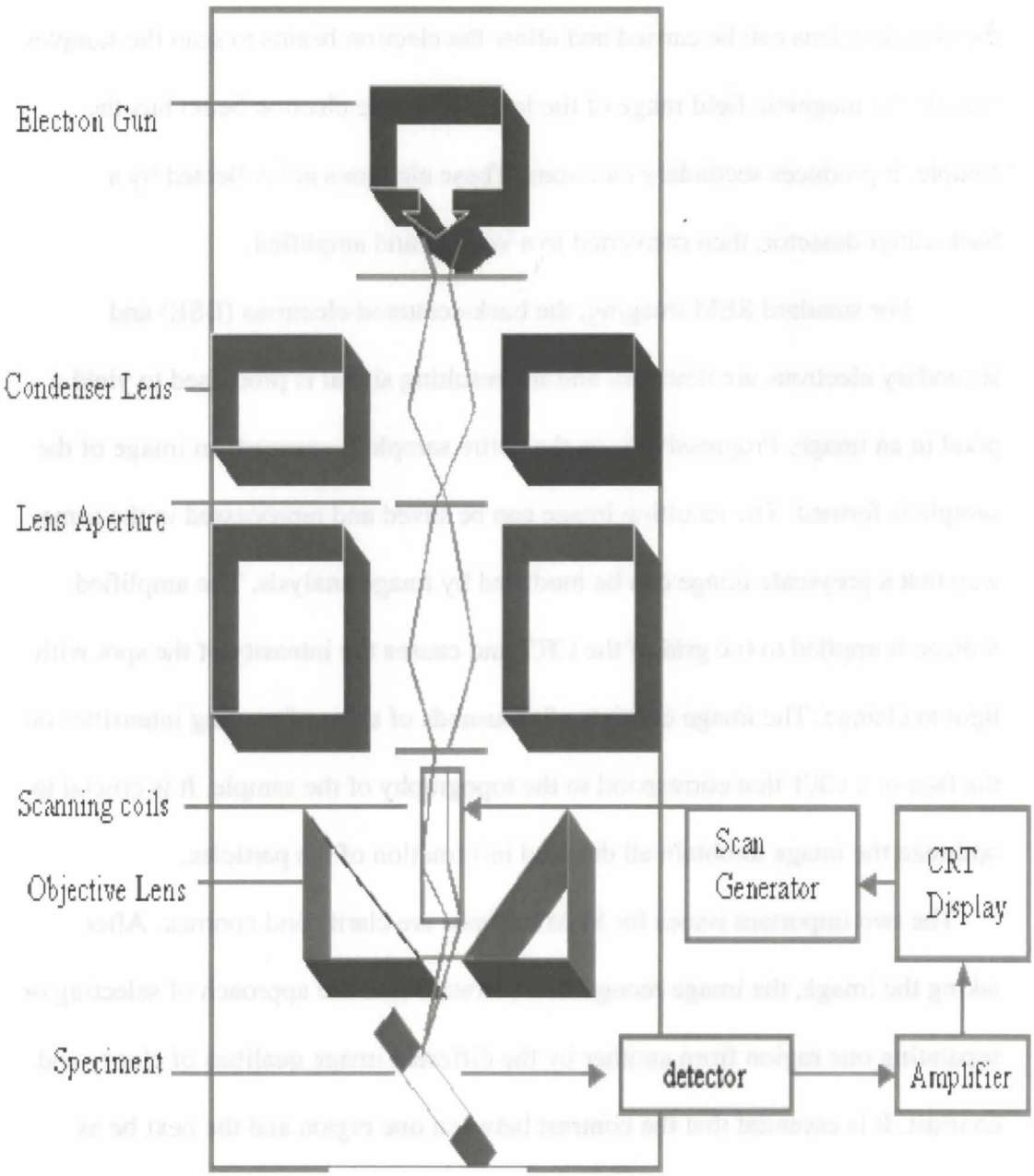


Figure 4.2: Schematic of scanning electron microscope

4.3 Composition of Sediment

4.3.1 Advantages of Neutron Activation Analysis

The Neutron Activation Analysis (NAA) facility at McMaster Nuclear Reactor was used for stormwater sludge composition analyses. It is an extremely sensitive multi-element analysis technique with great accuracy and precision. The ultimate sensitivity for many elements is found to be above other techniques. As this technique does not need any irradiation chemical treatment for the analysis, it is free from blank error caused by the use of contaminated reagents and eliminates the necessity for rigorous microchemical procedures in the determination of trace constituents. It is a non-destructive analysis that allows determination of many elements simultaneously at trace level in samples (Soete, et.al, 1972; Leninan, et al, 1971).

These advantages of NAA make it compatible to other methods of analysis. Inductively Coupled Plasma (ICP), the most common method used for analysis of sediment composition, requires calibration of elements for each analysis. Trace element determinations are usually required in the presence of significantly greater concentrations of other elements. In order to obtain the best determination limits for the elements, a minimum set sample dilution must be used. Less stability in the medium and long times needed for the techniques severely complicates calibration procedures, especially where changes in sensitivity with time vary across the spectrum (Date, 1985; Date, 1986). A sample is often digested by the addition of different chemicals and concentrate down to a

known volume before being analyzed by ICP (Bishop el.al, 2000). This may cause possible contamination of samples. Although ICP is able to analyze more elements than NAA, the complicated calibration procedure is a main draw back for this method. Other techniques such as DC arc plasma and RF arc plasma requires calibration for measurements (Belsterling, 1981; Knoll, 1989; Beck et al, 1969). Proton Induced X-ray Emission (PIXE) and X-ray fluorescence (XRF) and other radiation techniques are also used in many applications. X-ray fluorescence is able to measure some of the oxide in the samples as well. However, these methods can only be used for limited elements. Also, Neutron Activation Analysis has a detection limit lower than other method in most of the elements.

4.3.2 Theory of Neutron Activation Analysis

The sludge was naturally dried at room temperature under a fume hood and placed into a 10g container. The samples were irradiated in the core of the nuclear reactor. Figure 4.3 shows the principle of NAA. A neutron is injected into a sample and interact with a target nucleus by a non-elastic collision, then a compound nucleus are formed in a highly excited state. The excited nucleus emits nuclear particles or prompt gamma rays and undergoes a rapid de-excitation to a more stable configuration, typically within 10^{-14} s. The new nucleus is radioactive and will further de-excite by emitting decay gamma rays with a specific energy depending on each composition element. The NAA relies on the measurement of either these characteristic prompt or decay gamma rays for identifying elements and determining their amounts present in samples. The

technique is flexible with respect to the time of decay for different nuclei. Elements can be separated into two categories: long-lived and short-lived. For nuclei that take more than 10 hours to decay, it is called a long-lived element and the given reaction time will be longer. For nuclei that take shorter than a few hours to half decay it is called short lived. Long-lived nuclides are difficult to excite, therefore the irradiation time should be extensive. The delay time of long-lived elements is approximately one week. On the other side, easily excited nuclides have a short half-life and therefore, the cooling and counting time should be appropriate.

Prompt gamma is also used in Neutron Activation analysis but for element which emits gammy ray and beta particles faster than general short-lived elements.

Figures 4.4 and 4.5 show typical raw gamma energy spectrum results directly from NAA for long-lived and short-lived respectively. Each specific energy wavelength emitted from the sludge samples corresponded to each element. The standard reference material (SRM) was used for the calibration of intensity and the evaluation of techniques employed in the analysis of coal and similar materials. The standards for the sludge are SRM 1632b and 1633b. SRM 1632b consists of a 50g bottle of bituminous coal with a nominal sulfur content of 1.9%. A unit of SRM 1633b consists of 75g of powdered material. The total error in each standard was calculated to be slightly less than 1% at the 95% confidence level.

Thirty-two elements were detected in the sediment. Only twenty-four elements were above the detection limit. Elements below detection limit indicate that their existences were unknown and its concentration could not be quantified. Table 4.1 shows the detection limit for each element. Other expected major components of the sludge that could not be measured by NAA techniques are Si, C, N, O, Cu, Pb and H.

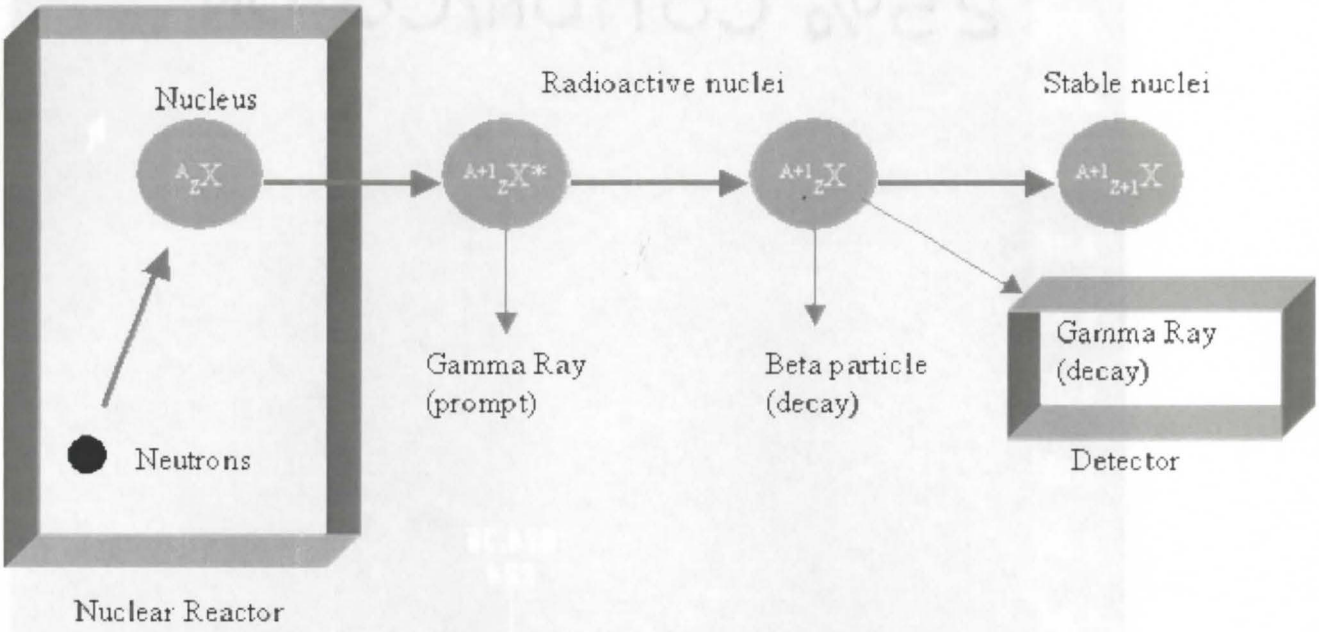


Figure 4.3: The principle of Neutron Activation Analysis

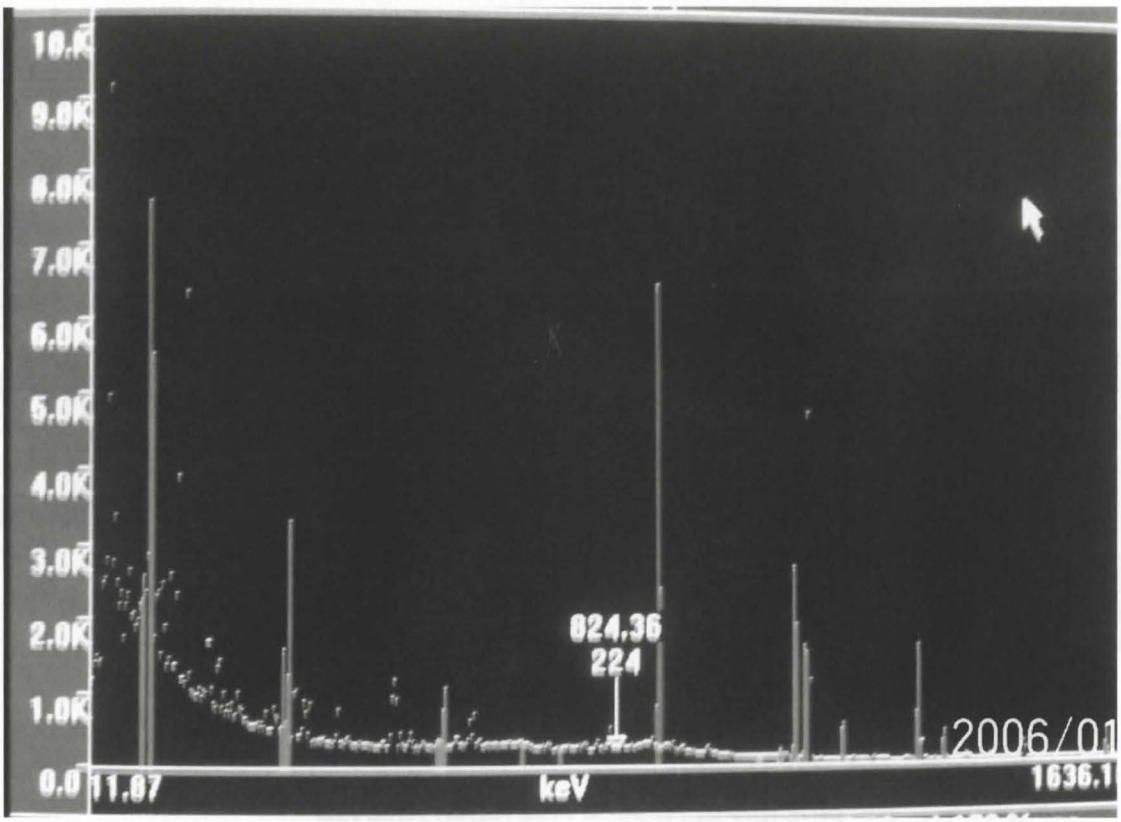


Figure 4.4: Typical gamma energy spectrum for long-lived result for Dartnell stormwater sediment sample.

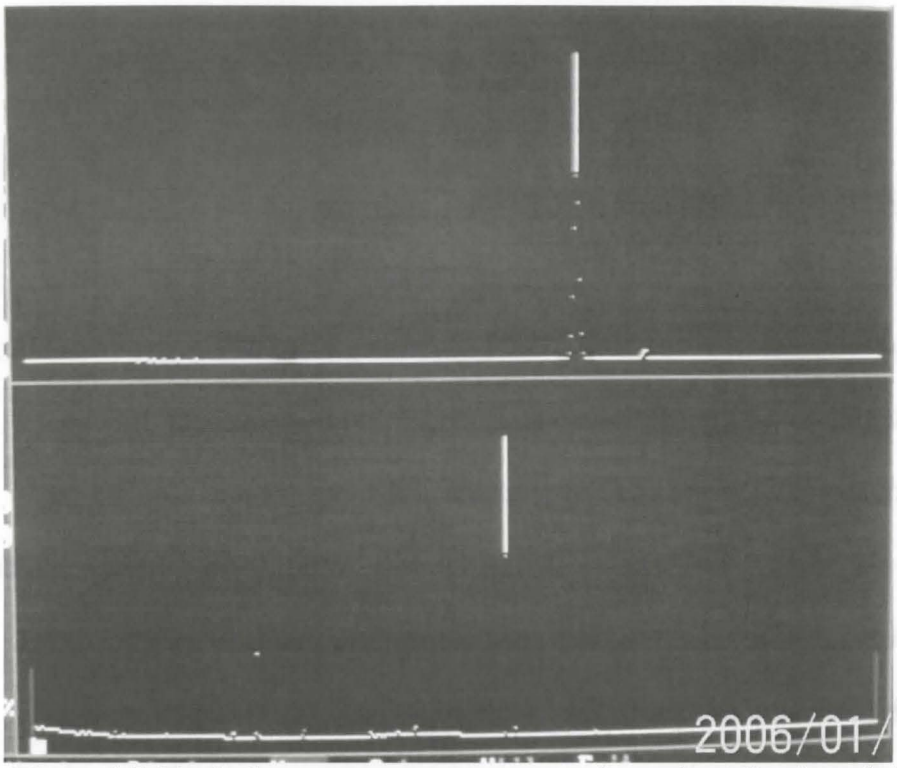


Figure 4.5: Typical gamma energy spectrum form short-lived result for Dartnell stormwater sediment sample.

Table 4.1:Detection limits of 33 elements in sediment determined by Neutron Activation Analysis.

Element	Limit (ppm)	Element	Limit (ppm)	Element	Limit (ppm)	Element	Limit (ppm)
Al	10	Co	1	K	1000	Sb	0.1
As	0.5	Cr	1	La	0.1	Sc	0.1
B	3	Dy	0.3	Mg	300	Sm	0.1
Ba	40	Eu	0.5	Mn	1	Ti	200
Br	2	Fe	1000	Mo	5	Th	0.3
Ca	1000	Ga	10	Na	10	V	0.5
Cd	1	Gd	1	Nd	1	W	1
Cl	10	I	10	S	5000	Zn	100

Chapter 5
Sludge Characterization

5.1 Sludge particle physical characteristics

Figures 5.1, 5.2, 5.3, 5.4 and 5.5 show the particle size distributions for Parkside road in summer, Waterdown road in summer, Waterdown road in winter, Dartnell road and Ancaster soccer field stormwater ponds in summer. Fifteen repeated samples for each site were conducted for the experiment. The sludge particle size distribution for Parkside road in summer, Waterdown road in summer, Waterdown road in winter and Dartnell road stormwater ponds in summer are all bimodal with maximum concentrations at 69μm, 45μm , 17μm and 20μm with another peak concentration around 831μm, 1258μm, 830μm and 831μm, respectively. The sludge particle size distribution for Ancaster soccer field stormwater pond is single mode with a maximum concentration of 20μm. The error percentage of fifteen repeated samples are within 10%.

The images from optical microscope showed that the particles in the dried sludge were irregular, and the sizes of each particle varied greatly. Some of the large particles were accumulation of smaller particles. Figures 5.6, 5.7, 5.8, 5.9 and 5.10 show the optical image of dried sludge of Parkside road in summer, Waterdown road in summer, Waterdown road in winter, Dartnell road and Ancaster soccer field stormwater ponds in summer. SEM captured more detailed images of the dried sludge compared to optical microscope. Figures 5.11 and 5.12 show the images of dried sludge in higher resolution and magnifications of 1000

and 2020 times, respectively. It clearly shows that the sludge consisted of two different structures. One structure is long, cylindrical materials and the other is scattered irregular material.

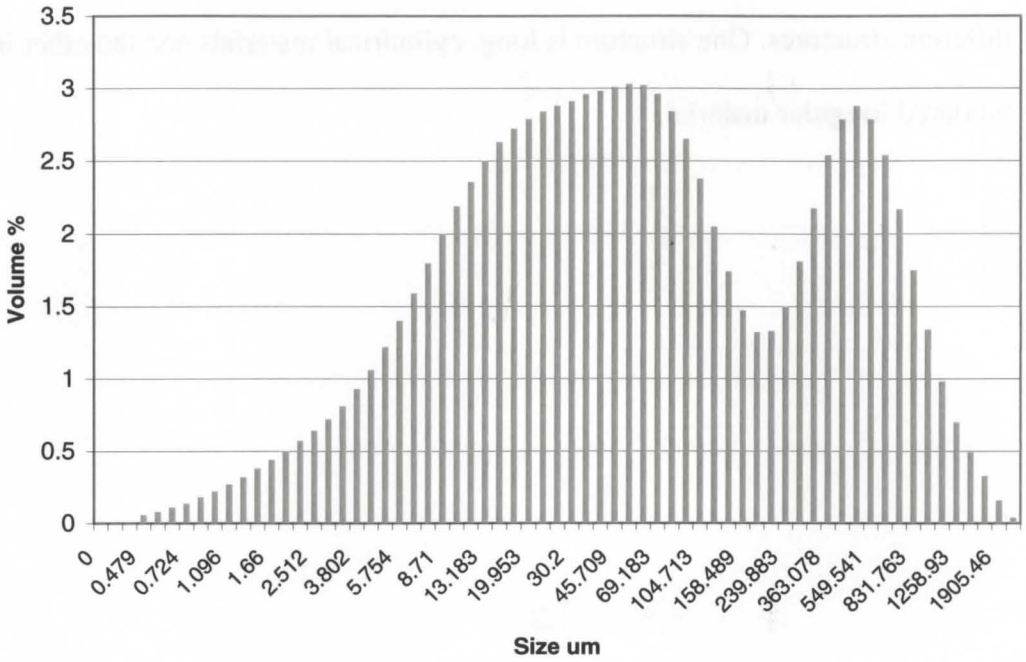


Figure 5.1: Particle size distribution for Parkside road stormwater pond sampled in summer

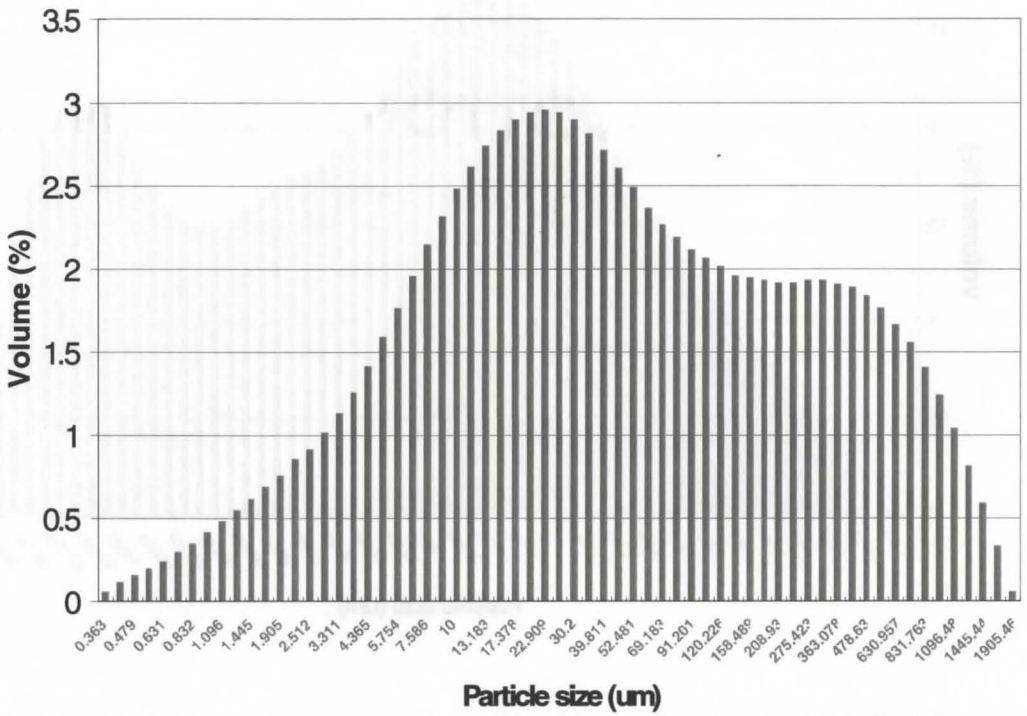


Figure 5.2: Particle size distribution for Waterdown stormwater pond sampled in summer

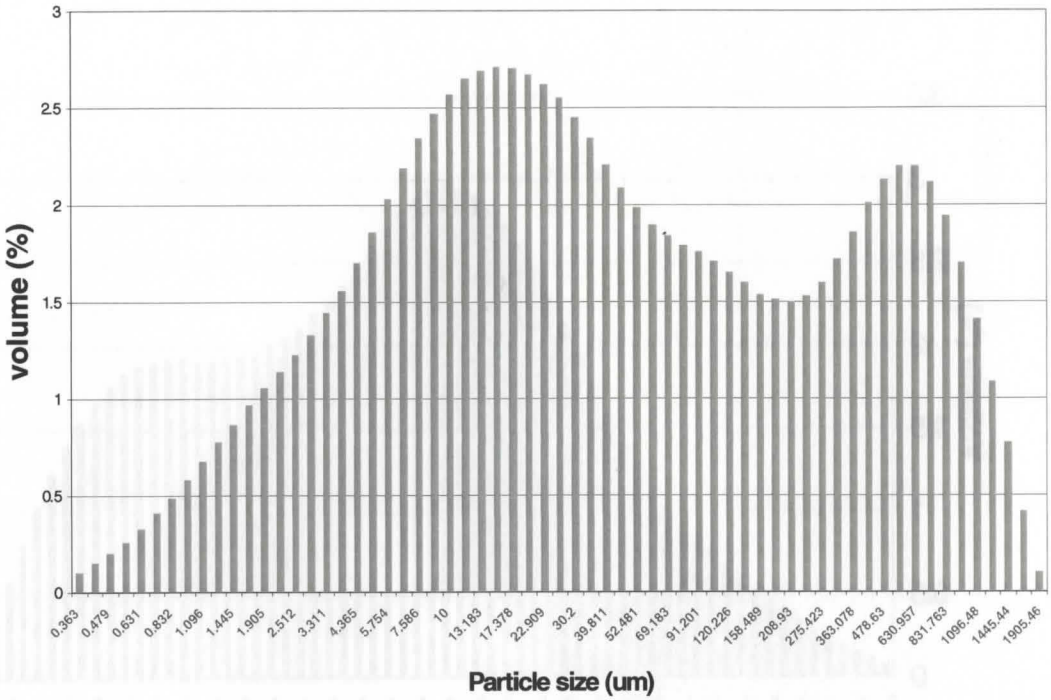


Figure 5.3: Particle size distribution for Waterdown stormwater pond sampled in winter

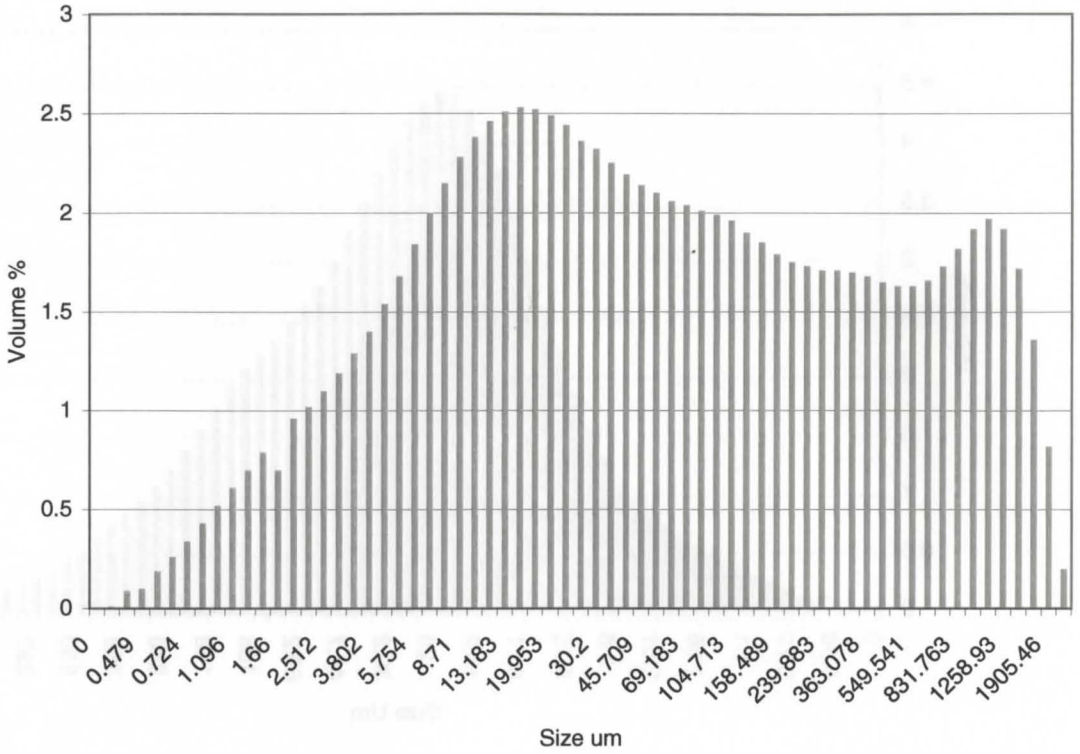


Figure 5.4: Particle size distribution for Dartnell road field stormwater pond sampled in summer

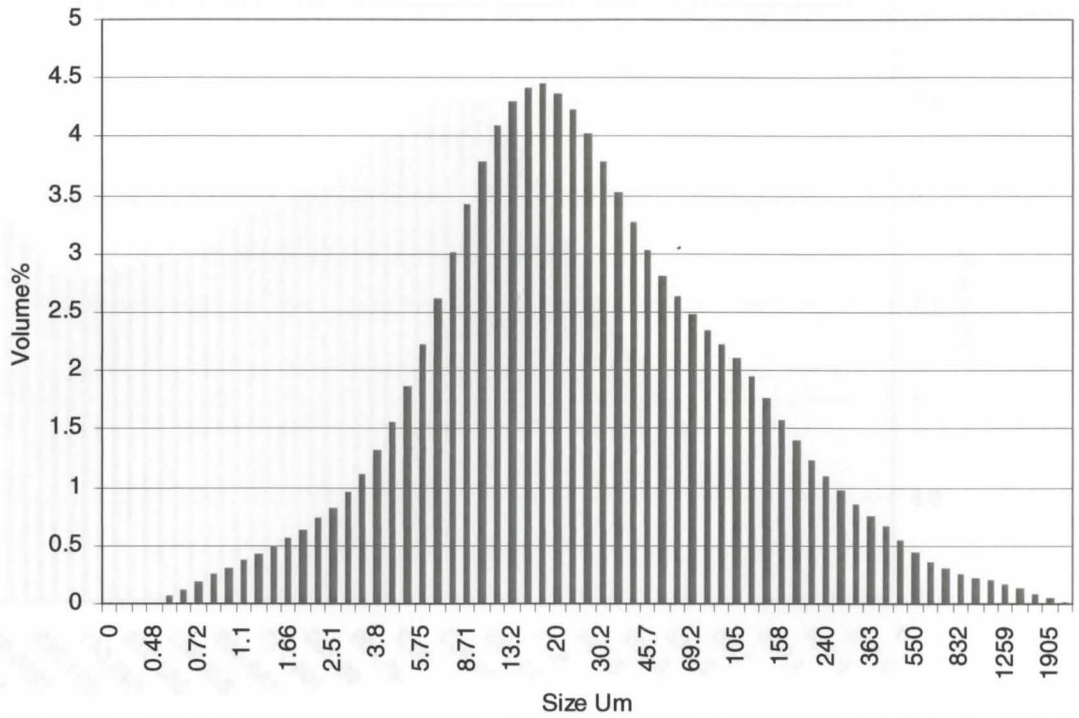


Figure 5.5: Particle size distribution for Ancaster Soccer field stormwater pond sampled in summer

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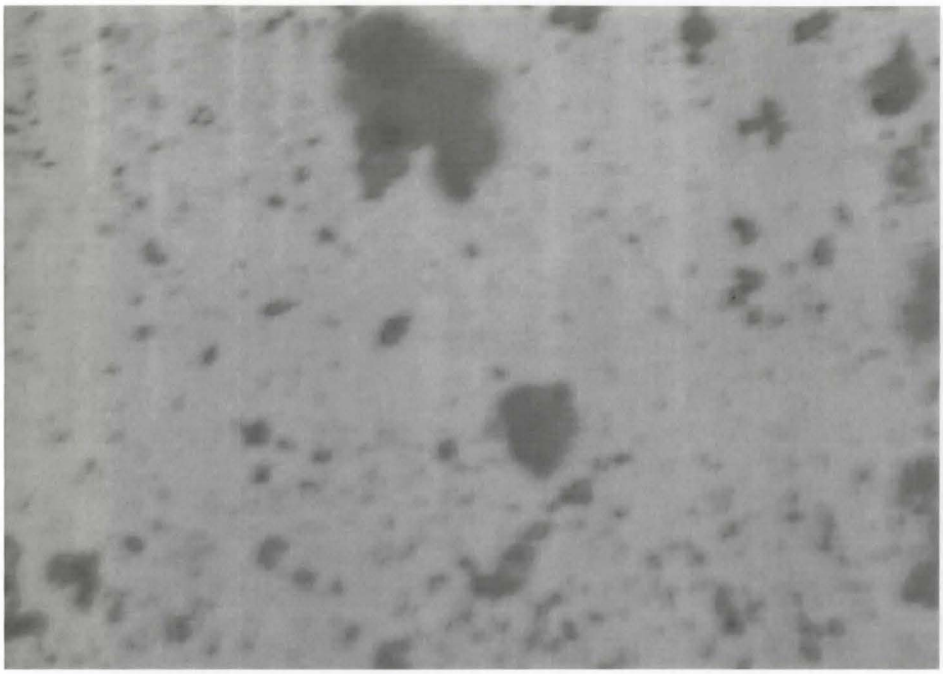

Figure 5.6: Image of dried sludge by optical microscope from Parkside stormwater pond sampled in summer.

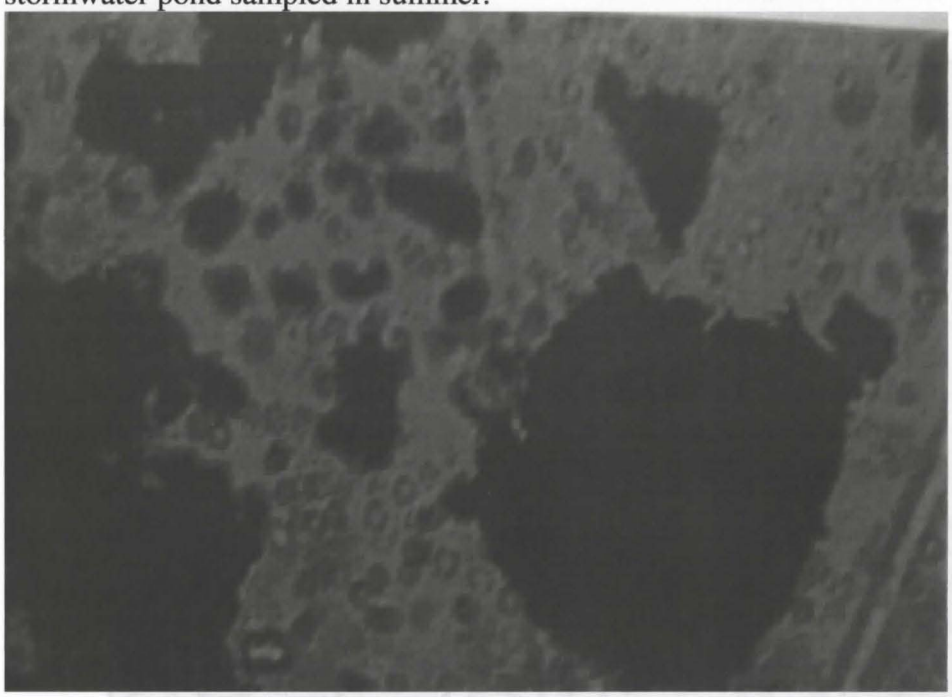

Figure 5.7: Image of dried sludge by optical microscope from Waterdown stormwater pond sampled in summer.

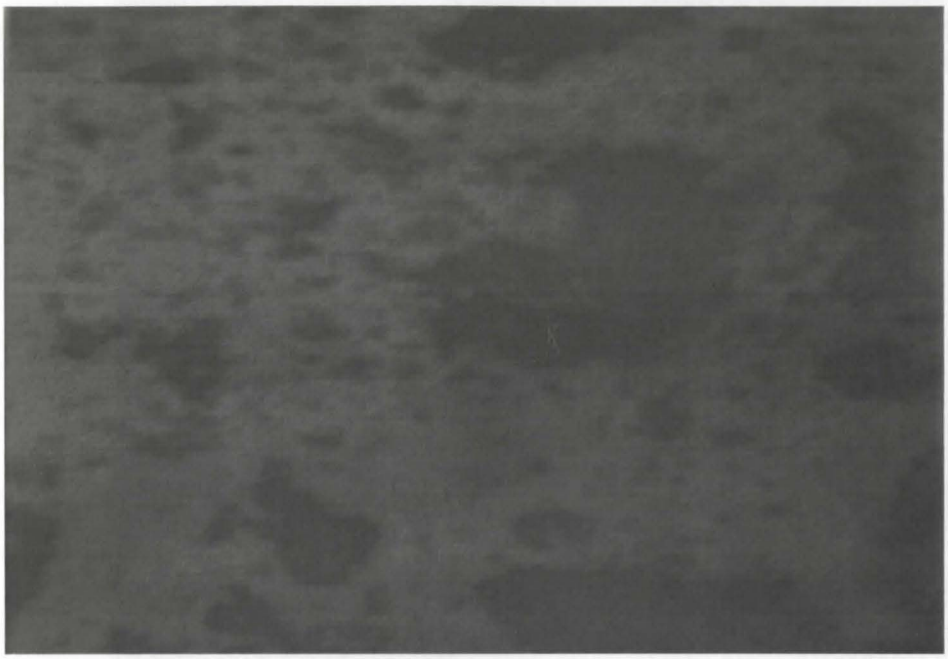

Figure 5.8: Image of dried sludge by optical microscope from Waterdown stormwater pond sampled in winter.

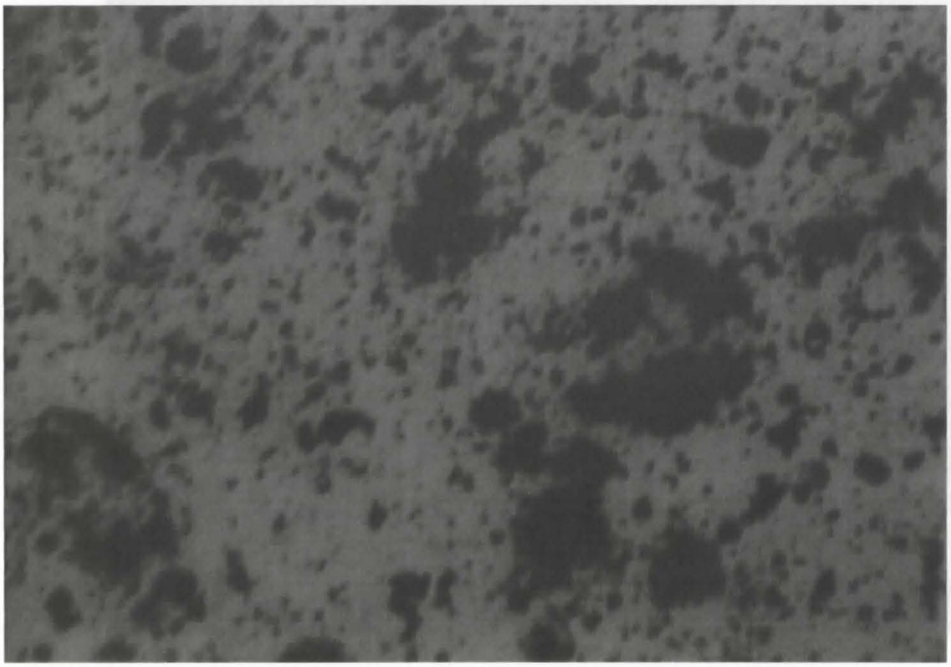

Figure 5.9: Image of dried sludge by optical microscope from Dartnell stormwater pond sampled in summer

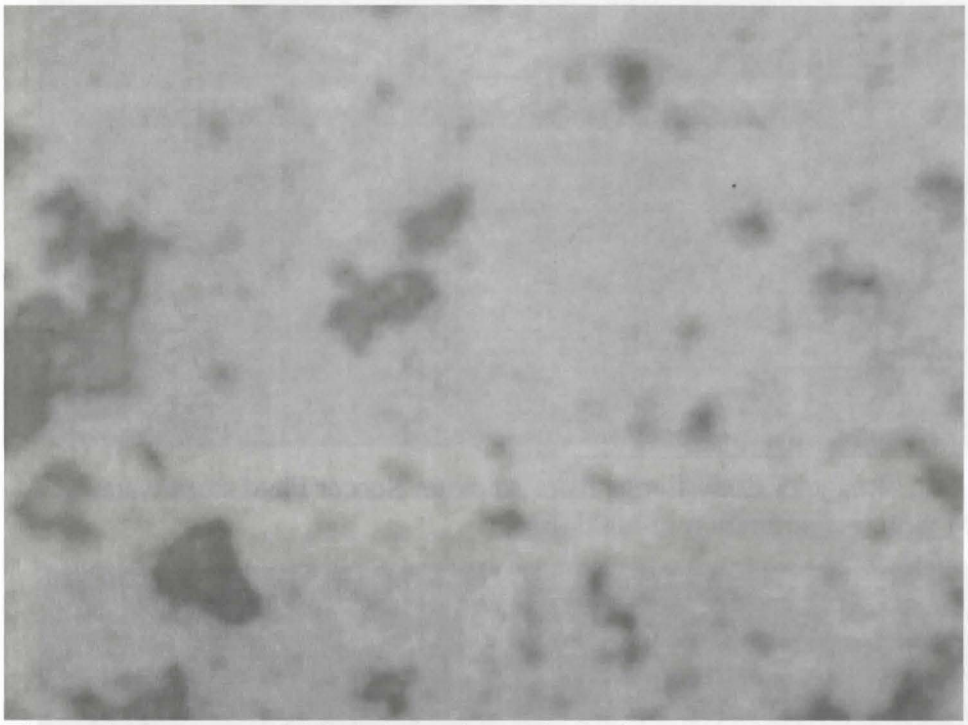

Figure 5.10: Image of dried sludge by optical microscope from Ancaster Soccer Field stormwater pond sampled in summer.

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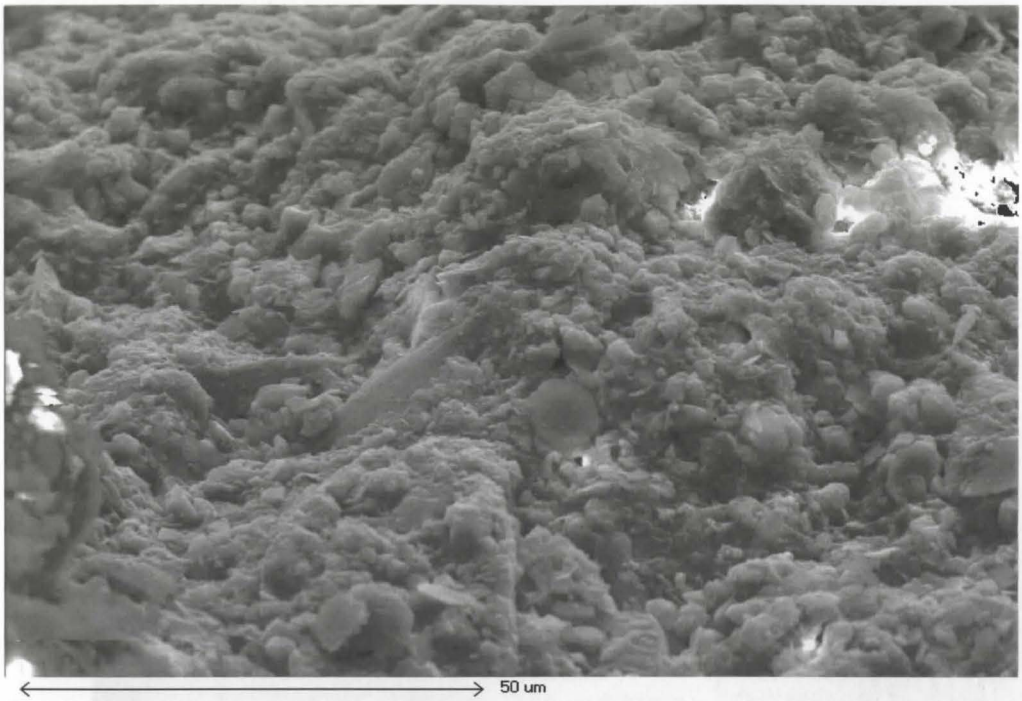

Figure 5.11: Image of dried sludge from Ancaster Soccer Field stormwater pond by SEM with magnification of 1000 times

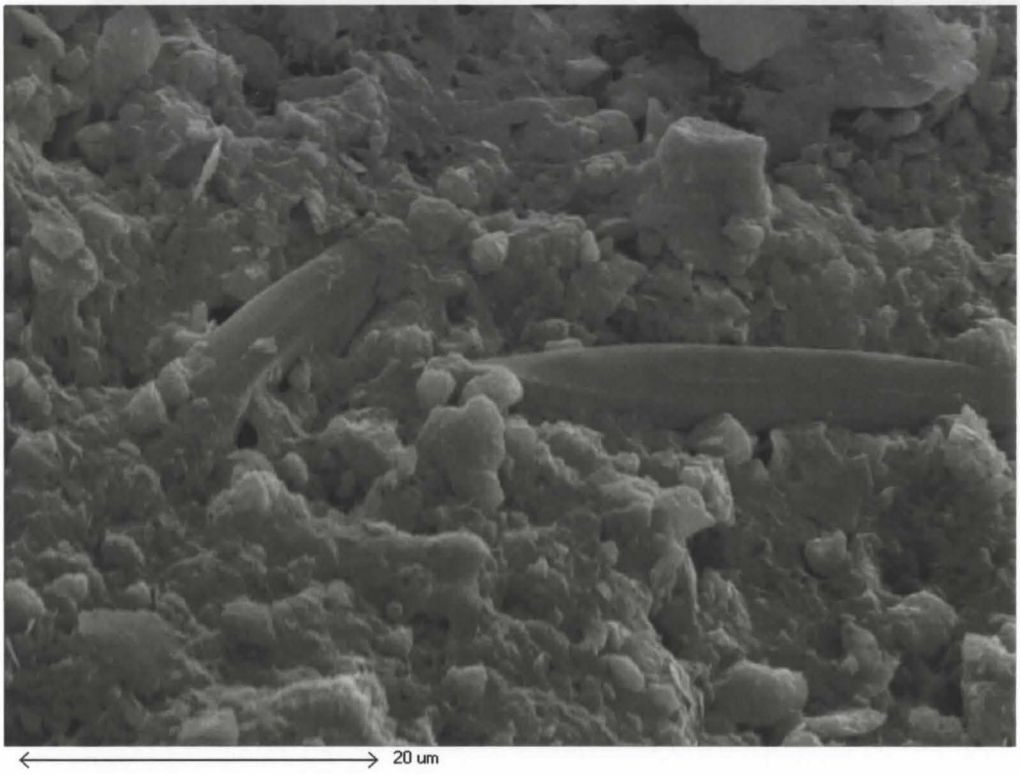

Figure 5.12: Image of dried sludge from Ancaster Soccer Field stormwater pond by SEM with magnification of 2020 times

5.2 Compositions of Stormwater Sediments

Thirty-two elements were observed in the sediment and nine among these thirty-two elements were below detection limit, while three elements are detected by prompt gamma by all were below detection limit. Comparisons between the concentration of each element in the four samples from the four stormwater ponds are shown in Figures 5.13, 5.14 and 5.15 the concentration ranges of 1000ppm and above, from 100 to 1000ppm and below 100ppm, respectively, where the standard deviations of each element are shown as bar in the figures. Three sets of sample were analyzed by NAA for each case. Nine elements were detected with a concentration higher than 1000 ppm, four elements had a concentration between 1000ppm and 100ppm, and the remaining ten elements had a concentration lower than 100ppm. The main compositions (above 1000ppm) of the dried sludge included Ca > Al > Fe > K > Mg > Na >Ti > Mn. The trace compositions (below 1000ppm) include Cl > Zn > Ba > Sr > Cr > V > La > Nd > As > Br > Co > Sc > Th > Sb > Sm > Eu. Since the concentrations of each element in five samples were fairly different, the descending order is just a rough estimation. Most elements have a quite similar pattern among the samples with some degree of deviation. A few elements such as Ca, Cr, Zn and Cl vary greatly within the samples.

Six regulated elements were detected by NAA. Table 5.1 shows the concentration of Cr, Fe, Zn, As and Mn of each pond compared to the LEL and

SEL of the Ontario Ministry of Environment (MOE). The assessment of Zn in all ponds sediment against the MOE sediment quality guidelines indicates a marginal-to-significant pollution. The concentrations of Fe in Dartnell and Waterdown stormwater pond indicate a marginal-to-significant pollution while the concentrations of Fe in the Ancaster and the Parkside stormwater pond in gross pollution. The concentrations of Cr in all ponds beside the Waterdown stormwater pond sampled in summer indicate a gross pollution. The concentrations of As in all ponds except Parkside stormwater pond are above the LEL. The concentration of Mn in all stormwater ponds is above LEL. The concentration of Cd is below detection limit in Waterdown winter sample.

Table 5.1: Comparison of the concentrations in ppm of Cr, Fe, Zn, As, Mn and Cd in all stormwater ponds to the LEL and SEL. (BDL = Below Detection Limit)

Element	LEL	SEL	Dartnell	Waterdown	Waterdown winter	Ancaster	Parkside
Cr	26	110	265	109	140	239	144
Fe	20000	40000	24441	32289	36851	49560	42673
Zn	120	820	204	251	214	511	165
As	6	32	13	9	11	16	5
Mn	460	1100	768	1090	946	772	825
Cd	0.6	10	-	-	BDL	-	-

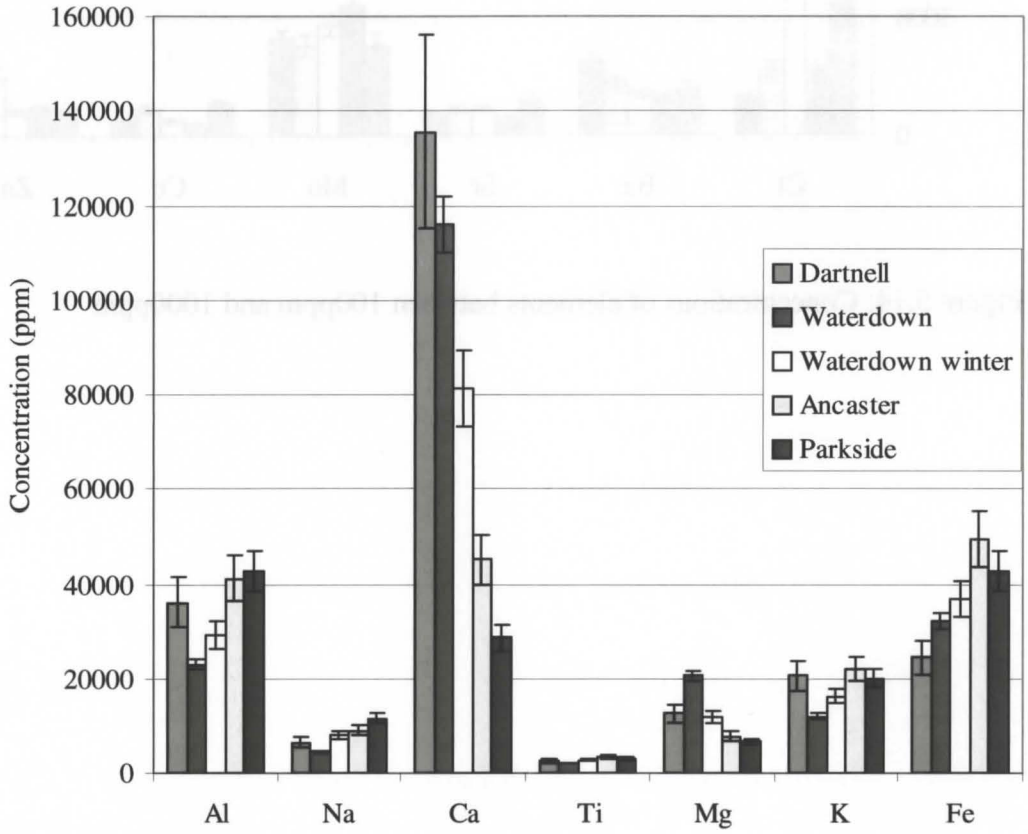

Figure 5.13: Concentrations of elements above 1000ppm

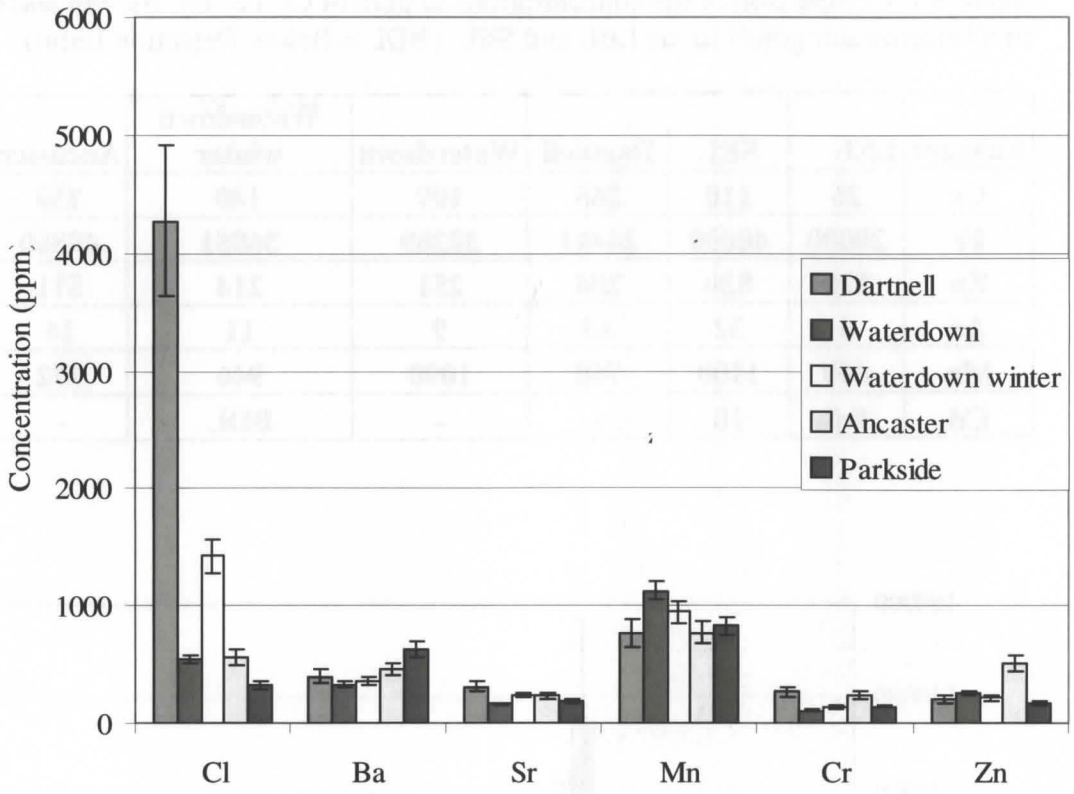

Figure 5.14: Concentrations of elements between 100ppm and 1000ppm

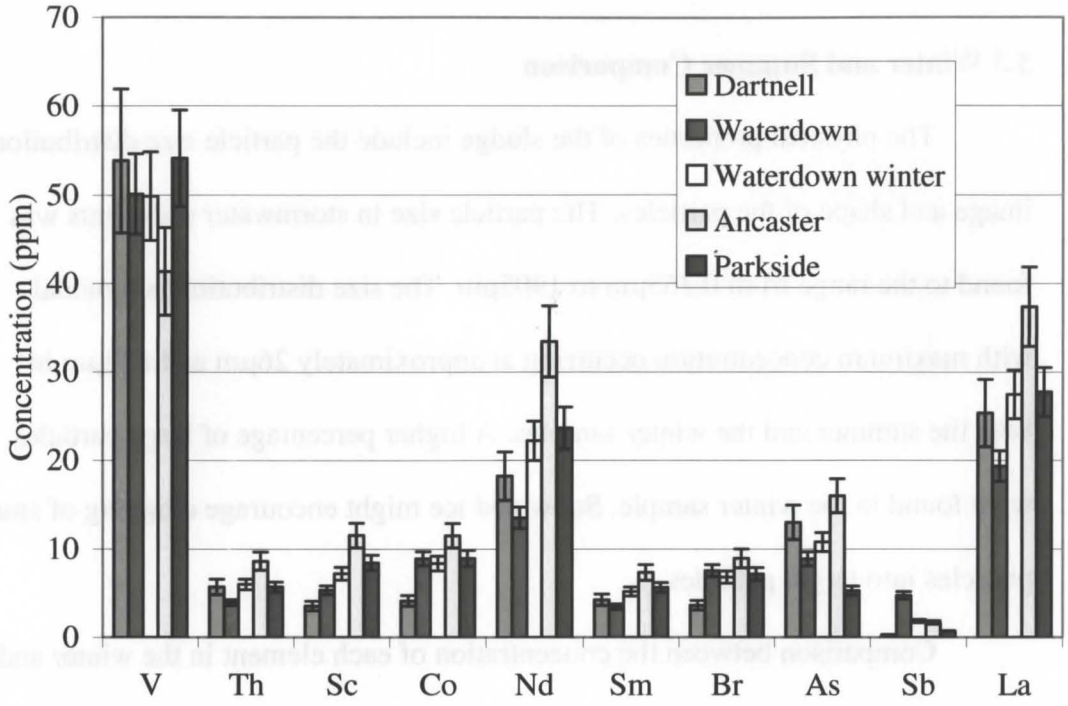

Figure 5.15: Concentrations of elements below 100ppm.

5.3 Winter and Summer Comparison

The physical properties of the sludge include the particle size distribution, image and shape of the particles. The particle size in stormwater sediments was found to the range from 0.363μm to 1905μm. The size distribution is bimodal with maximum concentration occurring at approximately 26μm and 830μm in both the summer and the winter samples. A higher percentage of large particles were found in the winter sample. Snow and ice might encourage clogging of small particles into larger particles.

Comparison between the concentration of each element in the winter and summer samples are shown in Figures 5.16, 5.17 and 5.18 for the concentration ranges of 1000ppm and above, between 100 to 1000ppm and below 100ppm, respectively. In the Waterdown stormwater pond, eight elements are detected with concentrations higher than 1000ppm, six elements have a concentration between 1000ppm and 100ppm, and the remaining ten elements have a concentration lower than 100ppm. The main compositions (above 1000ppm) of the dried sludge include Ca > Al > Fe > K > Mg > Na >Ti > Mn. The trace compositions (below 1000ppm) include Cl > Zn > Ba > Sr > Cr > V > La > Nd > As > Br > Co > Sc > Th > Sb > Sm > Eu. One of the major compositions, Si, which cannot be detected by NAA, but expected to present in stormwater sediment. Calcium, Aluminum, and Iron are naturally occurring and are often abundant within soils (Timothy, 2001), thus, high concentrations of these three elements are expected in

stormwater sediments. Also, the main compositions of residential soil are Ca, Fe, Al and Mg in the report of soil investigation in Port Colborne, Ontario in 2002 (MOE, 2002).

The compositions of elements present in the sediment are similar between summer and winter samples; although the concentrations of each element are slightly different. The concentrations of Na and Cl in winter samples are higher than those in summer samples; while the concentrations of Ca and Mg in the summer samples are higher than those in winter samples. Other elements have fairly similar concentrations in both seasons.

Road salts are used in Canada as de-icing and anti-icing chemicals for winter road maintenance. On average, five million tonnes of road salts are used each year as de-icers on roadways in Canada. The road salts used are mainly chloride salts, including sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$) and Potassium chloride (KCl) (Environment Canada, 2004). Sodium Chloride is the most common road salts among all the salts listed (Transportation Association of Canada, 1999). The addition of road salts may be the major reason why winter stormwater sediment samples have higher concentrations of Na and Cl.

Fertilizers and limestone are used for field crops in the summer. Fertilizers usually include nitrogen, phosphate and potash, magnesium, calcium and sulphur compounds (Ministry of Agriculture, Food and Rural Affairs, 2002). Ground limestone is in commonly used to correct soil acidity. Calcitic limestone

and dolomitic limestone consists largely of calcium carbonate and magnesium carbonate (Ministry of Agriculture, Food and Rural Affairs, 2002). Higher concentrations of Ca and Mg in both fertilizer and limestone might be the major reason that higher concentrations of both elements are observed in summer samples.

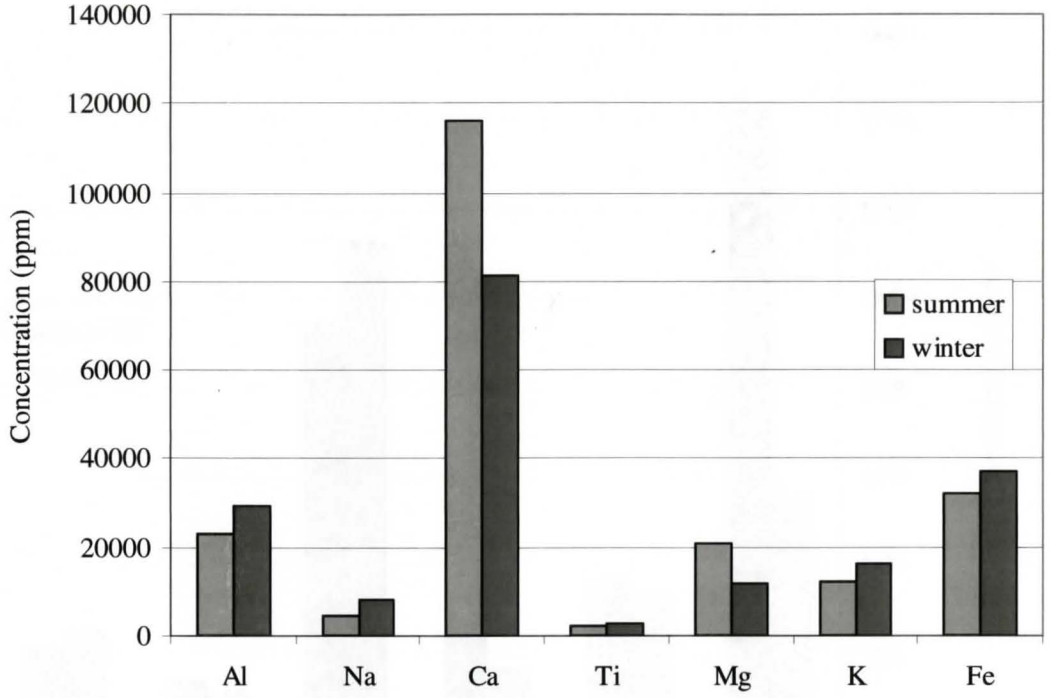

Figure 5.16: Comparison of summer and winter samples in Waterdown stormwater pond for elements with concentrations above 1000ppm

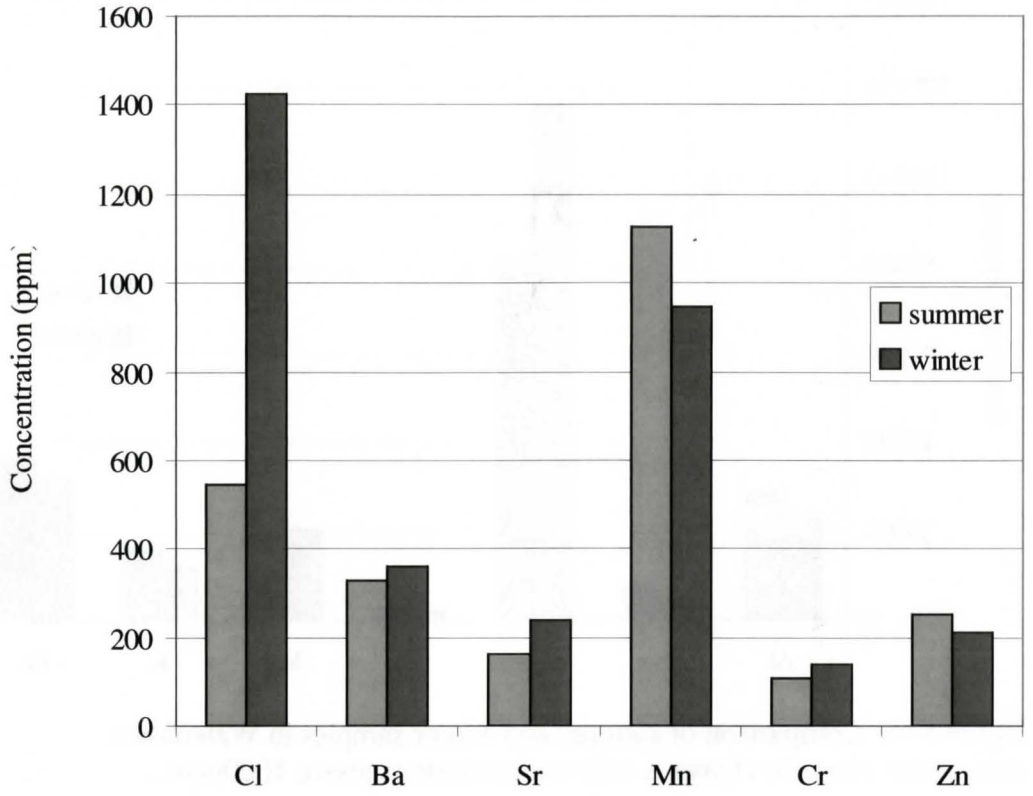

Figure 5.17: Comparison of summer and winter samples in Waterdown stormwater pond for of elements with concentrations between 100ppm and 1000ppm

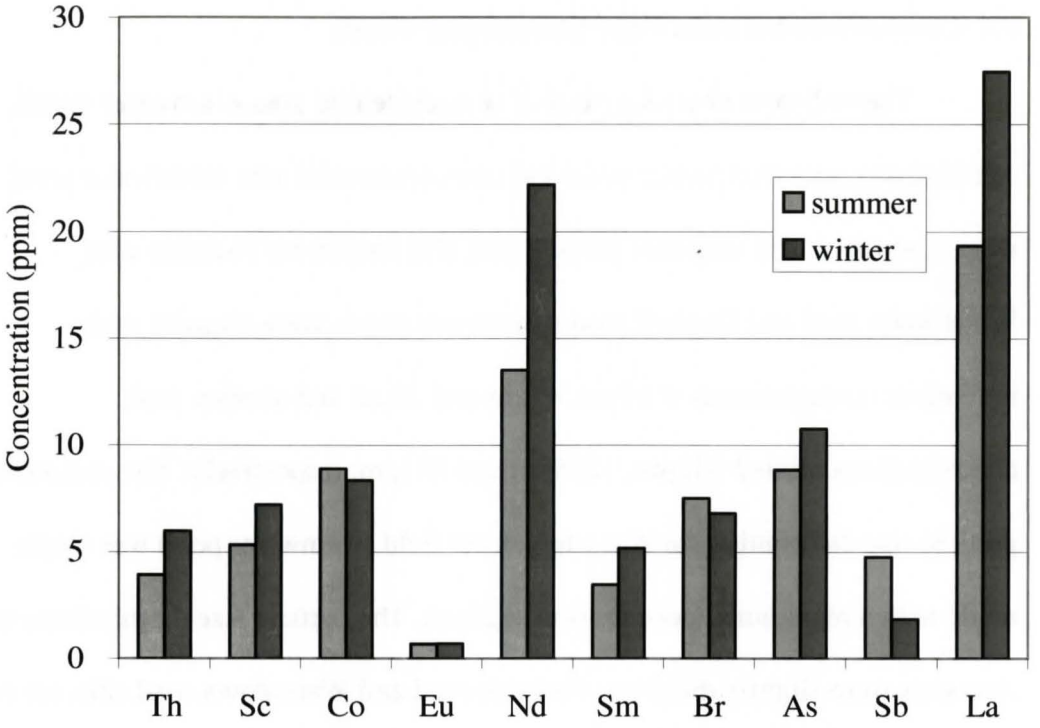

Figure 5.18: Comparison of summer and winter samples in Waterdown stormwater pond for elements with concentrations lower than 100ppm

5.4 Comparison between Four Stormwater Ponds

. The sediment characteristics of two residential area stormwater ponds, one highway area stormwater pond and one commercial area stormwater pond were compared. The sediment particle size distribution for Parkside road, Waterdown road and Dartnell road stormwater ponds were bimodal with maximum concentrations at 69μm, 45μm and 20μm and another peak concentrations around 831μm, 1258μm and 831μm, respectively. The sediment particle size distribution for Ancaster soccer field stormwater pond was single mode with a maximum concentration at 20μm. The particle size distributions of four sites were slightly different. Parkside road and Waterdown road sites are both located in the same residential area, and the particle size distributions of the two ponds are similar. The particle size distribution in Dartnell site was similar to the two residential area sites. Mostly small particles were present in the Ancaster Soccer field stormwater pond.

The particle size of different areas is largely determined by the natural soils present. A previous study suggested that land use affects the particle size distribution of sediments in stormwater ponds to some degree (Liebens, 2001; Ha, 2002). In areas where street sweeping is practiced, it may be related to the inability of rotary brush street sweepers to pick up fine materials such as clay and silt (Young. et al, 1996; Kidwell-Ross, 1988; Brinkmann at.el, 1999). Commercial streets are swept more often than residential streets, and sand is more often removed from commercial streets. Thus, fine materials are more readily available

for transport to the stormwater pond (Liebens, 2001). Among the four sites, smallest particles were presented in Ancaster Soccer field stormwater pond located in a commercial area. The highest volume of particles was observed in the Ancaster Soccer Field sites. Litters and waste from the mall in the area is one of the possible reasons for this increase in volume.

The quality of the sediment in the two residential area stormwater ponds, one highway stormwater pond and one commercial stormwater are pond, were also compared. Thirty-two elements were found in the sediment and nine among these thirty-two elements were below detection limit. Comparison between the concentrations of each element in sediments sampled from four stormwater ponds are shown in Figures 5.19, 5.20 and 5.21 for the concentration ranges of 1000ppm and above, between 100 to 1000ppm and below 100ppm, respectively. Seven elements were detected with a concentration higher than 1000 ppm, six elements had a concentration between 1000ppm and 100ppm, and the remaining ten elements had a concentration lower than 100ppm. The main compositions (above 1000ppm) of the dried sediments include Ca > Al > Fe > K > Mg > Na >Ti > Mn. The trace compositions (below 1000ppm) include Cl > Zn > Ba > Sr > Cr > V > La > Nd > As > Br > Co > Sc > Th > Sb > Sm > Eu. Since the concentrations of each element in the four samples vary significantly, the descending order is just a rough estimation. The concentrations of Ca, Cr, Zn and Cl in the four samples vary the most. Other elements have a quite similar pattern among the samples.

As the concentrations of different compounds are related to land use type, automobile densities and annual loadings for each metal from various sources (Shokouhian, 2001), the concentrations of each element in the same area are not necessary similar. One possible reason for why the concentrations of Cr, Zn, Mg and Ca differ greatly in the two residential area stormwater ponds in the same town is that the Waterdown site is located beside a main road while the Parkside site is located inside a living area. The road runoff clearly affects the Waterdown site in the summer-winter comparison section, as the concentration of Cl, which is a common deicing agent, is higher in winter.

The location where the sample is taken is another factor that could affect the result. In a previous study of the Harding Park stormwater pond in Richmond Hill, Ontario (Rochfort, 2000), four different sediment samples were taken from the sediment forebay, the main settling area, upstream and downstream of the pond outfall. The results showed that the concentrations of each element varied greatly.

Although the differences between land-usage are not apparent, it is within expectations that higher levels of chromium and zinc were observed in the Ancaster site, which is both located in a commercial/light industrial area. Chromium is used in steel, in plating and as a pigment in glass; zinc is used as a pigment, in car tires and in other industrial applications (Liebens, 2001).

The addition of road salts may be one of the major reasons for the higher concentrations of Cl in the Dartnall road site. Since the Dartnall road site is

located at the highway area, road salts are used as de-icing and anti-icing chemicals for winter road maintenance (Barret, 1998; Legret, 2006). The road salts in use are mainly chloride salts, including sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$) and Potassium chloride (KCl) (Environment Canada, 2004). These chemicals might be trapped inside the sediment for an extensive period of time, which would explain their presences in the sample.

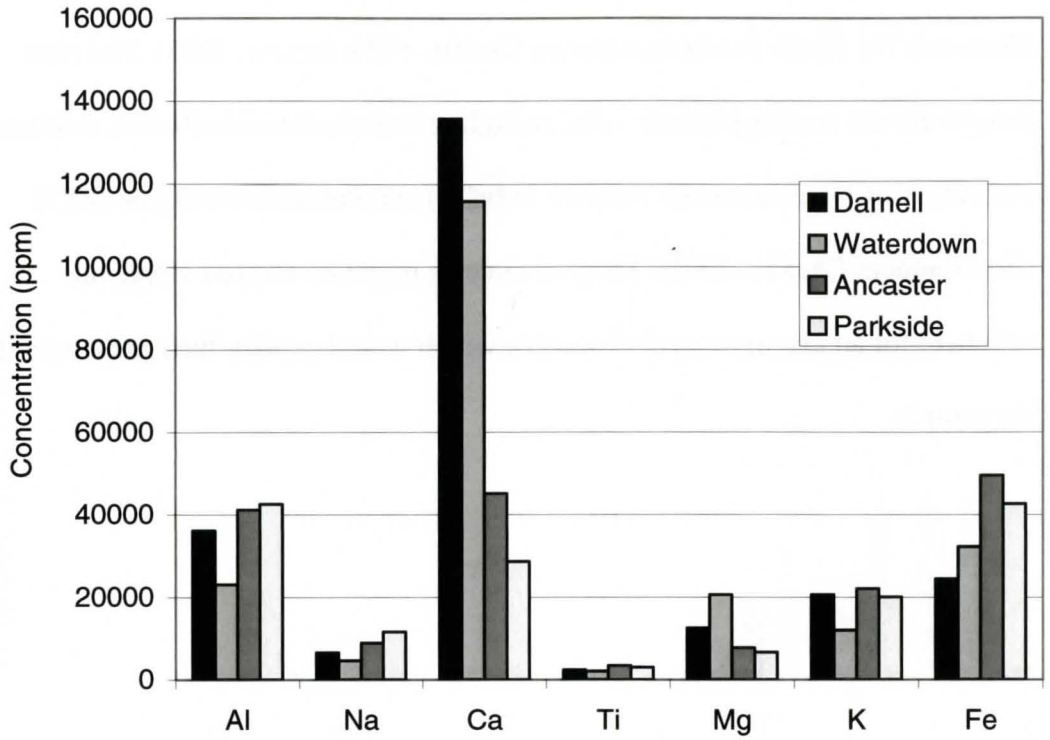

Figure 5.19: Comparison of four stormwater ponds in summer for elements with concentrations above 1000ppm

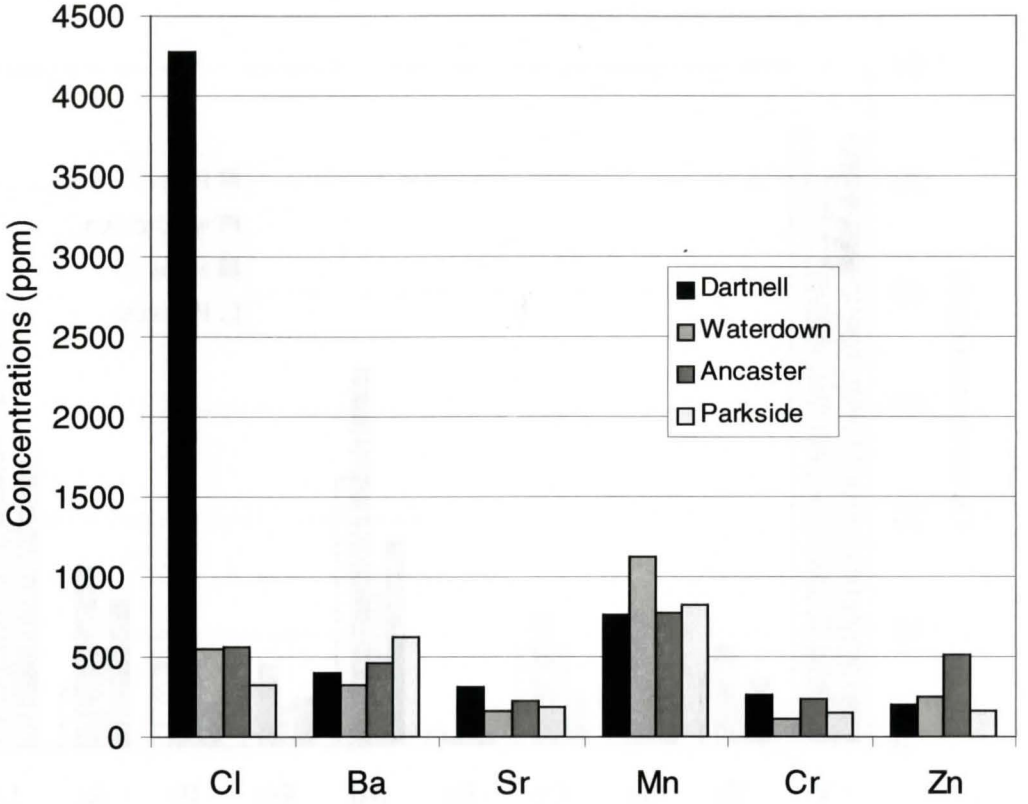

Figure 5.20: Comparison of four stormwater ponds in summer for elements with concentrations between 1000ppm and 100ppm

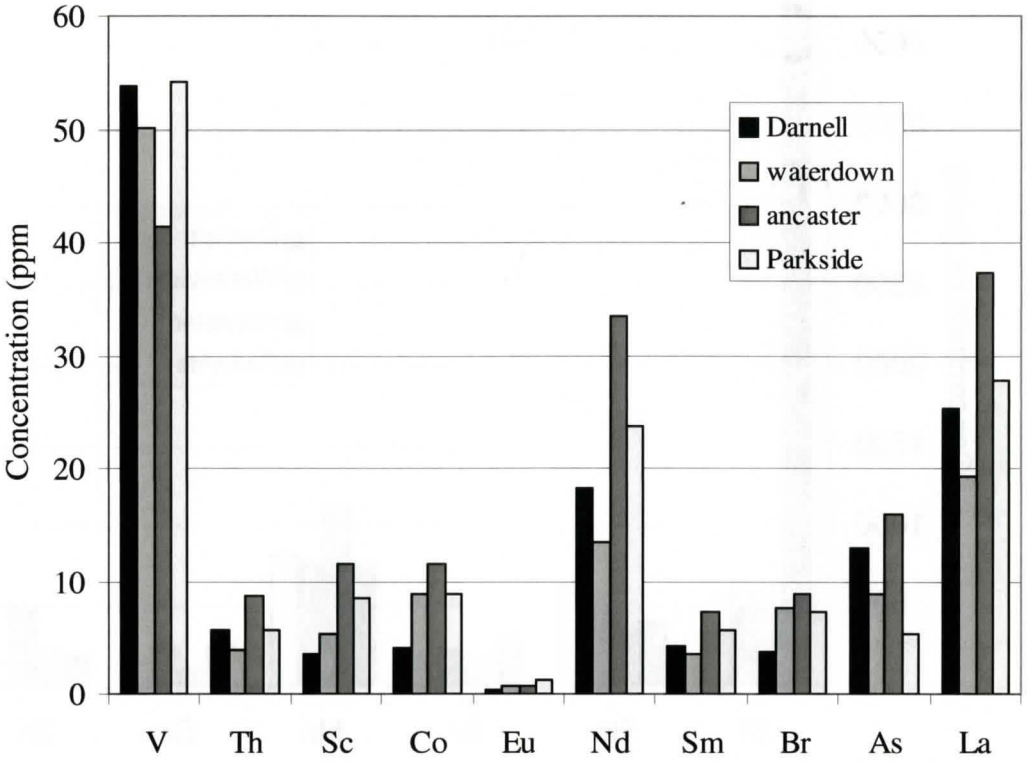

Figure 5.21: Comparison of four stormwater ponds in summer for elements with concentrations lower than 100ppm

Chapter 6
Preliminary Stormwater Sediment Treatment by Thermal Plasma

Thermal plasma technology is used for oxidation and melting of solid waste for volume reduction and to vitrify the noncombustible counter parts simultaneously into glassy slags with a very low leaching rate (Sawell et.al, 1988). Thermal plasma is used to convert bottom and fly ashes from municipal solid waste (MSW) and low level radioactive wastes (Jimbo et al, 1997;Tzenget al, 1998). Success of the technology has promoted thermal plasma as a treatment method for other solid wastes. Therefore, it may be feasible to use the thermal plasma technology to treat stormwater sediments.

6.1 Comparison of Elements in Storm Water Sediment (Sludge) and Municipal Sludges

Dried municipal wastewater treatment sludges (MS) have been treated by different thermal techniques successfully. A sludge melting system has been tested for the sludge from municipal sewage water treatment center in Japan. The system reduced waste volume to 1/30 of dehydrated sludge and detoxified waste into building construction materials. The physical and chemical properties of dried MS from Saseho and Maebashi, Japan (Chang et.al, 2003) were compared to the Dartnell site dried stormwater sludge in order to assess the possibility of using thermal plasma to treat stormwater sludge.

Physical properties including particle size and shape of the MS are compared to the dried stormwater sludge. The geometry of MS from Saseho and

Maebashi are very irregular and the maximum particle size is around 850-2000μm (Chang et.al, 2003). Although both MS and stormwater sludge particles are irregular in shape, stormwater sludge has a larger size distribution, with particle size ranges from 0.5μm to 2000μm, and has a bimodal distribution with maximum concentrations at 20μm and 831μm.

Compositions of dried MS were analyzed by NAA and compared to the dried storm water sludge in Figures 6.1, and 6.2. The ten common main compositions (above 1000ppm) are Ca > Al> Fe> Mg> K> Na> Zn> Cl> Ti> Ba. Common trace compositions (concentrations between 10ppm and 1000ppm) include 17 elements such as Mn> Sr> S> V>Cr > Br> La> Sb> Nd> Co> W > Th > Sc> Sm> As> Dy> Eu. Some compounds such as Mo and Rb are not detected in the dried stormwater sludge but are found in MS. The compositions of MS and stormwater sludge are similar, however, the concentrations of each element vary in some degree. In general, the concentration of most of the elements in stormwater sludge is slightly higher than those in MS samples, especially Fe, K, Mg, Mn, Cr and Sr. The concentration of Al and Zn in MS samples are much higher than in stormwater sludge. It is observed that MS samples from two different cities in Japan are different as well, indicating the sludge characteristics vary in different cities. Since the physical and chemical properties are quite similar between MS samples and stormwater sludge, the treatment of stormwater sludge by thermal plasma may be a potentially viable approach.

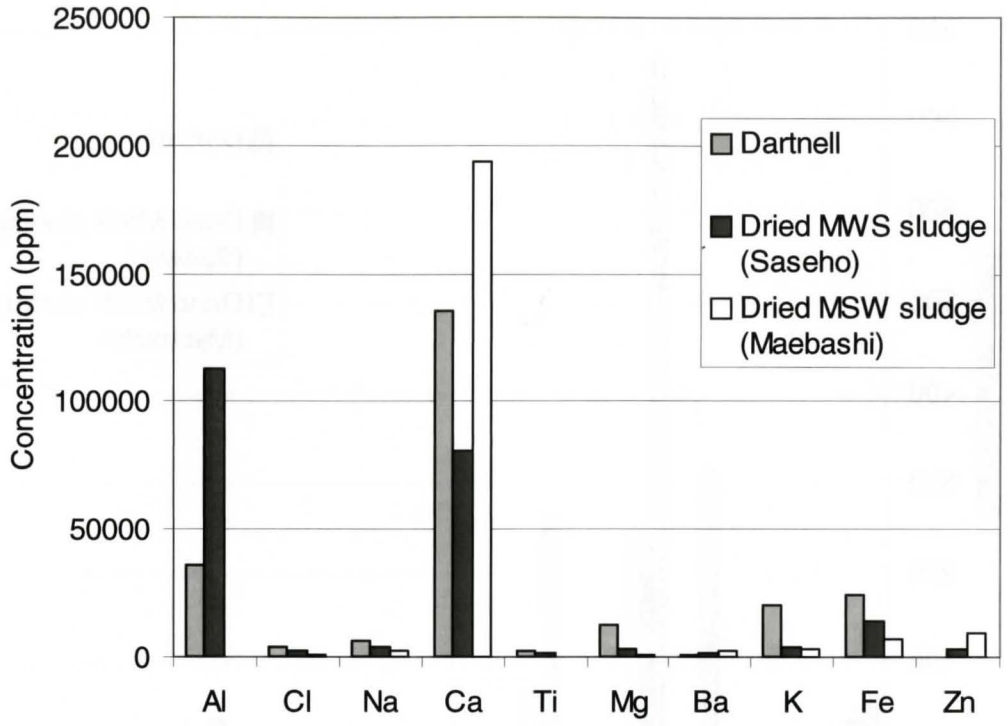

Figure 6.1: Comparison of main compositions between stormwater sludge and municipal sludges (MS).

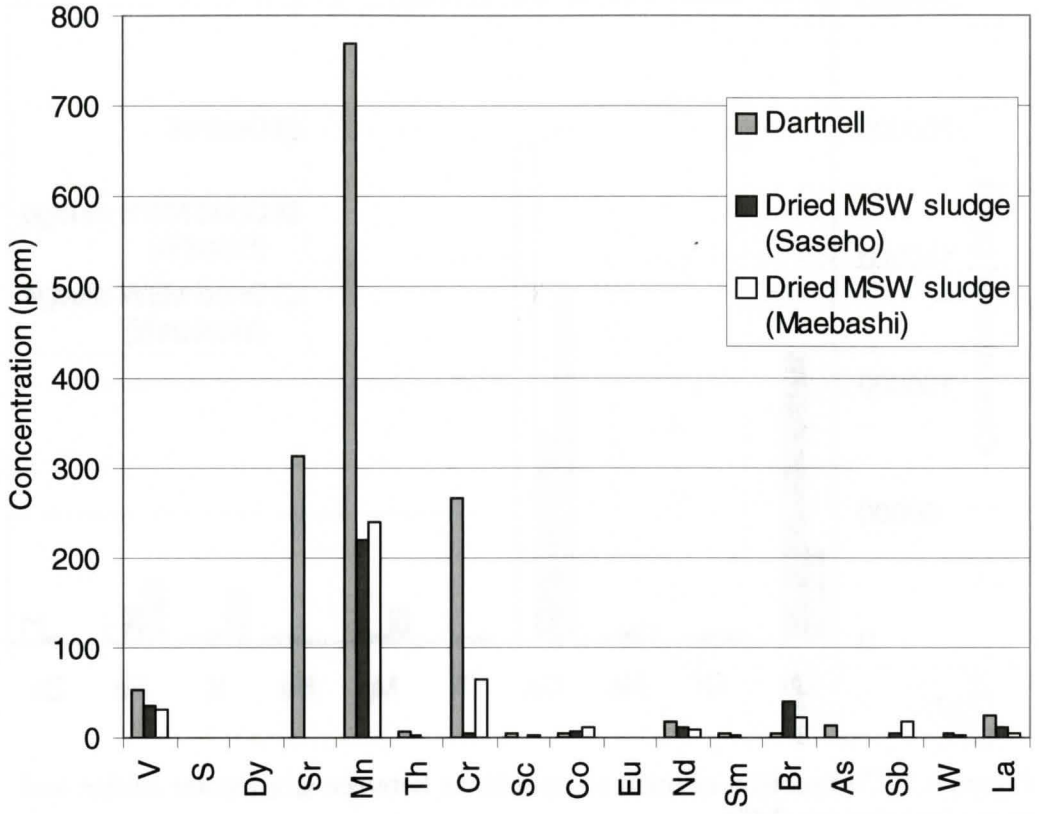

Figure 6.2: Comparison of trace compositions between stormwater sludge and municipal sludges (MS)

6.2 Experimental Apparatus

Plasma Torch Type Sludge Treatment System

A schematic of the plasma torch type sludge treatment system is shown in Figure 6.3. Dried stormwater sludge was placed into a 99.8% pure alumina made ceramic container with maximum operating temperatures of 1950°C in both oxidization and reduction atmospheres. The weights of sludge samples were mostly in between 20g to 30g. A ceramic container with a diameter of three inches and depth of two inches was placed 6cm below the torch. The heat was generated by a DC 10kW plasma torch (Beuthe el.al, 1997) and was ejected vertically through the top of the reactor chamber. Pure argon gas was used in the plasma torch, and air was injected through the anode in order to produce an oxidation environment. Typical plasma melt reactor temperature is between 1100°C and 1700°C, depending on the plasma torch operating power (Izumi et. al, 1996).

A constant-voltage power supply, in series with a resistor bank, was used to control the power to the plasma torch. A fixed current, with a voltage and power of 90A and 120V and 1.5 kW was provided to the plasma torch in the present processes for the treatment of stormwater sediment. A fixed argon gas flow rate of 17.5 L/min was injected into the torch without air for the creation of an anaerobic environment, and air flow rates varying from 2L/min to 5L/min controlled by a flow meter were used for different oxidation environments.

Treatment times of one hour, one and a half hour and two hours were examined for 0L/min and 2L/min air flow rates, and one hour for 5L/min air flow rate.

The exhaust gas was sampled down stream of the reaction chamber exit via a heat exchanger. The flue gas composition was measured by the Eurotron's GreenLine 8000 Combustion Gas Analyzer.

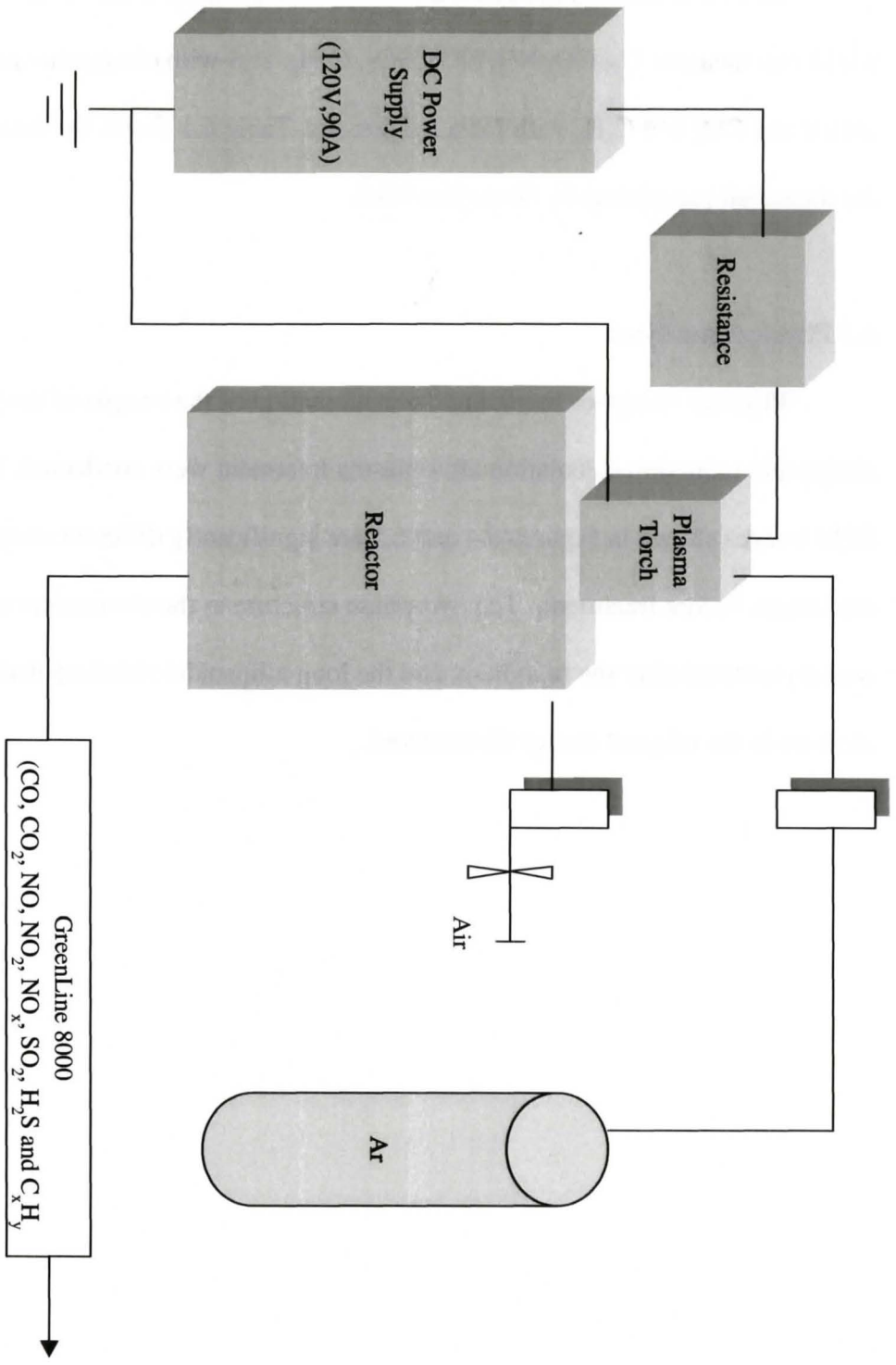

Figure 6.3: Schematic of thermal plasma system

Greenline 8000 by Eurotron Instrument is a portable emission gas analyzer which can measure O_2, CO, NO, NO_2, SO_2, C_xH_y, H_2S with electrochemical sensor and CO_2 and C_xH_y with Infra red sensors. Table 6.1 shows the details of the measured parameters by Greenline 8000.

6.3 Physical Analyses

Physical Analyses including the examination of the images of the treated sludge and reduction calculation after plasma treatment were conducted. The SEM images shown in Figures 6.4 and 6.5 are significantly different compared to the images before treatment. The two-phase structure in the stormwater sludge was crystallized after the treatment, and the long ellipsoidal structure that was obvious in the original sludge disappeared.

Table 6.1: Details of parameters measured by Greenline 8000

Parameter	Sensor	Range
O_2	Electrochemical	0 - 25%
CO	Electrochemical	0 - 8000ppm
CO%	Electrochemical	10%
NO	Electrochemical	0 - 4000ppm
NO_2	Electrochemical	0 - 1000ppm
NO_x	Calculated	0 - 4000ppm
SO_2	Electrochemical	1 - 4000ppm
CO_2	Infra-red	0 - 40%
C_xH_y	Infra-red	0 - 50000ppm
H_2S	Electrochemical	0 - 1000ppm

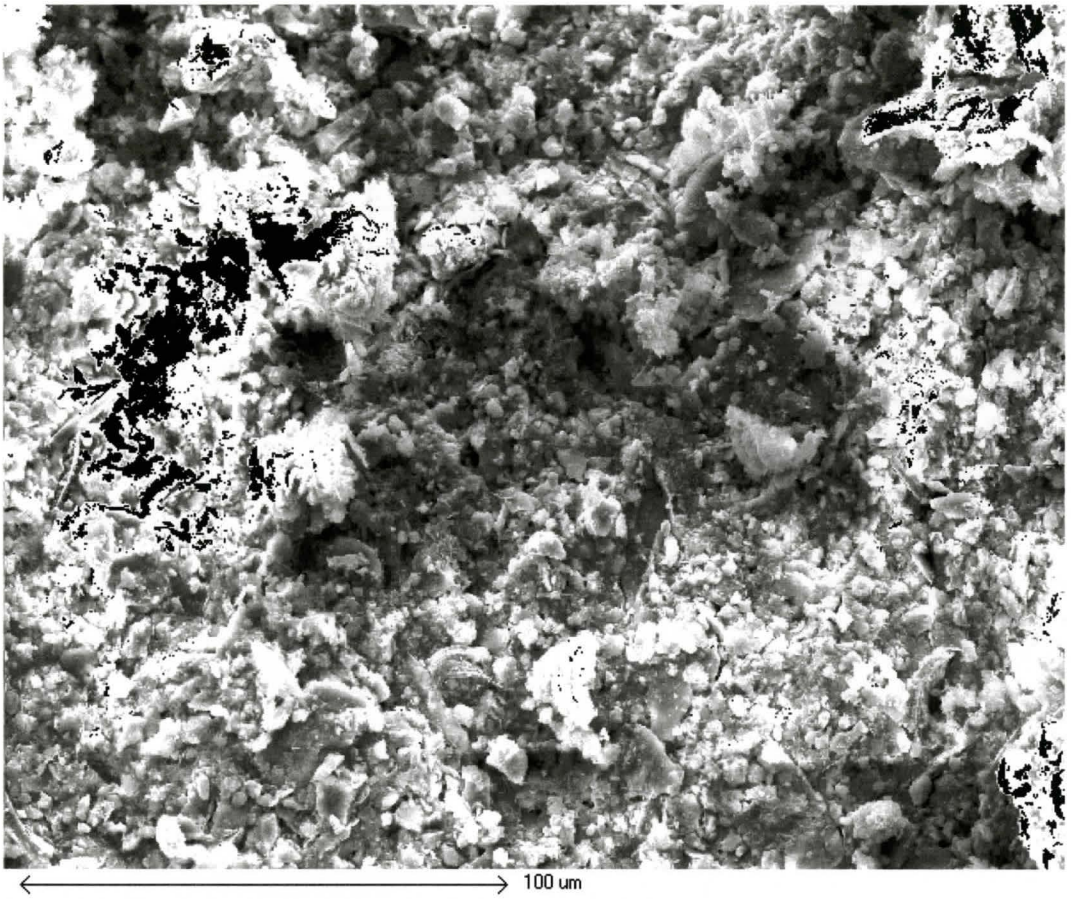

Figure 6.4: Image of plasma treated dried sludge from Ancaster Soccer Field stormwater pond by SEM with magnification of 526 times, with Argon flow rate of 17.5L/min, air flow rate of 2L/min in two hours.

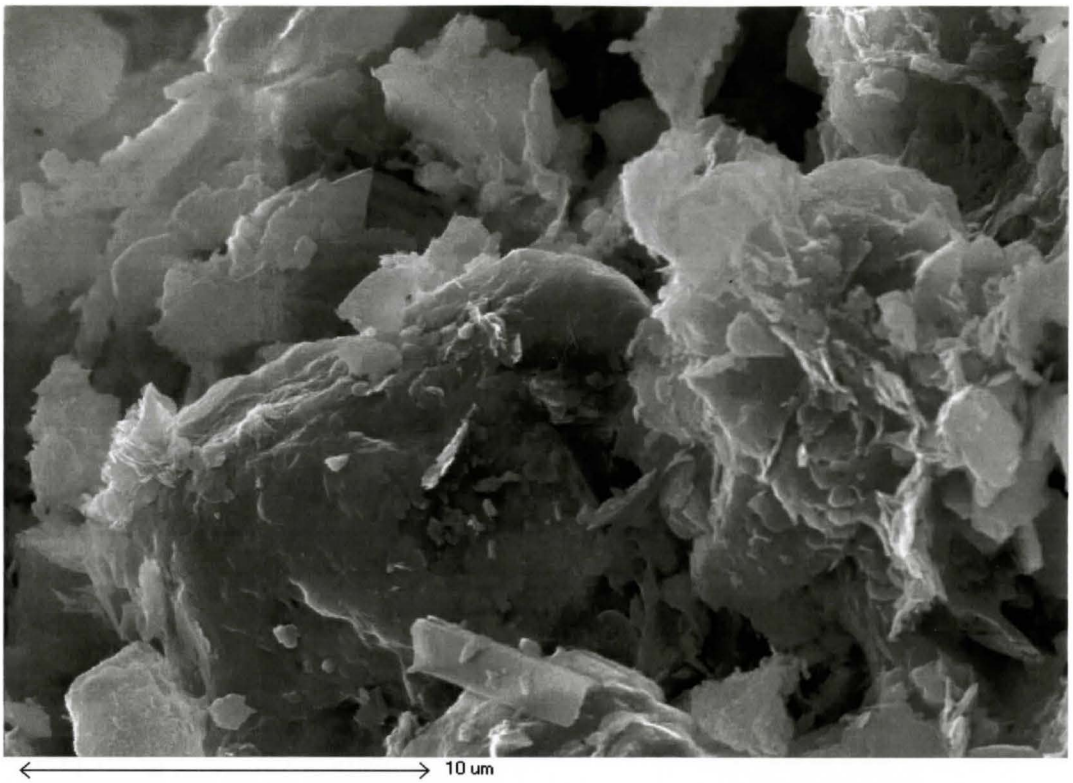

Figure 6.5: Image of treated dried sludge from Ancaster Soccer Field stormwater pond by SEM with magnification of 4000 times, with Argon flow rate of 17.5L/min, air flow rate of 2L/min in two hours.

Table 6.2: Raw data of weight on sludge before and after thermal plasma treatment.

Air flow rate L/min	Time (hr)	Weight before (g)	Weight after (g)	Percentage removal (%)
0	1	20.6	20.16	2.14
0	1.5	27.76	27.02	2.67
0	2	35.79	34.52	3.55
2	1	22.06	21.62	1.99
2	1.5	27.8	26.78	3.67
2	2	29.63	27.89	5.87
4	1	31.7	30.67	3.25
Air flow rate L/min		**Mean weight before (g)**	**Mean weight after (g)**	**Mean percentage removal (%)**
0		28.05	27.23	2.78± 0.51
2		26.50	25.43	3.85±1.35

The weights of sludge before and after each treatment are summarized in Table 6.2. The weight removed by the plasma treatment for different air flow rates and treatment times is shown in Figure 6.6. The maximum weight removal of 5.87% was achieved with 2L/min air flow rate and 2 hours of treatment time. In general, the percentage of weight removal increases with longer treatment times and higher air flow rates. The mean weight percentage removal by plasma treatments for 0L/min and 2L/min for one hour, one and a half hour and two hours are 2.78% ± 0.51% and 3.85% ± 1.35% respectively. Introducing oxygen into the system increases the oxidation of organic compounds, and thus resulting in a higher oxidation rate during the treatment.

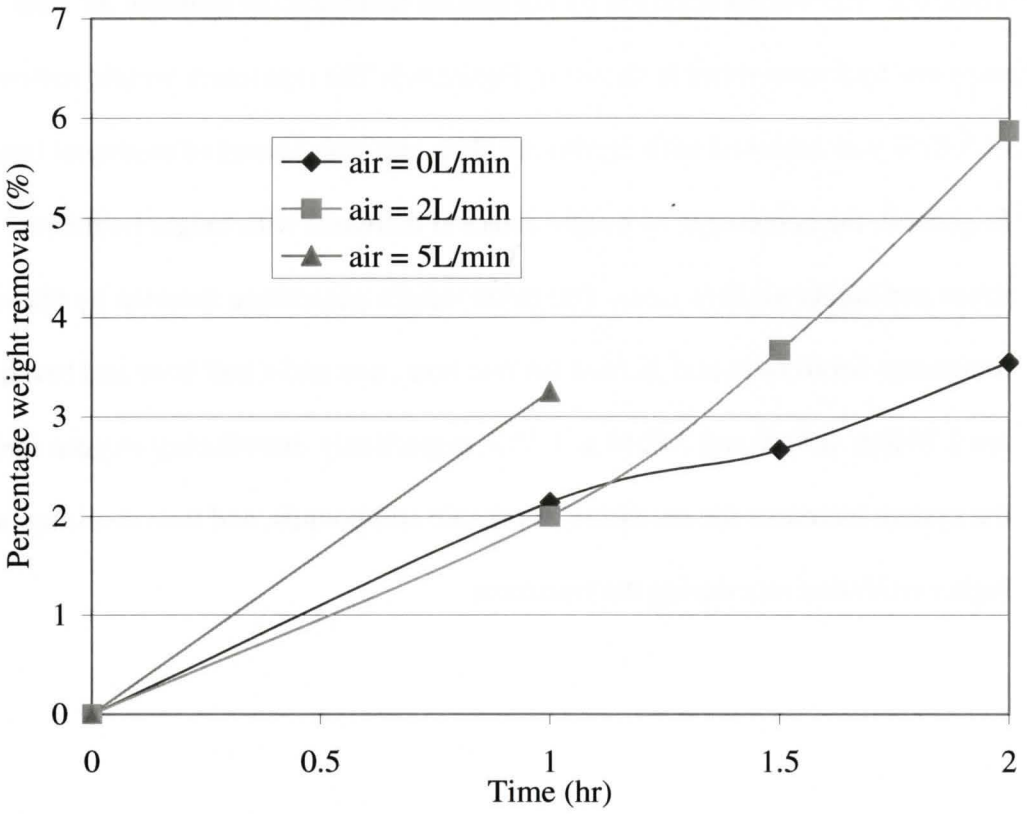

Figure 6.6: Percentage weight removal with different air flow rates as a function of treatment time, with Argon flow rate fixed at 17.5L/min.

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6.4 Plasma Sludge Treatment Gaseous By-product Analyses

The chemical properties, including total organic carbon (TOC) for the sediment before and after plasma treatment, the flue gas during the thermal plasma treatment and the NAA elementary analysis of the treated sludge, were analyzed.

TOC of the original and treated sludge were measured. First, all sludge were placed into an oven at 100°C, then they were placed inside a pissicusor for one day in order to remove all the water content inside the sludge. The sediments were weighted before and after being placed into another oven at 550°C for 30 minutes. Most of the organic compounds would be vaporized inside the oven and thus, the difference of weight would be the total amount of TOC in the samples.

The TOC of the Dartnell stormwater sludge is 7.65% by weight. The treated sludge of different air flow rates with respect to treatment time is shown in Figure 6.7. The TOC in the treated sample were lower than the original TOC in Dartnell stormwater sludge. The heat in the reactor oxidize the organic compounds in the sample into gas compounds, thus, reducing the amount of TOC. In general, the TOC percentage in the sample decreases as treatment time increases. This is consistent with the percentage weight removal in Section 6.3. The organic compounds may be gasified by oxidization or/and reduction, and hence, the weight of the sample decreases. It should be noted that the LEL level of TOC in sludge is 1% and the percentage of TOC in all samples are above this limit.

Thermal plasma is capable of incinerating organic parts with extreme high temperature in the treatment of MS (Jimbo, 1997;Tzeng, 1998). However, in our experiment, the samples still retain some TOC after the treatment, and the percentages of TOC are all above the LEL of the Ontario Ministry of Environment. The temperature profile of the treatment is shown in Figure 6.8. The highest operating temperature at one spot was around 300°C and it was much lower than the operating temperature of typical thermal plasma. The location of the ceramic reactor may need to be closer to the plasma torch for a higher operating temperature. The thickness of the sediment samples inside the reactor may affect the efficiency of the treatment. Heat from the plasma torch might only be able to reach the top part of the samples.

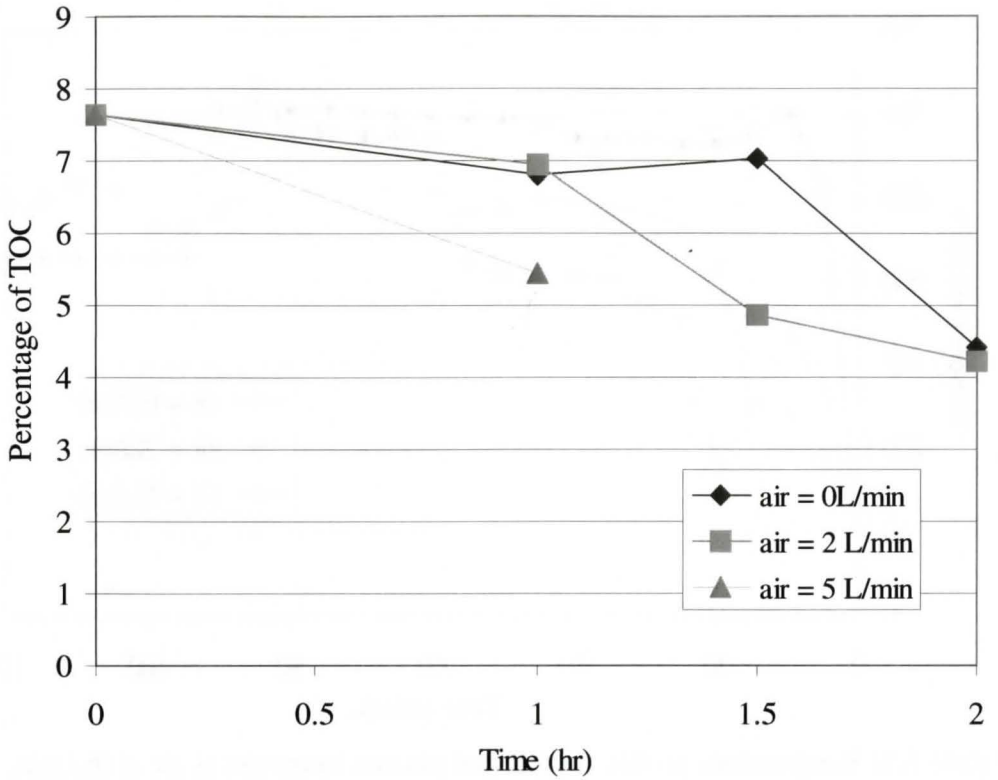

Figure 6.7: Percentage of TOC after plasma treatment for different air flow rates as a function of treatment time with Argon flow rate fixed at 17.5L/min.

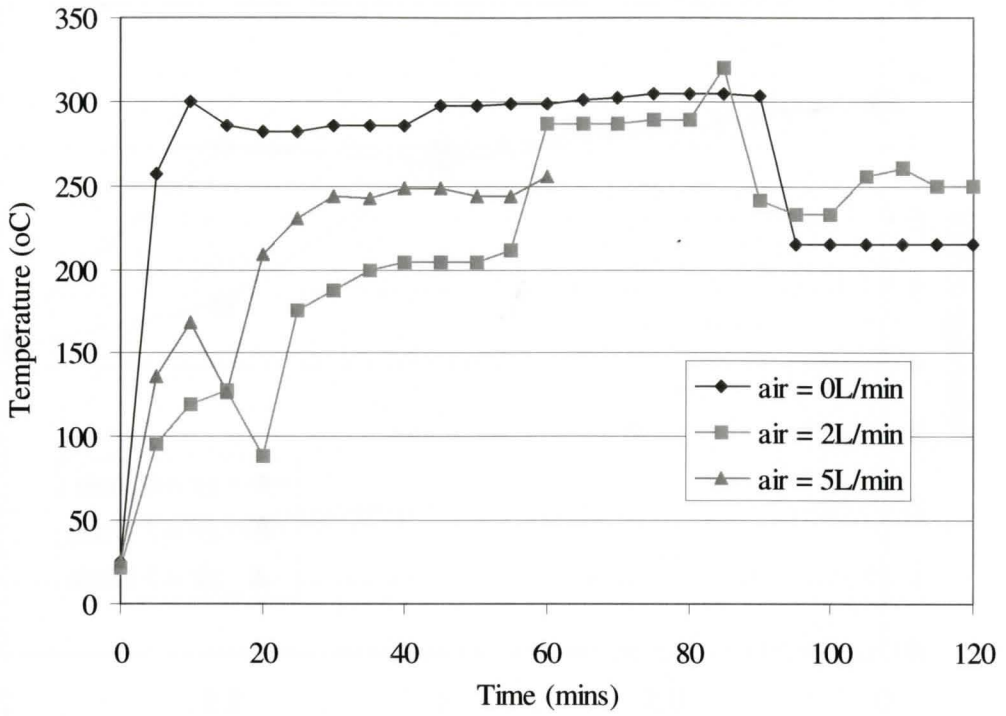

Figure 6.8: Temperature profile for thermal plasma treatment at air at 0L/min, 2L/min and 5L/min as a function of treatment time with Argon flow rate fixed at 17.5L/min.

Since the organic part of the sediment was converted to gases, it is necessary to investigate the gas content of the outlet to prevent toxic gases from being emitted into the environment. Figures 6.9 and 6.10 show the typical main compositions of emission gas for air flow rates of 0L/min and 2L/min with a treatment time of one and a half hours, respectively. Eight gas compounds including CO, CO_2, NO, NO_2, NO_x, SO_2, H_2S and C_xH_y were analyzed. The oxygen levels inside the reactor are dependent on the air flow rates, thus, they were fixed during the experiment.

The emission gas components for treatment with the absence of air are shown in Figure 6.9. It showed that oxidation occurred for the first 30 minutes and pyrolysis started at 65 minutes after the treatment. Oxide compounds in the sample were combusted and released oxygen for the reactions to produce NO_x, SO_2 and CO in the first 30 minutes, and as there was no oxygen applied to the system, pyrolysis started and converted some carbon and sulphur compounds to hydrocarbon and H_2S.

Figure 6.10 shows a higher oxidation rate in 30minutes of treatment with the presence of oxygen in the reactor. The concentration of the oxide compounds such as CO, NO, SO_2, NO_2 and CO_2 are much higher with the present of air. Most of the oxide compounds in the samples were combusted in the first 30 minutes. Since oxygen was provided constantly during the treatment, oxidations continue in the later part of the treatment and thus a constant concentration of oxide compounds were generated during the later part of the treatment.

More detailed comparisons of each gas compound are shown in Figures 6.11 through 6.18. The result clearly shows that the carbon and sulphur compounds in the sludge were oxidized into gas compounds during the treatment. The generation of NO, NO_2 and NO_x might be from the nitrogen-compounds in the sample. The concentration of CO, NO, NO_2, SO_2, CO_2 and C_xH_y were much higher in an oxidizing environment. It is reasonable that the generation of most of the oxide compounds such as SO_2, NO, NO_2, NO_x and CO_2 in 5L/min of air flow rate were in the highest concentration as there were more oxygen provided for the oxidation. It was observed that CO concentrations increased with increasing oxygen. The increased oxygen concentration in the chamber had a direct effect on the CO concentration (Ara et al, 2005). Most of the CO is formed by dissociation, via negative ions or electrons of CO_2. The increase in concentration of CO might be caused by the increased availability of CO_2 from the increased air flow rate (Chang et al, 1997; Beuthe et al, 1997; Chang et al, 1992).

NO, NO_2 and CO_2 were not produced while H_2S and C_xH_y were generated in the pyrolysis stage which occurred after 60 minutes with the absence of air. Hydrocarbons and sulphur were easier to react to the oxygen released by the oxide compounds than nitrogen, thus the production of CO and SO_2 were more prevalent in the early oxidation stage. The generation of H_2S was at the highest in the pyrolysis stage with the absence of air.

The generation of hydrocarbon was at the highest for air flow rate of 2L/min. Hydrocarbon compounds are easier to oxidize to CO or CO_2 if sufficient

air is provided, and thus the generation of hydrocarbon for air flow rate of 5L/min was quite low compared to smaller air flow rates.

Although the weight removal reached maximum with the presence of air, more toxic gas compounds were produced with increasing gas flow rates. Maximization of the efficiency of weight removal and minimization of the amount of toxic gas emission must be considered.

The concentrations of flue gas emitted from plasma treatment are compared to the guideline for combustion and air pollution requirements for new municipal waste incinerators from the Ontario Ministry of the Environment (MOE, 2004). Although this guideline is not designed for stormwater sludge thermal plasma treatment, it can serve as a reference for the level of toxicity of the flue gas. Table 6.3 shows the parameters and emission limits of the guidelines. The concentration of SO_2 in the flue gas with the absence of air is above the limit. The concentrations of SO_2, NO_x and hydrocarbon in the flue gas with air flow rate of 2L/min are all above the emission limit. The concentrations of SO_2 and NO_x in flue gas with air flow rate of 5L/min are above emission limit. An efficient removal of these toxic gases must be considered in the development of treatment processes.

Table 6.3: Parameters and emission limits of the Ontario Ministry of Environment

Parameter	Emission Limit (ppm)
NO_x	110
SO_x	21
HCl	18
Organic matter	100 (undiluted)

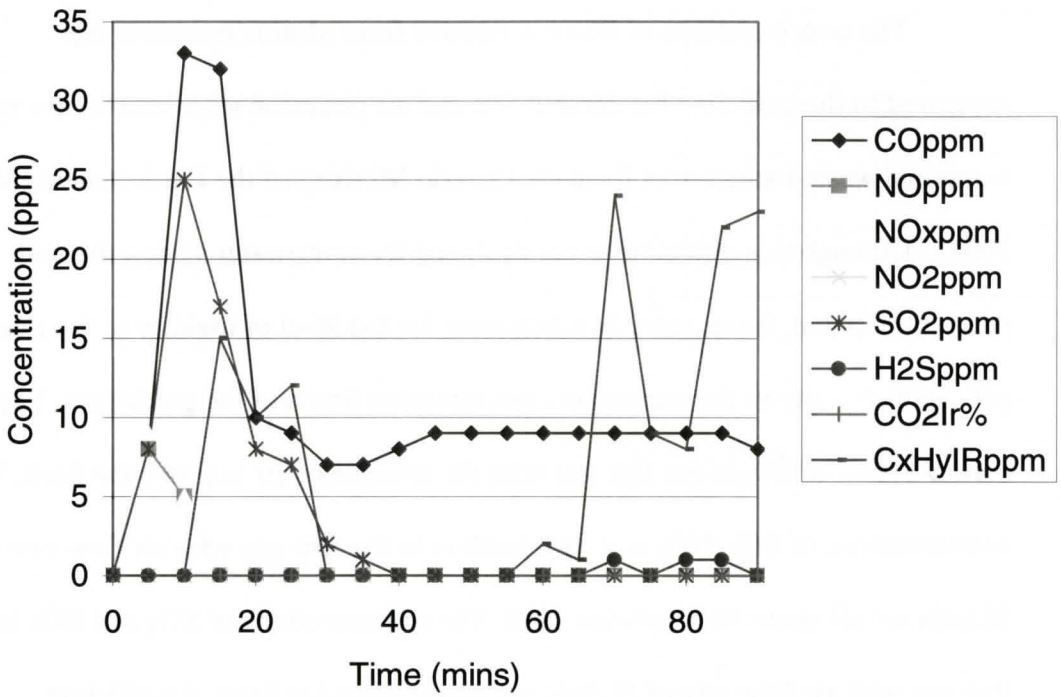

Figure 6.9: Emission gas components for air flow rate of 0L/min and Argon flow rate of 17.5L/min in one and a half hour

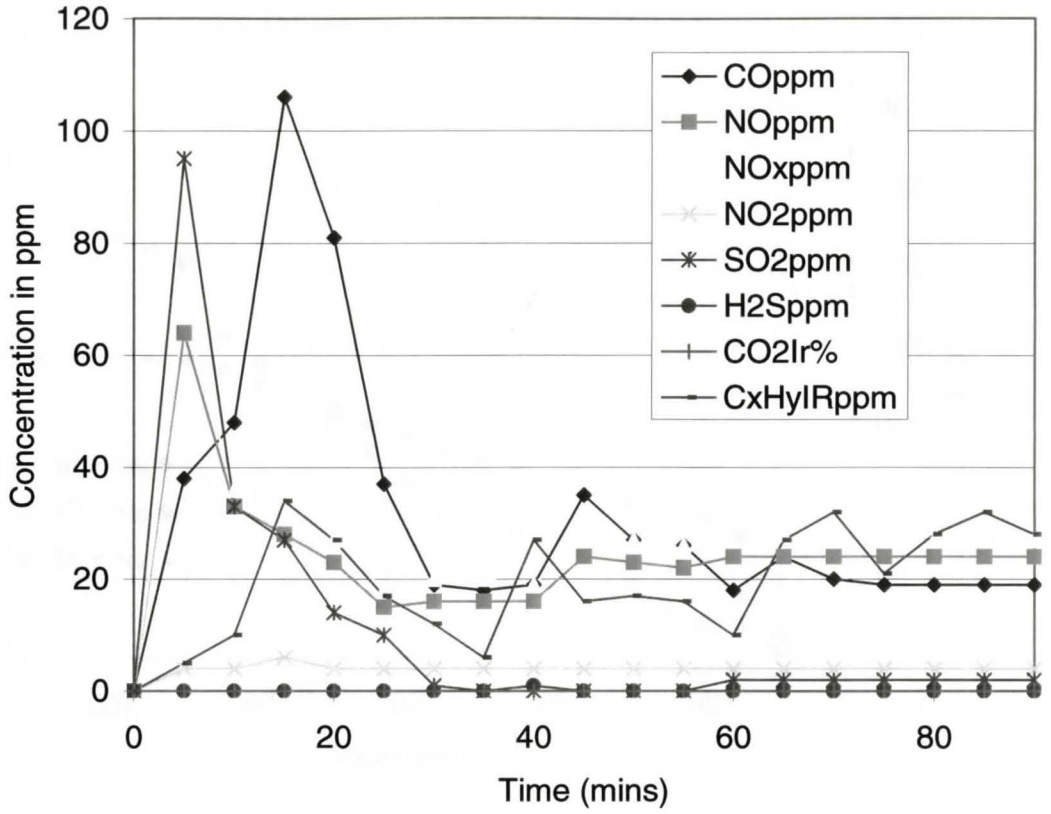

Figure 6.10: Emission gas components for air flow rate of 2L/min min and Argon flow rate of 17.5L/min in one and a half hour

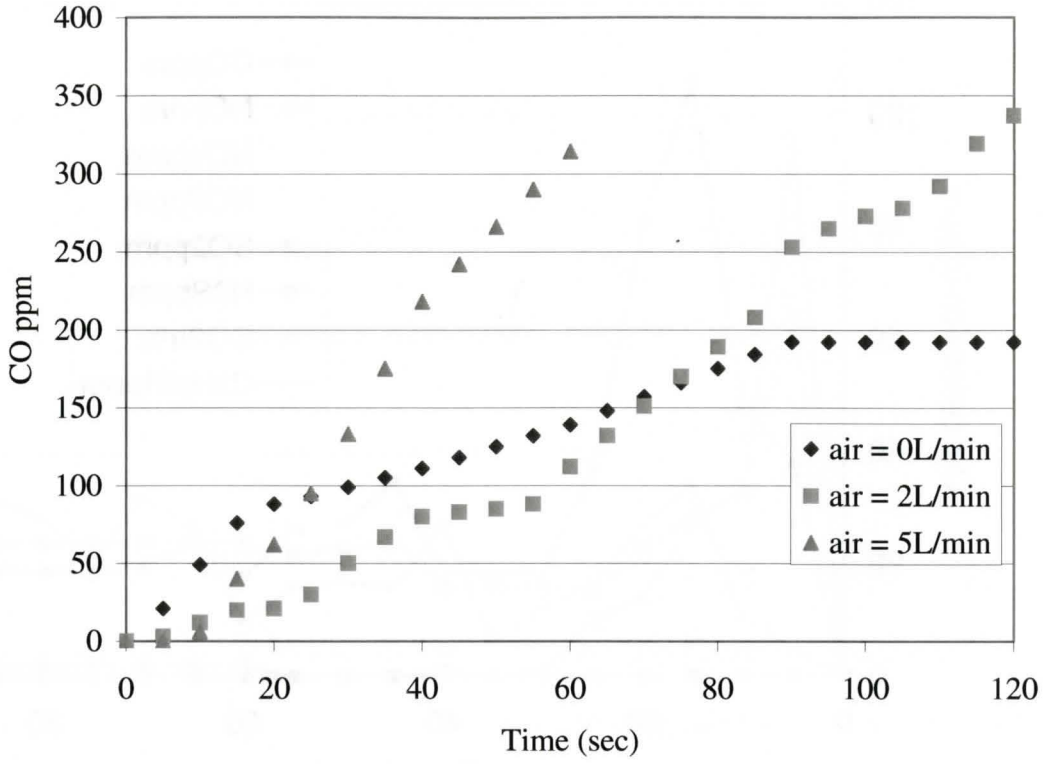

Figure 6.11: Concentration of CO for different air flow rates (Argon flow rate fixed at 17.5L/min with respect to time)

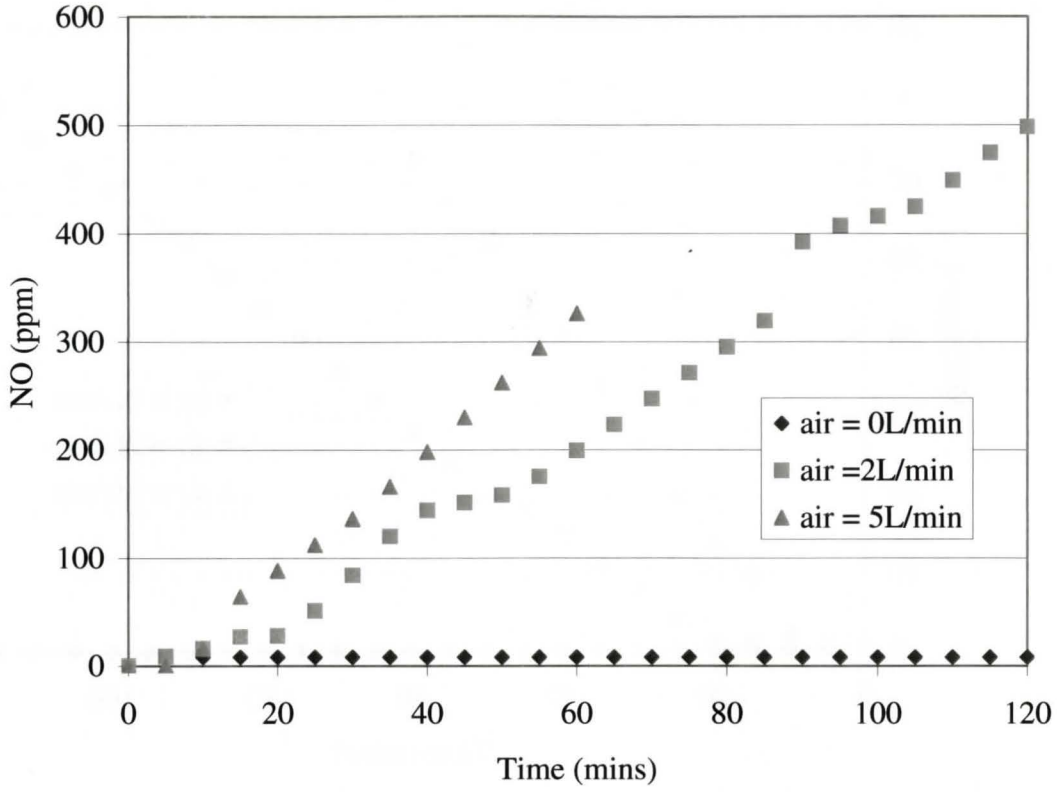

Figure 6.12: Concentration of NO for different air flow rates (Argon flow rate fixed at 17.5L/min with respect to time)

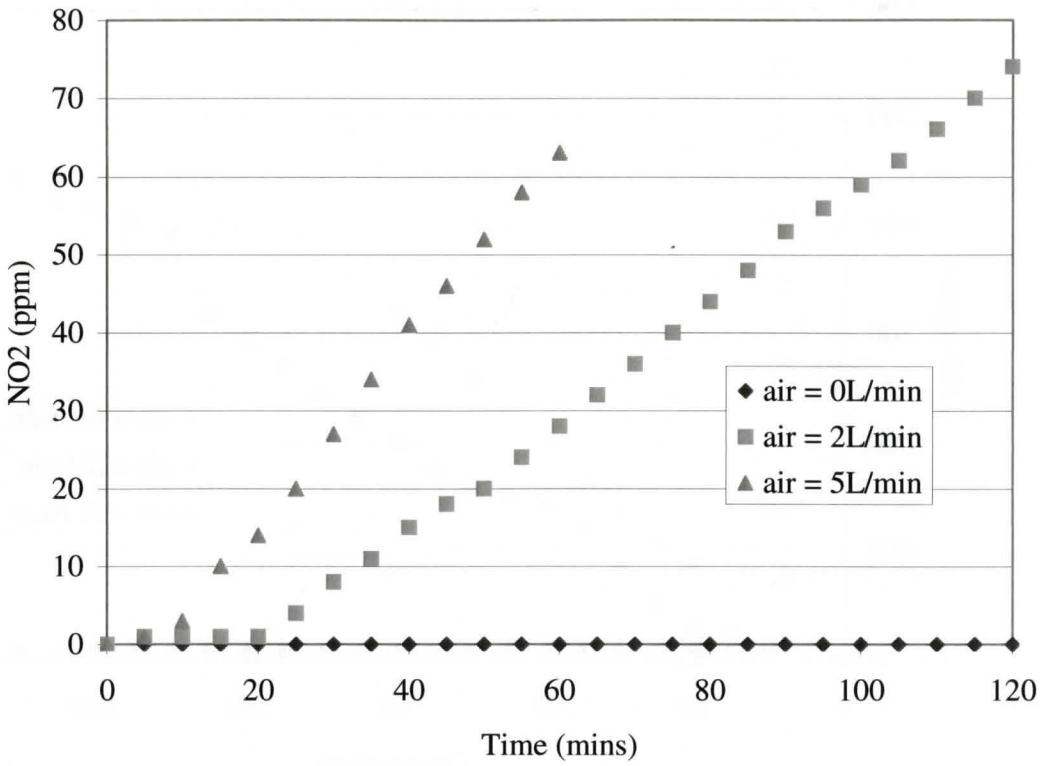

Figure 6.13: Concentration of NO_2 for different air flow rates (Argon flow rate fixed at 17.5L/min with respect to time)

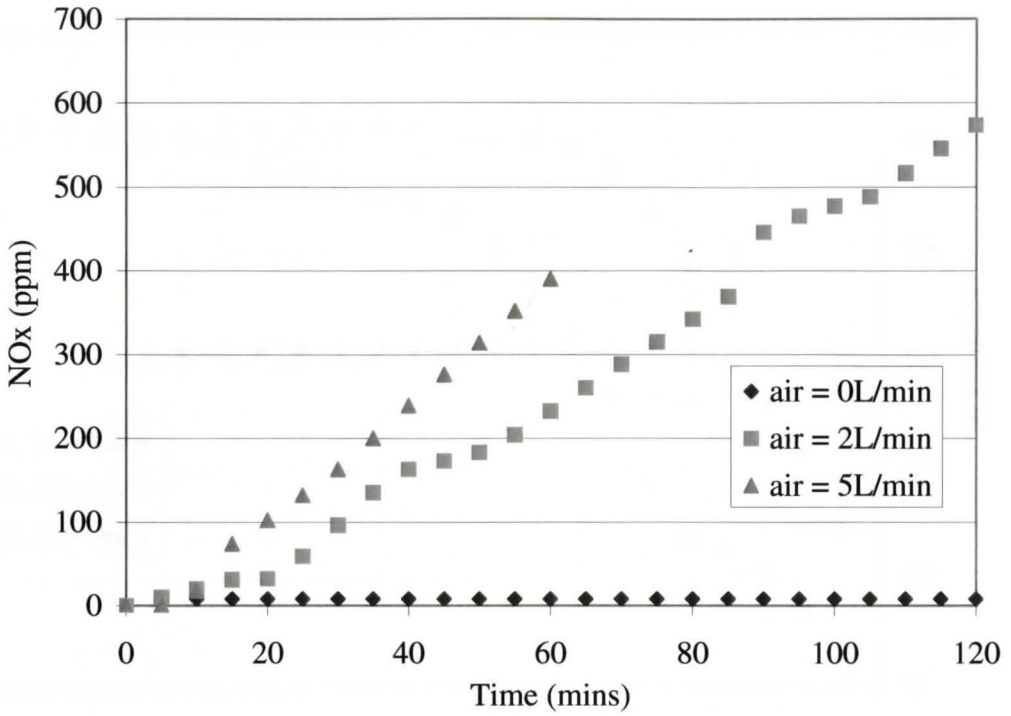

Figure 6.14: Concentration of NO_x for different air flow rates (Argon flow rate fixed at 17.5L/min with respect to time)

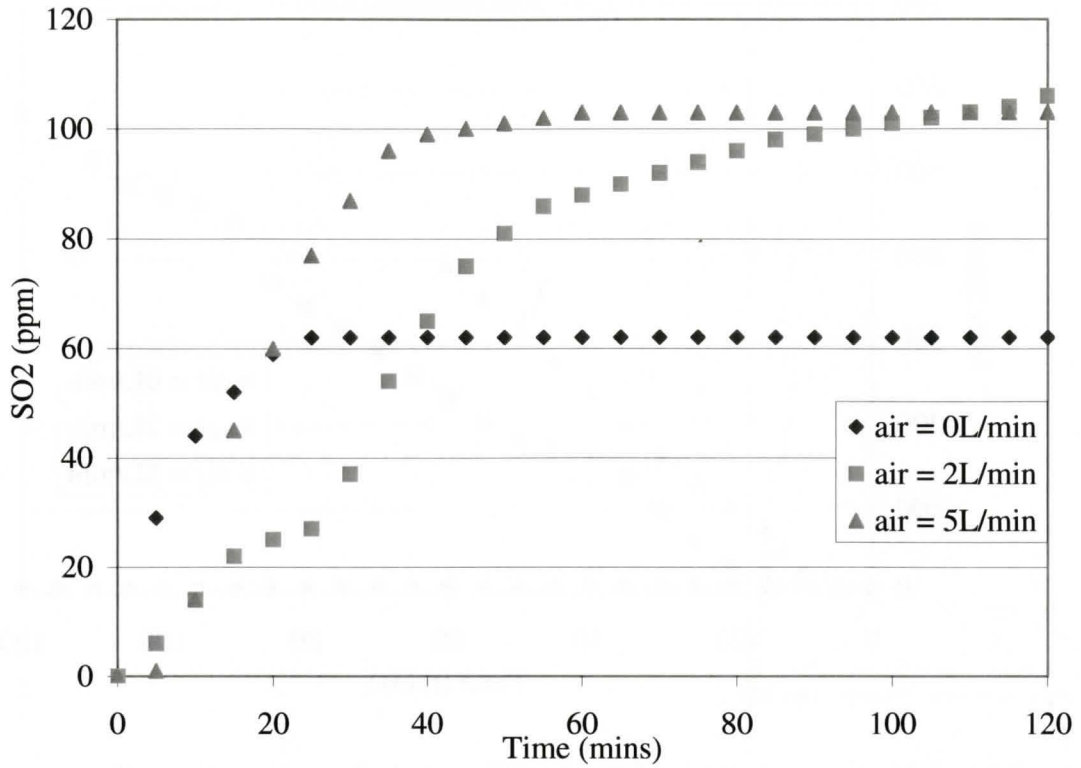

Figure 6.15: Concentration of SO_2 for different air flow rates (Argon flow rate fixed at 17.5L/min with respect to time)

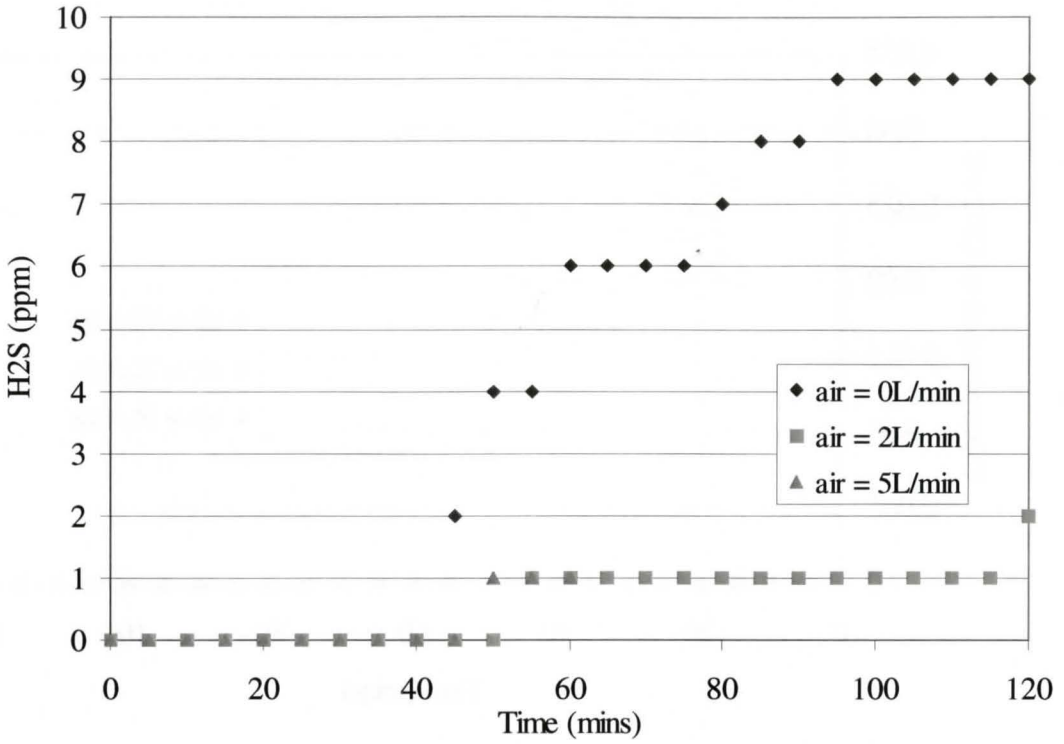

Figure 6.16: Concentration of H_2S for different air flow rates (Argon flow rate fixed at 17.5L/min with respect to time)

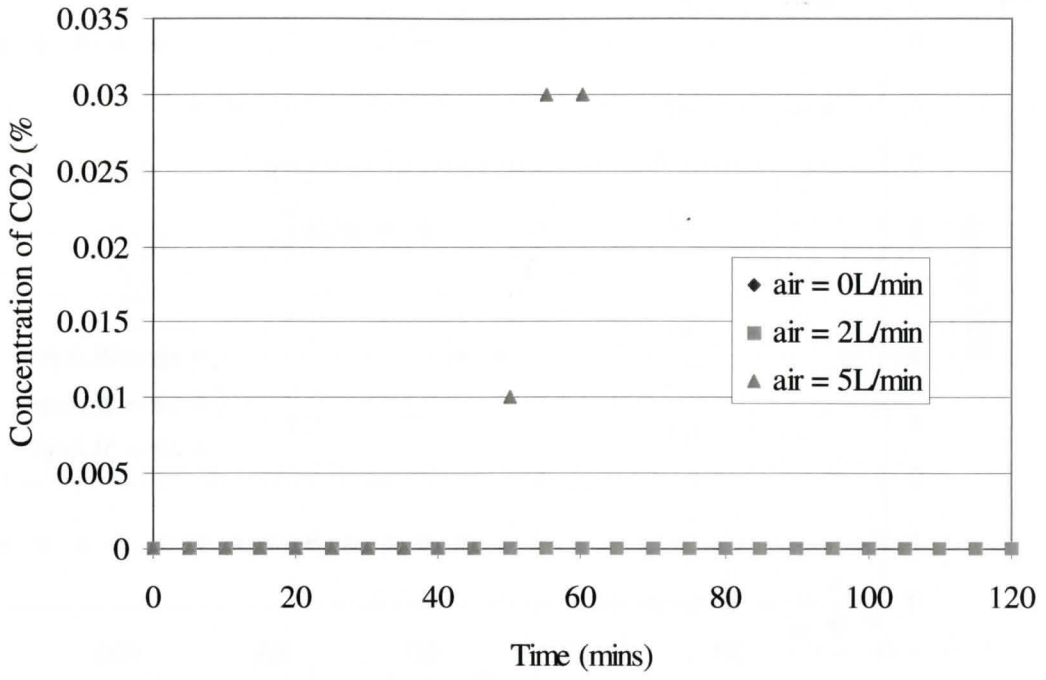

Figure 6.17: Concentration of CO_2 for different air flow rates (Argon flow rate fixed at 17.5L/min with respect to time)

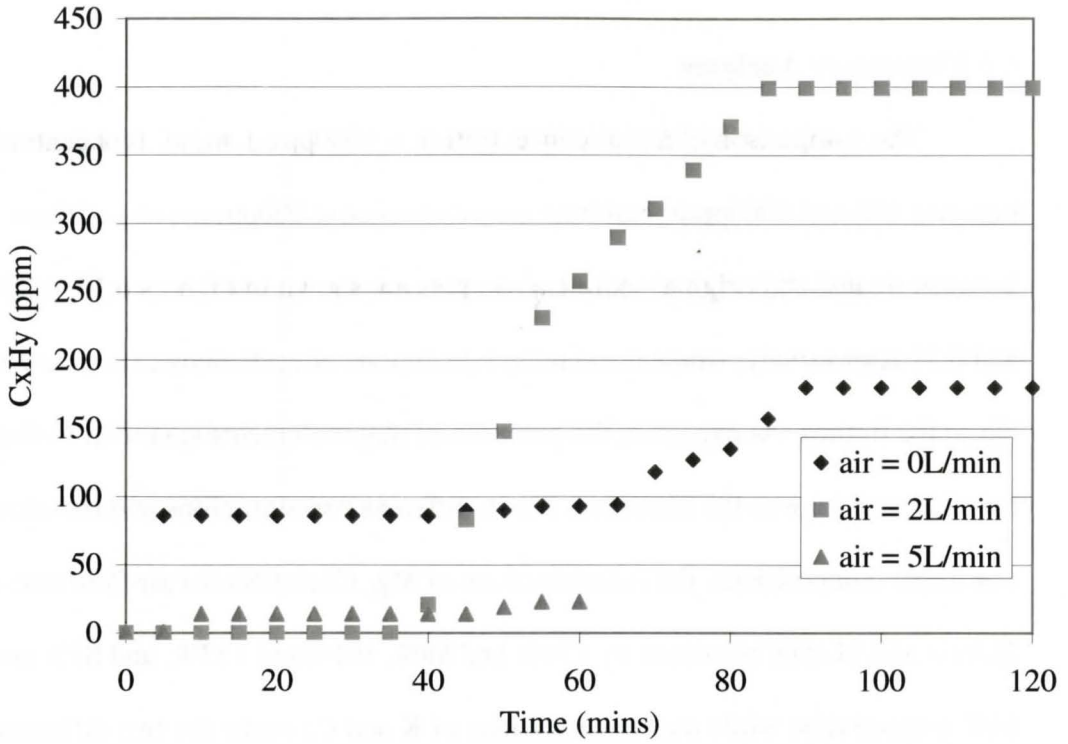

Figure 6.18: Concentration of C_xH_y for different air flow rates (Argon flow rate fixed at 17.5L/min with respect to time)

6.5 Elementary Analyses

The comparison of main (concentration > 1000ppm), minor (concentration between 100 and 1000ppm) and trace (concentration < 100ppm) compositions between treated and original sediment samples are shown in Figures 6.19, 6.20 and 6.21 respectively, where the standard deviations of each element are shown as bar in the figures. As expected, the presence of major elements is similar to that of the sediment prior to the treatment, but in different concentrations and enrichment. For major compositions, the concentrations of Mg, Cl and Na for air flow rate of 2L/min and 0L/min increased by 174% and 88%, 105%and 133%, and 83% and 61% respectively; while the concentrations of K and Ca under the two different air flow rates decreased by 23% and 35%, and 12% and 2%, respectively. For minor compositions, the concentrations of Cr, Sr, Ba and Mn fluctuate between 10-50% while Zn decreases by 25% and 29% respectively with the presence and absence of air. Enrichments of trace elements are observed after the treatment, with the exception of As and Nd. As it can be observed from Figures 6.19, 6.20 and 6.21, a deviance between main concentrations of elements does occur under oxidizing and reducing environments. This can be possible explained by the fact that in the presence of oxygen the formation of binary or tertiary oxides greatly decreases the volatilization of metals (Reich. J, 2003).

Zn, K and Nd are very volatile, and decrease in concentration after the treatment. Conversely, Na and Cl, being two of the most volatile elements,

increases in concentration instead. Elements exist in different chemical forms, whether pure metals, oxides, sulphites, carbonates, chlorides, hydroxides or other (Megy et al, 1997), and volatility depends on the chemical form of the elements.

The solid sediments were converted to an unleachable slag in the previous study of the treatment of MS by thermal plasma (Chang, et.al., 2003; Chang, et.al, 2005). However, as the operating temperature of the system did not reach above 1100°C, the process of melting inorganic compounds into slag could not be achieved. The plasma treatment system needs to be optimized for the treatment of stormwater sediment. Higher argon flow rate, higher plasma torch power and longer treatment time may be tested in future experiment. Also, low heat transfer from the plasma torch to the bottom of the reactor may further explain the failure of the melting process. The ceramic reactor may need to be in closer proximity to the plasma torch, or redesigned to enhance the heat transfer from the plasma torch to sediment.

Thermal plasma treatment of stormwater sludge still has a great potential as a treatment method since it can treat both organic and inorganic part of the contaminated stormwater sediments. Organic materials in the sediments are combusted and thus, reduce the volume of the waste. Inorganic materials in the sediments, including some toxic elements or compounds, are trapped inside the unleachable slag and can be reused as a building material. Extraction and recycling of some metals in the sediments can be accomplished. With the modification of the reactor and optimization of the plasma treatment system, the

efficiency of the combustion of organics may be increased; conversion of inorganic compounds into unleachable slag and extraction of metals may also be achieved.

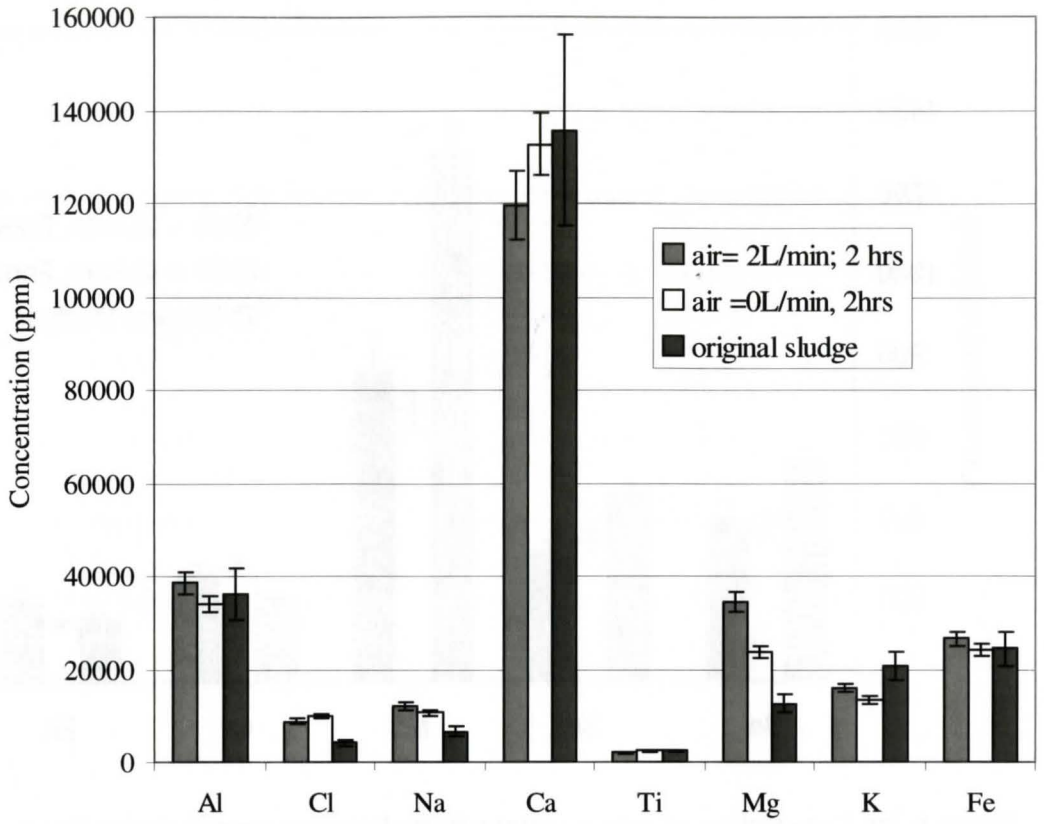

Figure 6.19: Comparison of main compositions between treated sludge (air = 2L/min and 0L/min in 2 hours, Argon flow rate fixed at 17.5L/min) and original sludge.

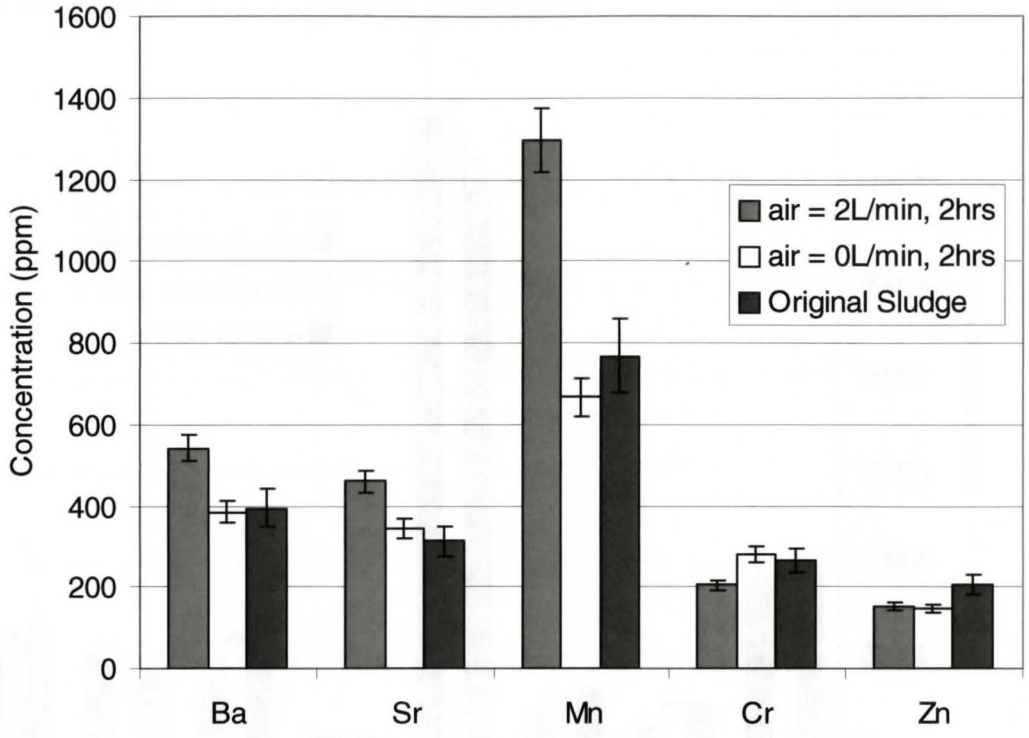

Figure 6.20: Comparison of minor compositions between treated sludge (air = 2L/min and 0L/min in 2 hours, Argon flow rate fixed at 17.5L/min) and original sludge.

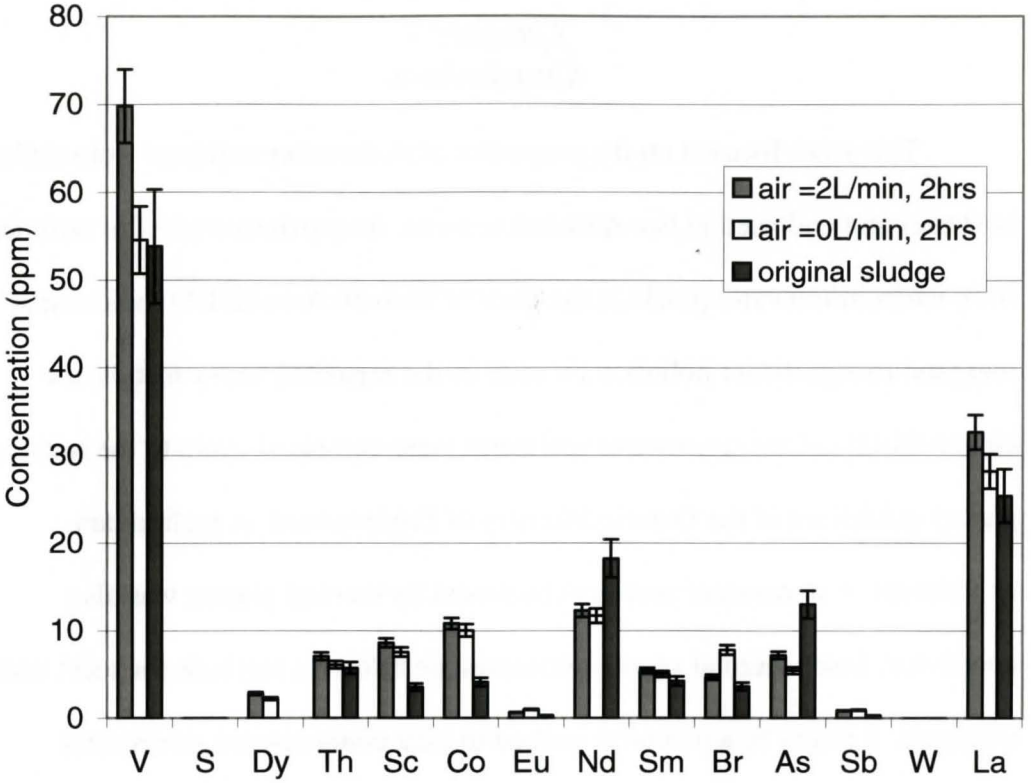

Figure 6.21: Comparison of trace compositions between treated sludge (air = 2L/min and 0L/min in 2 hours, Argon flow rate fixed at 17.5L/min) and original sludge.

Chapter 7
Conclusions

This work focused on the properties of stormwater sediment from different land uses and collected in two different seasons. As previous studies of sediments from varies stormwater ponds in the Greater Toronto Area (GTA) indicated a marginal-to-significant pollution by most of the regulated heavy metals, the characteristics of the stormwater sediments were compared again to the sediment quality guidelines of the Ontario Ministry of Environment. A preliminary experiment of stormwater sediment treatment by thermal plasma was also conducted. Since thermal plasma processes are effective methods for solid waste treatment, it might be a potential method to treat contaminated stormwater sediments as well.

Four different stormwater ponds around the city of Hamilton, Ontario, Canada were sampled in the summer of 2005. Two of the stormwater ponds are located in the town of Flamborough, Ontario, Canada. The remaining two ponds are located beside Dartnall Road and Ancaster soccer field in Hamilton. The first two ponds are located in residential areas and the last two ponds are located in commercial and industrial (highway) areas. For the one stormwater pond located in Waterdown Road, Flamborough, the sediments were taken on January and July in 2005 for winter and summer conditions respectively. Particle size and image of the sludge were analyzed by a laser particle size analyzer, a scanning electron

microscope and an optical microscope, while elementary characteristics were analyzed using neutron activation multi-element analysis (NAA).

The images from optical microscope showed that the particles in the dried sludge were irregular, and the sizes of each particle vary largely. Using scanning electron microscope (SEM), it was shown that two different structures of particles are present in the sediments. One is long, cylindrical material and the other is scattered, irregular material. The sediment particle size distribution for Parkside road, Waterdown road in the summer, Waterdown road in the winter and Dartnell road stormwater ponds were bimodal with maximum concentrations at 69μm, 45μm , 17μm and 20μm with another peak concentrations around 831μm, 1258μm, 830μm and 831μm, respectively. The sediment particle size distribution for Ancaster soccer field stormwater pond is single mode and has a maximum concentration at 20μm. By using neutron activation multi-element analysis (NAA), thirty-two elements were found in the sediment and nine among these thirty-two elements were below detection limit. The main compositions (above 1000ppm) of the dried sediment are Ca > Al > Fe > K > Mg > Na > Ti> Mn. The trace compositions (below 1000ppm) include Cl > Zn > Ba > Sr > Cr > V > La > Nd > As > Co > Sc > Br > Sm > Th > Eu. The concentration of Cr, Fe, Zn, As, Mn and Cd of each pond were compared to the LEL and SEL of the Ontario Ministry of Environment. The assessment of Zn in all ponds sediment against the MOE sediment quality guidelines indicates a marginal-to-significant pollution. The concentrations of Fe in Dartnell and Waterdown stormwater pond indicate a

marginal-to-significant pollution while the concentrations of Fe in Ancaster and Parkside stormwater pond in gross pollution. The concentrations of Cr in all ponds beside Waterdown stormwater pond sampled in summer indicate a gross pollution. The concentrations of As in all ponds except Parkside stormwater pond are above the LEL. The concentration of Mn in all stormwater ponds is above LEL. The concentration of Cd is below detection limit in Waterdown winter sample.

The size distribution is bimodal with maximum concentrations at approximately 26μm and 830μm in both the summer and winter samples from the Waterdown Road pond. However, a higher percentage of the large particles were found in the winter sample. Snow and ice may encourage clogging of small particles into larger particles. The compositions of elements present in the sediment are similar between summer and winter samples although the concentrations of each element are slightly different. The concentrations of Na and Cl in winter samples are higher than in summer samples, while the concentrations of Ca and Mg in summer samples are higher than in winter samples. The addition of road salts might be the major reason that winter stormwater sludge samples have higher concentrations of Na and Cl while Ca and Mg in fertilizer and limestone might be a major reason that results in higher concentrations of both elements in summer samples.

The sediment characteristics of two residential area stormwater ponds, one highway area stormwater pond and one commercial stormwater pond were also

compared. The particle size distributions in the residential area and highway area were similar, while a high percentage of smaller particles were observed in the commercial area. The concentrations of Ca, Cr, Zn and Cl in the four samples varied the most. Other elements have a quite similar pattern among the samples.

Although the differences between land-uses were not apparent in the stormwater sediment characteristics, some general effects could still be observed. It is within expectations that higher levels of chromium and zinc were observed in the Ancaster site, which is located in a commercial/light industrial area. The concentrations of Cl in highway/ commercial area were the highest among the four ponds as road salts are usually used in winter times. One possible reason that the concentrations of Cr, Zn, Mg and Ca differ greatly in the two residential area stormwater ponds in the same town is that the Waterdown site is located beside a main road while Parkside site is located inside a living area. The road runoff clearly affects the Waterdown site in summer-winter comparison as the concentrations of Na and Cl, which is a common deicing agent, are in higher concentrations in the winter.

A preliminary thermal plasma treatment was conducted on Dartnell stormwater sediment, which is located in a highway/ commercial area. The mean weight percentage removal by plasma treatment for 0L/min and 2L/min of air flow rate are 2.78% ± 0.51% and 3.85% ± 1.35%, respectively. The maximum weight removal of 5.87% was achieved with 2L/min air flow rate and two hours of treatment time. After the treatment, the two-phase structure in the stormwater

sludge was crystallized and only one structure was left in the sediments. The TOC in the treated sample were lower than the original TOC in Dartnell stormwater sediment. TOC percentage in the sample decreases with longer treatment time. Eight gas compounds including CO, CO_2, NO, NO_2, NO_x, SO_2, H_2S and C_xH_y emitted during the treatment process. The thermal plasma treatment that operated in an oxidizing environment yields more oxide compounds; while the process that operated in a reducing environment yields less oxide compounds and no NO, NO_2 and CO_2.

Chapter 8: Recommendations for Future Research

This work has been successfully conducted for the characterization of the physical and chemical properties of stormwater sediments sampled during different seasons and from different land-uses. Although the effect of land-uses on stormwater sediments is not apparent in this study, some differences were still observed. One of the possible reasons that the land use effect is not obvious is that the stormwater sediment characteristics also depend on the exact location of sampling within the pond. Because only about 2 liters of sediment samples were collected from a relatively huge area of each stormwater pond, the sediment characteristics may have large fluctuations even among samples collected from the same pond but at different locations within the pond. In future studies, samples may be taken at multiple locations at each pond (e.g., from the sediment forebay, main settling area, upstream of the pond outlet). As heavier elements are more condensed in the bottom of the sediment, different compositions would be found at varying depths. Sampling of the top, middle and bottom layers may also be considered.

Although neutron activation analysis (NAA) can detect multi-elements instantly, some regulated metals can only be detected by other analytical methods. The use of ICP accompanied with NAA to investigate the level of all regulated heavy metals is recommended for future studies.

Modifications of the preliminary plasma treatment process experimented in this study are necessary. The operating temperature in the plasma must be above 1000°C for the melting of inorganic part into unleachable slag.

Recovery of high concentration of heavy metals in stormwater sludge is another potentially feasible idea to reduce the cost of treatment (Legret, 2006; Haugsten, 2000; Izaumikawa, 1996). Sieving may be used to separate sediment particles and smaller particles may be treated using thermal plasma. It is expected that greater adsorption of heavy metals is on finer particles (Allan, 1986). This is in agreement with the observation of substantially higher metal concentrations in the fine sediment fraction (<45μm) in stormwater pond (Marsalek, 1997). As the organic compounds in the sediment are not sufficient enough to self-generate the power needed for treatment, mixing of stormwater sludge with other high organic-compound concentration solid wastes is recommended.

The emission of toxic gases during the treatment is another major concern. Significant amount of N, Cl, S components in stormwater sediment will be converted to NO_x, HCl and SO_x in the process. Conversion of CO to harmless CO_2 should be included in the design. Hydrocarbon in flue gas must be burned before emitting to the atmosphere. Some gas control systems should be introduced at the exit. Selective Catalytic Reduction (SCR) can be used to treat NO_x and SO_x and calcium injection can be used to eliminate HCl (J.S Chang, el. Science and Technology Network, 2005). High efficiency particulate air (HEPA) filters can be

inserted in the exit to capture volatile and semi-volatile materials in the off-gas stream.

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