The Potential Role of Bacteria as a Bioremediation Technique at the Sydney Coke Ovens Site

by

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ABSTRACT

The main objectives of this research were to ascertain whether bacteria are naturally occurring in the local groundwater and soils and to determine the potential role and effectiveness of these bacteria in degrading polycyclic aromatic hydrocarbon (PAH) in a bioremediation program at the Coke Ovens site in Sydney Nova Scotia. Samples were enumerated for sulphate reducing bacteria, iron reducing bacteria, aerobic heterotrophic bacteria and fermentative/acid producing bacteria. In addition the tolerance of these bacteria types was evaluated by adding various concentrations of naphthalene to soil sub samples. Both aerobic and anaerobic bacteria were detected to be naturally occurring at the site, however, the populations of different types of bacteria varied. PAH concentrations were also variable throughout the site with the Coke Batteries and Domtar areas having the highest concentrations in the groundwater and soil, respectively. It was found that increasing concentrations of naphthalene did not have an affect on the bacteria population densities. It is therefore difficult to conclude whether PAH degrading bacteria are present without further studies.

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LIST OF ABBREVIATIONS

AHB	aerobic heterotrophic bacteria
APB	acid producing bacteria
BTEX	benzene, toluene, ethylbenzene, xylene
CFU	colony forming unit
HDPE	high density polyethylene
HM PAH	High molecular weight polycyclic aromatic hydrocarbons
IRB	iron reducing bacteria
LM PAH	low molecular weight polycyclic aromatic hydrocarbons
MPN	most probable number
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
SRB	sulphate reducing bacteria
SRBB	sulphate reducing bacteria with benzoate
STPA	Sydney Tar Pond Agency
STPCO	Sydney Tar Pond and Coke Ovens site
SYSCO	Sydney Steel Corporation
US EPA	United States Environmental Protection Agency

1.0 INTRODUCTION

Environmental concerns arise as a result of industrial practices such as mining and the processing of raw materials. In the past, little attention was given to the protection of the environment and as a result mine and industrial processing sites have been contaminated with toxic chemicals such as polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and heavy metals. Today, it is a large expense for government and industry to clean up these sites to reduce the risks to people and the environment.

Mining and processing of raw materials can involve the generation of waste products and materials that are deposited on the earth's surface. Waste rock is generated and piled on the surface in a waste dump where it is tiered and stepped to minimize erosion. However, the exposure to precipitation can result in acid mine drainage which has the potential to contaminate groundwater and surface water. In the processing of metal rich rock, a slurry of fine particles suspended in water can be generated and is typically pumped to a dam or settling pond where the water evaporates. The remaining fine particles can be toxic because they may contain unextracted sulphide minerals. Slag is another waste product that is harmful to the environment. It is the by-product produced during the smelting of ore to purify metals and can contain a mixture of metal oxides and some metal sulphides or other elements. Slag can be stock piled on site for reprocessing in order to extract other metals or be disposed of at a landfill. These materials generate pathways for contaminants to enter the environment through unnatural means. By increasing their mobility, air, water and soil are at risk of becoming toxic to the earth's flora and fauna.

Sydney, Nova Scotia was home to a large steel making complex for 100 years. Closure of the site in 2001 led to the removal of the steel plant facilities and initiated a clean-up program for the four-hundred hectare property. The site included a coke oven plant where an estimated 560,000 tonnes of soil have been contaminated with coal by-products including, heavy metals, volatile organic compounds, PCBs and PAHs.

Coal from the Cape Breton Region was used to provide coke, a fuel and reducing agent, for steel production in Sydney. The use of coal at this site had many harmful effects. The coal was brought to the site and stock-piled before processing in designated areas. Coal naturally contains low levels of uranium and thorium which can be released into the environment when left in high concentrations in one area. Also, over the 100 years huge amounts of coal were heated and processed to coke, which generated many harmful waste products such as fly ash, bottom ash, boiler slag, and flue gas desulfurization, all of which contain toxic contaminants. One group of contaminants, PAHs, were generated at the site as a result of the incomplete combustion of coal. During the 100 years of operations, high levels of these contaminants were produced and remain on the site. It is unclear what effects this may have had on the local microbial ecology in the Coke Ovens site.

PAHs are a class of hazardous organic chemicals that are formulated from two or more fused aromatic rings, and are known to have toxic effects on human health (Monna et al, 1993). These harmful compounds enter the environment through two potential pathways, 1) adsorbed onto particles that are emitted from the incomplete combustion of carbon-containing fuels or 2) from coal tars (Bouchez et al., 1996). Extensive industrial coal

liquefaction and gasification during most of the 20th century has left massive amounts of soil contaminated with PAHs (Johnsen et al., 2005). Typically, these contaminated sites were located in urban regions so that coal gas could be efficiently distributed to customers. As a result, many contaminated sites are found in or near cities where they create a large public health hazard.

PAHs have low aqueous solubility and low vapour pressures; therefore, these compounds are more prevalent in soil as opposed to water or air. The mobility of PAHs in soil and groundwater decreases with increasing molecular weights because as the molecular weight increases the PAHs become less soluble and less volatile (Brauner et al., 2002). Studies have shown low molecular weight PAH compounds are able to biodegrade under certain environmental conditions, while PAH compounds with higher molecular weight tend to be recalcitrant (Brown et al, 1999).

From the 1970s to 1990s the more traditional approach to remediation was to excavate contaminated soil and transfer it to a landfill for disposal. In the case of contaminated groundwater, the pump and treat method was used. Since the 1990s, various land reclamation techniques have been applied such as capping, incineration, soil washing, bioslurry reactors, composting, air sparging and bioventing, phytoremediation and bioremediation. The type of remediation technique chosen for a contaminated site depends on site specific conditions. It is important to characterize a site in order to determine its potential for the use of the different remediation technologies.

The US EPA defines bioremediation as a treatment process that uses naturally occurring microorganisms (e.g., yeast, fungi, and bacteria) to break down or degrade hazardous

substances into less toxic or non-toxic substances (Sylvia et al, 2005). A range of bioremediation techniques can be used, anything from allowing natural bioremediation to occur in situ with no intervention, to the excavation of contaminated material for an off-site treatment such as landfarming or lastly by the use of bioreactor tanks (Sylvia et al., 2005). Depending on the technique chosen, the process of bioremediation may result in varying degrees of transformation or degradation of contaminants. For example, in biotransformation, a parent compound can be transformed into a daughter compound that is less toxic. Alternatively, mineralization may occur, the process of complete biodegradation of an organic contaminant to its inorganic constituents, typically carbon dioxide and water (Sylvia et al., 2005). Studies have shown a variety of bacteria, fungi and yeasts can degrade contaminants. In nature mixed groups of organisms function together to degrade hydrocarbons as different organisms can attack the same hydrocarbon using a similar or different pathway.

The degradation of PAHs occurs through oxidation, where an electron is transferred from the organic compound to a substance known as an electron acceptor or oxidant. This process is biologically mediated, where microorganisms catalyze electron transfer (Madsen et al, 1997). The free energy and carbon released from the reactions are used by the microorgansms to generate more adenosine triphosphate and biomass. The degradation of contaminants occurs at a faster rate with oxygen as compared to other electron acceptors. As the oxidant, oxygen thermodynamically releases the most energy compared to other final electron acceptors, such as nitrate, manganese (IV) oxide, iron (III) hydroxide, sulphate and carbon dioxide (Madsen et al., 1997). When oxygen is limited and aerobic processes decrease then other final electron acceptors can be utilized.

PAHs have been shown to degrade under anaerobic conditions, including methanogenic conditions, sulphate-reducing conditions and nitrate reducing conditions (Chang et al., 2002).

A potential pathway for the degradation of naphthalene under anaerobic conditions by the pseudomonas species has been proposed (McD Francis and Gould, in prep). Through dioxygenase enzymes molecular oxygen is incorporated into the compound to form cis-naphthalene dihydrodiol, which through ring fission leads to the formation of intermediate compound salicylate. Under anaerobic conditions, Zhang and Young (1997) reported for the first time that carboxylation is the initial key in the reduction of naphthalene and phenanthrene under sulphate reducing conditions. The breakdown of both naphthalene and phenanthrene results in the formation of the intermediate compound carboxylic acid which is further broken down to carbon dioxide and water (see Figure 1) (Zhang and Young, 1997; Meckenstock et al., 2000).

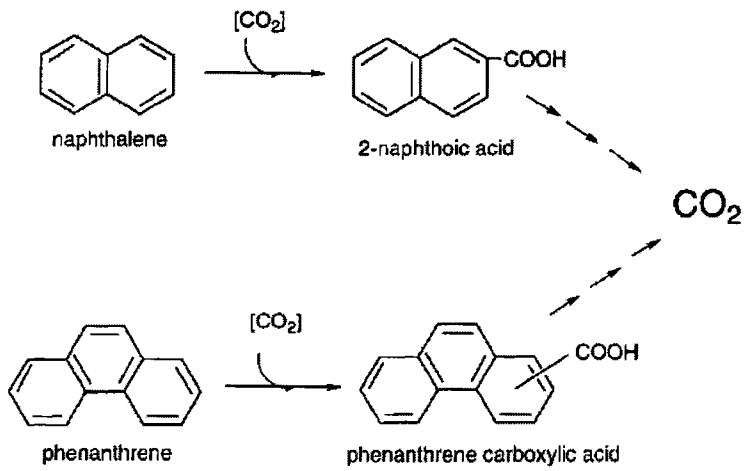

Figure 1: Proposed summary pathways for the anaerobic metabolism of naphthalene and phenanthrene in the sulfidogenic enrichments. (Zhang and Young, 1997)

Landfarming is a bioremediation treatment process that is performed in the upper soil zone or in biotreatment cells. This type of treatment can be used *in situ* or *ex situ* to remediate contaminated soils, sediments or sludge (Sylvia et al., 2005). In landfarming, natural microbial communities are stimulated under aerobic conditions to degrade contaminants by the addition of oxygen and nutrients (Straube et al., 2003). Physical mixing of soils is used to improve aeration and the addition of nutrients can also be done to stimulate degradation (Straube et al., 2003). In *ex situ* treatment, contaminated material is transferred to cells underlain with an impermeable barrier to collect potential leachate. Similar to *in situ* treatments, soil is tilled, fertilized and irrigated. Once contaminant levels decrease to the desired concentrations, soils can be removed and disposed of in landfills or reintroduced to the original site. Studies have shown landfarming to be a common technique for the remediation of PAH-contaminated soils (Straube et al., 2003). For example, Mendonca and Picado (2002) showed that landfarming of two, three and four ringed PAHs was successful at a Coke Ovens site in Portugal. Total PAHs were reduced by 64% in three months (1141mg/kg to 415mg/kg). The reduction was due to the biodegradation of low molecular weight PAHs.

As part of a large scale remediation program, the Sydney Tar Pond Agency (STPA) evaluated four cleanup options for the Coke Ovens site provided in the Remedial Action Evaluation Report (2003). Option 1 involved *in situ* containment and *in situ* treatment through bioremediation. *In situ* treatment would reduce the concentrations of contaminants in the surficial soils prior to the placement of a contaminant cap of cover.

The cover would limit the concentration of contaminants in contact with the surface water. The second option is the complete removal and *ex situ* containment of contaminated materials in a new containment facility (landfill) built on the site. Option three for the site involves *ex situ* treatment; contaminated soils and sediments are excavated and undergo soil washing and the subsequent destruction of the concentrated contaminants through co-burning. Option four requires the *ex situ* treatment of soil through thermal desorption or pyrolysis and similar to option three, contaminants will be destroyed by co-burning.

In the Environmental Assessment Report, the STPA proposed to use three methodologies to remediate the different sections of the Coke Ovens site, including the destruction of organic contaminates by excavation and incineration, treatment of contaminated soils by landfarming and containment of contaminated soils in situ.

Many studies have proven that remediation techniques, such as landfarming, are effective on soils containing naturally occurring bacteria. However, in highly contaminated sites it is not clear whether indigenous bacteria would be present in sufficient quantities to bioremediate the contaminants of concern. In order to determine the potential use of naturally occurring bacteria as a bioremediation technique for the Coke Ovens site in Sydney, it is important to characterize the natural microbial communities within the soil and groundwater, determine the levels of contaminants and assess the degradation ability of the microbial community. By characterizing the Coke Ovens site, it is possible to assess whether biodegradation is a viable remediation option for sites with similar site conditions.

1.1 Study Objectives

The main objectives of this research are:

- to ascertain whether bacteria are naturally occurring in the soils and groundwater of the Coke Ovens site in Sydney;
- to characterize the microbial ecology of the soils in terms of type and abundance of different groups of soil bacteria; and,
- to determine the potential role and effectiveness of these bacteria in a bioremediation program, based on their tolerance to various concentrations of naphthalene at the Coke Ovens site.

These objectives were achieved by:

1. Evaluating the soil and groundwater samples for the presence or absence of anaerobic and aerobic bacteria including aerobic heterotrophic bacteria (AHB), sulphate reducing bacteria (SRB), iron reducing bacteria (IRB) and fermentative/acid producing bacteria (APB) using the most probable number (MPN) technique (Cochran, 1950);
2. Determining the concentration of various PAH compounds at each soil and groundwater sampling location;
3. Evaluating the tolerance of naturally occurring bacteria at the Coke Ovens site to known concentrations of naphthalene.

1.2 Study Area

The study was conducted at the old Sydney Steel Corporation (SYSCO) steel manufacturing complex, now known as the Sydney Tar Ponds and Coke Ovens site (STPCO). This is located in the heart of Sydney, Nova Scotia, Canada on the east coast

of Cape Breton Island (Figure 2). It is surrounded by commercial, light industrial property, the capped Municipal Waste Disposal site/Municipal Ash Industrial Disposal site and residential land (Dillon-ADI, 2004).

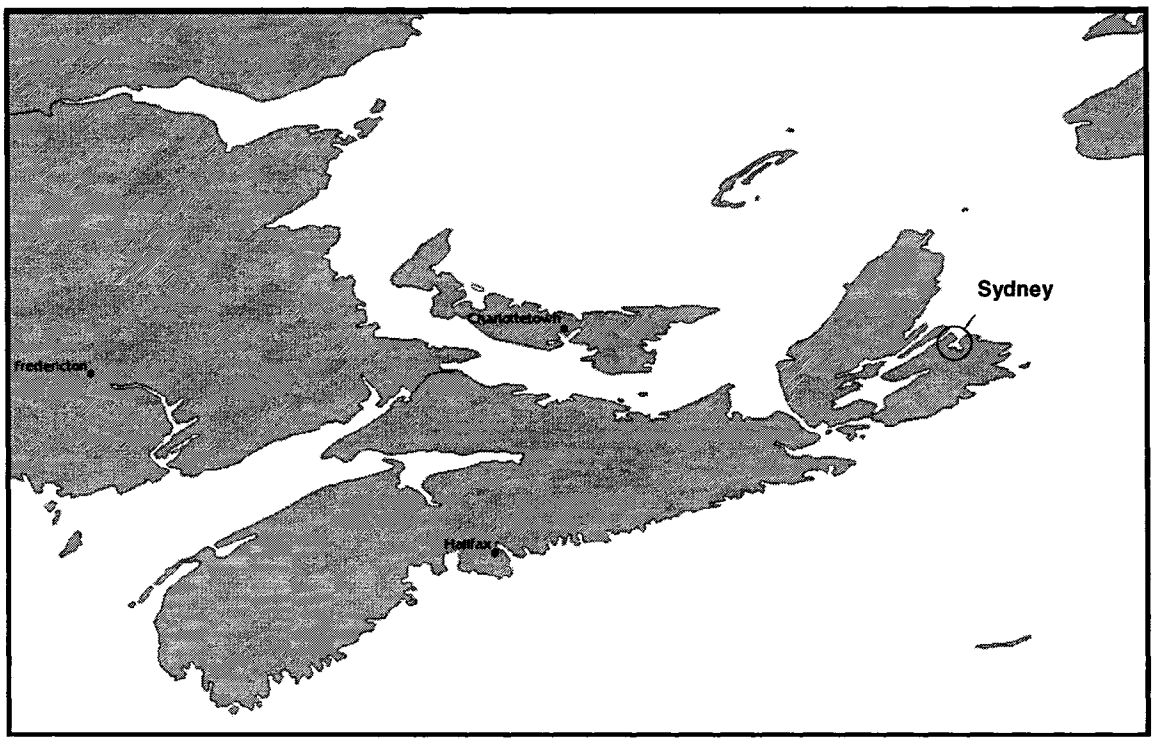

Figure 2: Location of the study area, Sydney, Nova Scotia, Canada

The site is located within the Muggah Creek Watershed. The watershed is approximately 1.8 kilometers long. Muggah Creek is an estuary at the downstream end of the watershed, and has been divided into the North Pond which empties into the South Arm of Sydney Harbour and the South Pond which is separated from the North Pond by a berm and weir structure. The Coke Ovens Brook crosses the site and enters from the east and migrates westward across the site and then south to the Coke Ovens Brook Connector which discharges into the South Tar Pond (Figure 3).

The Muggah Creek Estuary used to be a pristine environment, but during the steel mill operations, the North and South Ponds were infilled with slag and sludge migrating down the Coke Ovens Brook. Over time the infilling operations encroached upon the former salt marsh and changed the configuration of the natural shoreline of the harbour. Another source of contamination is the municipal landfill to the east of the Coke Ovens site. Leachate contaminated groundwater migrates eastward through the Coke Ovens site, where other contaminates are introduced, and discharges at the South Pond. The leachate contaminated groundwater is characterized by high concentrations of major ions and trace metals with few organic contaminants, but as it moves through the Coke Ovens site organic contaminants increase.

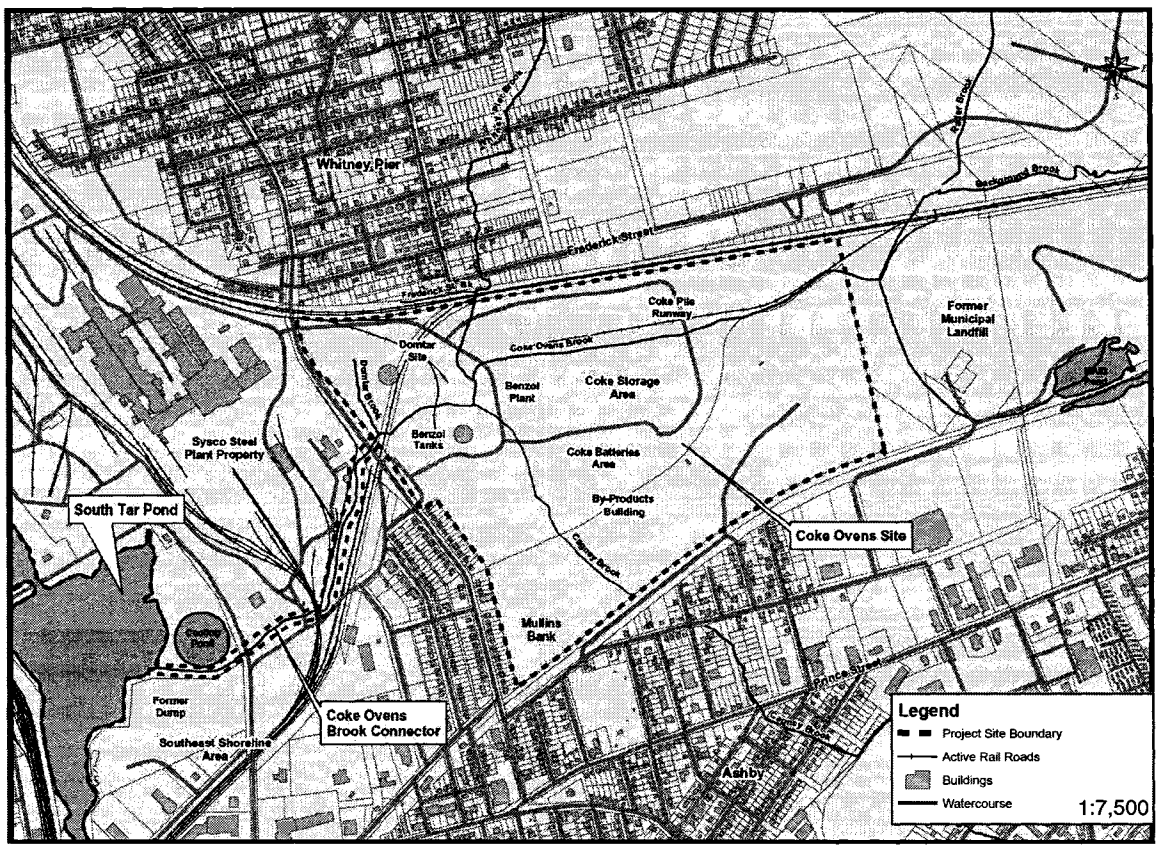

Figure 3: Coke Ovens site plan showing surrounding features (from AMEC, 2005b)

1.2.1 Site History

In 1901 American industrialists opened this steel manufacturing complex in the port town of Sydney, NS. The SYSCO complex was an active producer of steel until 2001. Sydney was an ideal location for such a large operation because of its proximity to a good harbour for shipping, plenty of cooling water, proximity to local coal fields and limestone deposits and nearby iron ore from Bell Island, Newfoundland.

The manufacturing complex contained many other industries operating at the site including a coal tar plant, a cement plant, an asphalt paving company, a fuel gas and oil company, metal processors and a brick manufacturing company, all of which produced wastes that have contributed to the contaminants in the area's soil, sediments, surface and groundwater and air. Prior to the last 20 years, little was known about the negative environmental effects of industrial waste and the steel manufacturing industry provided a wealth of jobs for local residents making the stockpiled waste by-products seem like a harmless trade-off for prosperity.

As part of the steel manufacturing complex, a Coke Ovens site processed coal from the local Sydney Coal Fields into coke to supply the steel processing plant with fuel from 1901 to 1988. After 1988 the steel plant converted to an electric arc process that does not use coke. The by-products of coke production operations included coal tar, ammonia, sulphur, light hydrocarbons and polyaromatic hydrocarbons. Other sources of contaminants include the storage of raw coal and coke products, flue dust from the blast furnaces and ovens, and coal tars. These waste materials were stockpiled in storage areas at the plant site or deposited onto the soil or into the watercourses on site. As a result, the

soil and groundwater within the SYSCO manufacturing complex is contaminated with coal by-products. In 1999, concerned residents who lived on Frederick Street, directly north of the Coke Ovens site, were relocated due to fears of exposure to the toxic contaminants on the site.

1.2.2 Coke Ovens Site

The Coke Ovens site is approximately 68 hectares and contains over 560,000 tonnes of contaminated soils. There are five main areas within the Coke Ovens site including the Domtar area, the Benzol Plant and tanks area, the Coke Storage area, the Coke Batteries area and Mullin's Bank area (Figure 3). The five sites were described in detail in the Remediation of Sydney Tar Ponds and Coke Ovens Sites: Environmental Impact Statement, (AMEC, 2005b). The sites are summarized below.

The first area is the Domtar site, which includes the in-ground Tar Cell containing 25,000 tonnes of tars and contaminated soil, and other widespread coal tars. In the summer months, tar oozes onto the surface and solidifies in solid golf size balls. The Domtar site was in operation from 1903 to 1963 and contained tar lagoons, an above ground petroleum storage tank farm with 17 tanks, oil/tar distilling units, an administration building and load-out platform with rail sidings.

The second area is the Benzol Plant and tanks area. It was constructed to remove BTEX components from the coking gas produced from the coking plants. Operations involved pumping oil through shallow subsurface lines to secondary coolers/condenser buildings at each Coke Plant (AMEC, 2005a). The oil would come into contact with the gas to allow

the BTEX to absorb onto the oil. The resultant benzolized oil was pumped back to the Benzol Plant for final processing and extraction. The Benzol Plant facilities included above ground benzol storage tanks, light oil underground tanks, distillation building, and subsurface drains. The site was operational for at least 73 years.

The third area is the coal pile runway and Coke Storage area. In 1901 the first Coke Plant (Oven No. 1) was built in the coal pile runway area and in 1911, the coke operations were relocated to the southern region of the Coke Ovens site. After the Coke Ovens were relocated, this area was used to temporarily store coke on a 1.6 hectare pad between 1966 and 1988. Remaining infrastructure includes footings for the ovens, a water tank, and water line.

The fourth area is the Coke Batteries and By-Products Buildings. The Coke Plants included a number of coke batteries and ovens. By 1953, the batteries contained a total of 114 vertical slot ovens with an estimated capacity of 600,000 tonnes of coke per year. Raw coal was fed through charging holes on the top of the batteries and heated to 1,200°C with little oxygen for 18 to 24 hours. "Cooked" coke was pushed into a car and transferred to a quenching tower, where it was water cooled in the by-products building. Once cooled, the coke was returned to the batteries and fed by conveyor to the crushing and screening plant for sorting. Coarser components were taken to the blast furnaces and fines were either used in the sinter plant/boilers or discarded. The precipitated tars were stored in tanks and transferred to the Domtar area. BTEX components were also extracted (using unbenzolized oil) and pumped to the Benzol Plant in shallow subsurface pipelines. Numerous ruptures of the pipeline have been reported over the operational life

of the site. A sulphur plant was also located in this area. Raw sulphur was used to produce sulphuric acid for the extraction of ammonia sulphate from gases produced in the ovens. Over the 70 year period large quantities of hazardous materials were transferred, used, and stored in the By-Products Buildings area. Building and structures included exhaust stations, coolers, scrubbers, service shops and a transfer station. The site was significantly disturbed by the construction of buildings, support structures, the Cagney Brook underdrain, site operations and demolition activities. The batteries were demolished in the 1980s, however, some brick and steel remain and it is assumed the oven basements are flooded.

The fifth area is the Mullin's Coal Bank. This site was used to temporarily store coal prior to shipment overseas from the 1930s to 1980s. This area contained a rail accessible transfer bank and coal pads. Cagney Brook was diverted through the site in an underground tunnel system which extended to Coke Ovens Brook.

1.2.3 Geology

The local bedrock geology consists of the Palaeozoic age Carboniferous System. Within this system the Canso Group Point Edward Formation is overlain by the Morien Group South Bar Formation (NSDNR, 1986). The Morien Group South Bar Formation, in the vicinity of the STPCO site, is comprised of grey sandstones and pebbly sandstones with minor conglomerates and rare coal, while the Canso Group Point Edward Formation consists of red and minor grey-green variably calcareous siltstone and sandstone with minor limestone. The coal resources of Nova Scotia are spread over several coalfields and coal districts, however the major portion of Nova Scotia's coal is within the Sydney

coalfields of Cape Breton Island (NSDNR, 1986). Local coal deposits that have been mined over the last century are typically found in intermittent seams within the Morien Group.

The surficial geology of the study area is comprised of Wisconsinian age ground moraine (till) deposits derived from local bedrock (NSDNR, 1992). The till contains a sandy matrix with numerous boulders and is typically two to four metres thick. The till is characterized by a stony, sandy matrix composed of material derived from the local bedrock (NSDNR, 1992). Fill material covers most of the site and is typically 1 to 3 metres thick (NSDNR, 1992). More recent deposits since glaciation, such as peat bogs/organic deposits and alluvial deposits, would also be expected in the area; however, due to industrial development and activities over the site, most of the more recent natural deposits have been removed during development or buried by fill placement.

1.2.4 Hydrogeology

Groundwater flow in the Coke Ovens site is in an east to west direction from the closed municipal landfill site towards the South pond (see Figure 3). The local groundwater at the Coke Ovens site is complicated by a remaining underlying infrastructure, which promotes lateral and vertical migration of contaminants. There are four hydrostratographic units within the Coke Ovens site. The first unit is the fill which has a geometric mean hydraulic conductivity of 4.0×10^{-4} cm/sec. It is typically 1 to 3 metres thick and has extensive contamination with coal tar. The till is typically 2 to 4 metres thick, but is thin or absent in the southern end of the site. The geometric mean hydraulic conductivity of the till is 1.7×10^{-4} cm/sec. The underlying bedrock is mainly comprised

of sandstones of the Morien Formation that are bounded to the west by an eastward dipping contact with the shales/mudstones of the Canso Formation. The Morien Formation and Canso Formation have fracture hydraulic conductivities of $5.5x10^{-5}$ cm/sec and $6.6x10^{-6}$ cm/sec, respectively. The geological contact is oriented approximately in a north – south direction and is situated in the west part of the Coke oven site in the Domtar area. The Canso Formation prevails to the west of the contact and is overlain by the Morien Formation to the east.

2.0 METHODOLOGY

2.1 Field Methods

The following sections describe the methods followed during the collection of soil and groundwater samples at five locations in the Coke Ovens site during a site visit in September 2006. In consultation with the STPA, the sampling program was designed to include the five subareas of the Coke Ovens site. Five sample locations, each representative of its subarea, were sampled for soil and groundwater. Field parameters were no obtained during sampling because the equipments was not available at the site.

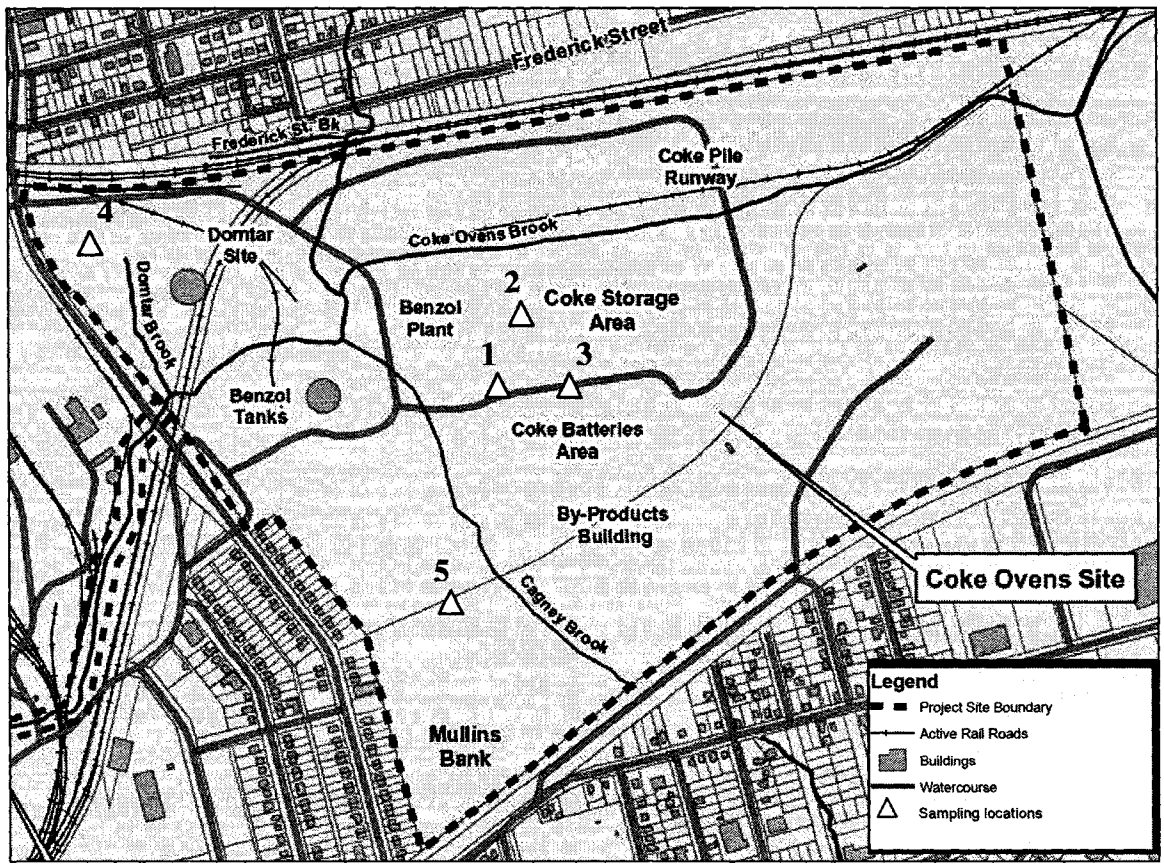

Figure 4: Sampling locations within the Coke Ovens site (modified from AMEC, 2005b).

2.1.1 Groundwater Sampling

Five groundwater monitoring wells were sampled in different sections of the Coke Ovens site (see Figure 4). Sample location 1 was in the Benzol Plant area at monitoring well COBP-001-MWB. Sample location 2 was in the Coke Storage area at monitoring well COCS-004-MW. Sample location 3 was in the Coke Batteries Storage area at COCB-003-MWA. Sample location 4 was in the Domtar area at CODT-002-MW. Sample location 5 was in the Mullin's Bank area at COMB-005-MW. All groundwater locations were screened in the shallow bedrock with the exception of COCB-003-MWA, which was screened in the till/fill layer.

All groundwater samples were collected using HDPE 1.6 cm ID tubing with a waterra foot valve. Two samples from each well were collected, one of the standing water and one after five minutes of purging (approximately two well volumes). Each sample, before purging and after purging, consisted of two 250 mL amber bottles and one 500 mL HDPE plastic bottle. The sample bottles were completely filled leaving minimal headspace. Samples were transported from Sydney, NS to Ottawa, ON in coolers with ice packs to ensure the samples remained between 4°C and 10°C until they were refrigerated. Samples were stored in the Earth Sciences Laboratory at Carleton University, Ottawa, ON until they were transported to the CANMET Laboratories to be prepared for microbiological analysis and Caduceon Environmental Laboratories for PAH analyses.

2.1.2 Soil Sampling

Soil samples were collected within 2 metres of each groundwater sample (see Figure 4). Samples were collected at surface and at 25 cm below ground surface using a hand trowel and shovel. For each sample, two 500 mL wide mouth glass jars were completely filled leaving minimal headspace and sealed with Teflon-lined lids. Samples were transported from Sydney, NS to Ottawa, ON in coolers with ice packs until to ensure the samples remained between 4°C and 10°C they were refrigerated. Samples were stored in the Earth Sciences Laboratory at Carleton University, Ottawa, ON until they were transported to CANMET Laboratories to be prepared for microbiological analysis and Caduceon Environmental Laboratories for PAH analysis.

2.2 Laboratory Methods

2.2.1 PAH Analysis

Groundwater and soil samples were sent to Caduceon Environmental Laboratories in Ottawa, Ontario for PAH analysis. Samples were analysed following the US EPA standardized method 8270 using a gas chromatograph/mass spectrometer. Samples were extracted with dichloromethane.

2.2.2 Microbiology

Ten groundwater and soil samples were analysed for aerobic heterotrophic bacteria (AHB), iron-reducing bacteria (IRB), sulphate-reducing bacteria (SRB) and fermentative/acid producing bacteria (APB) at the CANMET Laboratories in Ottawa, Ontario. Enumerations of IRB, SRB and APB were completed using the most probable number (MPN) technique (Cochran, 1950) and expressed as MPN/g or MPN/mL, while

the AHB were counted and expressed as CFU/g or CFU/mL of sample material. These culture-based techniques may under estimate the metabolically active bacteria by an order of magnitude and does not consider the slow-growing, non-culturable, or inactive microorganisms and bacteria that require specific redox or nutrient conditions not provided by the chosen culture media (Bhupathiraju et al., 1999). However, the selective media culture based methods used in this study provide an overall assessment of the functional groups of bacteria present at the site. These methods were selected in consultation with Dr. D.W. Gould of CANMET where the microbiology analysis was completed.

AHB were enumerated by plate count on minimal media agar. The collected samples were serially diluted using nine millilitres of 10% NaCl in test tubes. For each sample, one gram of soil or groundwater was added to the test tube in the first dilution series. A 10-fold dilution series was used for each sample, transferring one millilitre aliquots through the dilution series. The spread plate method was used for dilutions 10^{-2} to 10^{-6}. 0.1 millilitre aliquots were transferred to solid minimal media agar plates (3g/L trypticase soy broth and 20g/L agar) in triplicate. A flame sterilized glass rod was used to spread the sample on the surface of the agar. Inoculated plates were inverted and incubated at 27°C for 72 hours. After 72 hours the colonies were counted and expressed as CFU/g.

The growth media for IRB was composed of 5g $NaHCO_3$, 3g NH_4Cl, 1.2g NaH_2PO_4, 0.2g $CaCl_2$ $4H_2O$, 0.2g KCl, 0.2g $MgCl_2$ $6H_2O$, 0.01g $MnCl_2$ $4H_2O$, 0.002g Na_2MoO_4, 3.68g ferric EDTA and 3g peptone (Gould, 2003). These ingredients were added to two litres of deionized water in a two litre Erlenmeyer flask. The pH was adjusted to 7.0

using either HCl or NaOH to alter the pH as required. The liquid broth was heated to approximately 100°C and aerated with nitrogen gas for approximately one hour.

Two sets of SRB enumerations were completed using different modifications to Postgate medium C (Postgate, 1979) as described by Benner et al. (1999). The first growth medium and reducing agents (SRB) were composed of 1g KH_2PO_4, 2g NH_4Cl, 9g, Na_2SO_4, 0.08g $CaCl_2$ 6H2O, 0.12g $MgSO_4$ $7H_2O$, 5.87g Na lactate, 2.56g Na acetate, 2g yeast extract, 0.008g $FeSO_4$ $7H_2O$, 0.6g Na citrate dehydrate and 0.4% resazurin. These ingredients were added to two litres of deionized water in a two litre Erlenmeyer flask. The pH was adjusted to 7.5 using H_2SO_4 to decrease the pH and/or NaOH to increase the pH, as required. The liquid broth was heated to approximately 100°C and aerated with nitrogen gas for approximately one hour.

The second growth medium (SRBB) was composed of 1g KH_2PO_4, 2g NH_4Cl, 9g, Na_2SO_4, 0.08g $CaCl_2$ 6H2O, 0.12g $MgSO_4$ $7H_2O$, 0.1g yeast extract, 10g sodium benzoate, 0.008g $FeSO_4$ $7H_2O$, and 0.4% resazurin. These ingredients were added to two litres of deionized water in a two litre Erlenmeyer flask. The pH was adjusted to 7.5 using H_2SO_4 to decrease the pH and/or NaOH to increase the pH, as required. The liquid broth was heated to approximately 100°C and aerated with nitrogen gas for approximately one hour.

The IRB and SRB growth mediums were distributed into 20 millilitre serum bottles in an anaerobic chamber. Nine mL of growth medium was transferred into the serum jars using a nine millilitre pipette. Each serum jar was sealed with a rubber stopper and metal cap. All serum jars containing growth medium were then autoclaved to sterilize and to

ensure there was no oxygen present. A 10-fold dilution series was used for each sample with five replicates. For each sample, one gram of soil or groundwater was added to five test tubes in the first dilution series in the anaerobic chamber. Using a 10 millilitre syringe, a one millilitre aliquot was transferred from the first dilution to the second dilution. Each dilution was sequentially inoculated to a final dilution of 10^{10} for IRB and SRB samples and 10^{8} for SRBB samples. Inoculated samples were stored in the anaerobic chamber at room temperature for 28 days.

The APB growth medium was composed of 10 grams dextrose, 2 grams beef extract, 20 grams protease peptone, 10 grams NaCl and 0.2 grams bromothymol blue. These ingredients were added to two litres of deionized water in a two litre Erlenmeyer flask as describer in Hulshof et al. (2003). The pH was adjusted to 7.2 using HCl to decrease the pH and/or NaOH to increase the pH, as required. The liquid broth was heated to approximately 100°C and stirred for approximately one hour. Test tubes were filled with nine millilitres of the liquid broth using a nine millilitre pipette. A 10-fold dilution series was used for each sample with five replicates. All inoculation and dilution procedures were completed in a laminar flow hood using sterile pipette tips. For each sample, one gram of soil or groundwater was added to five test tubes in the first dilution series. Starting with the first dilution, the test tube was vortexed three times and a one mL aliquot transferred to the second dilution. Each dilution was then sequentially inoculated in the same manner to a final dilution of 10^{10}. The test tubes were incubated for 96 hours at room temperature. A positive result was indicated by a change in colour from blue/green to yellow, indicating a change in pH below 6. The number of APB in each sample was determined using the MPN technique.

Soil samples with similar PAH concentrations were combined to generate a composite sample of the Coke Ovens site. Eight 500 millilitre glass jars were filled with 50 grams of the composite sample. Four solutions were mixed with various concentrations of naphthalene. Each solution was mixed with acetone to generate 100 ppm, 1,000 ppm and 10,000 ppm naphthalene concentration solutions. 5 millilitres of each solution was added to two composite sample jars. 5 millilitres of acetone (0 ppm naphthalene) was added to two sample jars to represent a control sample. One set of composite samples was stored in the anaerobic chamber while the other set was placed in a laminar flow hood under aerobic conditions. The samples were incubated for approximately 6 weeks.

Each composite sample was analysed for APB, IRB and SRB enumerations using the methods described above with the following exceptions. 0.1 gram of bromothymol blue was added to the APB growth media instead of 0.2 gram. There was a slight variation in the SRBB growth medium. The sodium benzoate concentration was reduced by half and replaced with pyrogallol. The growth medium for the second SRBB was composed of 1g KH_2PO_4, 2g NH_4Cl, 9g, Na_2SO_4, 0.08g $CaCl_2$ 6H2O, 0.12g $MgSO_4$ $7H_2O$, 0.1g yeast extract, 5g sodium benzoate ($NaC_6H_5CO_2$), 5g pyrogallol ($C_6H_6O_3$), 0.008g $FeSO_4$ $7H_2O$, and 0.4% resazurin for 2 litres of medium.

3.0 RESULTS

3.1 Soil Samples

3.1.1 Soil PAH Analysis

Table 1 presents the results of PAH analysis completed at each soil sampling location at surface and at 0.25 metres depth. As can be seen in Table 1, the Domtar site exhibited the highest concentrations of individual PAHs constituents ranging from 2.8 to 145 ppm at surface and 3.7 to 89.3 ppm at depth. In comparison, the background station in Mullin's Bank exhibited lower PAH concentrations by 2 to 3 orders of magnitude, ranging from 0.007 to 0.242 ppm at surface and 0.006 to 0.215 ppm at depth. The Battery Storage area contained the second lowest concentrations, ranging from 0.03 to 0.62 ppm at surface and from 0.04 to 0.77 ppm at depth. The Benzol Plant and Coke Storage areas exhibited similar intermediate PAH concentrations. The PAH concentrations in the Benzol Plant area at surface ranged from 0.23 to 4.15 ppm and from 0.03 to 7.77 ppm at depth. The Coke Storage area ranged from below laboratory detection limit to 5.6 ppm at surface and from 0.04 to 4.7 ppm at depth.

Due to the variability in the PAH concentrations at the site, there was no dominant PAH constituent. The low molecular weight PAHs tended to have the highest concentrations at each site, with the exception of pyrene in the subsurface at the Coke Storage area. The total low molecular weight PAHs had higher concentrations than high molecular weight PAHs with the exception of the Domtar site which had higher concentrations of high molecular weight PAHs.

Table 1: PAH concentrations (ppm) in soil samples from the Coke Ovens site at surface and at 0.25 metres depth below surface.

	Benzol Plant		Coke Storage		Coke Batteries		Domtar		Mullin's Bank	
Parameter (ppm)	**S**	**D**	**S**	**D**	**S**	**D**	**S**	**D**	**S**	**D**
Acenaphthene	0.23	0.3	0.4	0.23	0.03	0.06	8	5.2	0.008	0.006
Acenaphthylene	0.29	0.03	< 0.2	0.04	0.03	0.04	4.3	4.5	0.007	0.026
Fluorene	0.43	0.44	0.3	0.37	0.05	0.08	14.2	9.7	0.017	0.024
Methylnaphthalene,1-	2.3	3.98	1.7	2.29	0.38	0.43	2.8	3.7	0.147	0.029
Methylnaphthalene,2-	4.15	7.77	3.4	4.7	0.62	0.77	4.6	5.2	0.242	0.044
Naphthalene	2.88	4.61	2.6	3	0.6	0.77	5.9	5.7	0.22	0.058
Anthracene	0.66	0.06	0.82	0.14	0.06	0.14	86.5	37.7	0.011	0.073
Fluoranthene	2.93	0.31	5.6	0.63	0.32	0.75	145	89.3	0.071	0.215
Phenanthrene	3.02	1.94	3.8	1.75	0.4	0.65	106	63	0.118	0.201
LMPAH	**16.89**	**19.44**	**18.62**	**13.15**	**2.49**	**3.69**	**377.3**	**224**	**0.841**	**0.676**
Benzo(a)anthracene	1.57	0.15	2.6	0.3	0.2	0.41	64.5	39.2	0.03	0.081
Benzo(b+k)fluoranthene	2.08	0.28	4.2	0.82	0.33	0.61	105	85.9	0.049	0.11
Chrysene	1.42	0.34	2.4	0.45	0.21	0.34	74.7	52.9	0.036	0.073
Pyrene	2.16	0.29	3.9	0.5	0.26	0.6	108	59.1	0.054	0.142
Benzo(a)pyrene	1.36	0.12	2.6	0.37	0.19	0.35	70.1	56.3	0.033	0.08
Benzo(g,h,i)perylene	0.76	0.12	2.3	0.26	0.14	0.25	40.1	37	0.02	0.041
Dibenzo(a,h)anthracene	0.33	0.11	0.7	0.13	0.06	0.08	15.7	12.7	0.009	0.018
Indeno(1,2,3,-cd)pyrene	0.99	0.06	2.2	0.26	0.18	0.25	48.8	40.2	0.024	0.053
HMPAH	**10.67**	**1.47**	**20.9**	**3.09**	**1.57**	**2.89**	**526.9**	**383.3**	**0.255**	**0.598**
TOTAL	**27.56**	**20.91**	**39.52**	**16.24**	**4.06**	**6.58**	**904.2**	**607.3**	**1.096**	**1.274**

Notes:
S = surface
D = at 0.25 metres depth
LMPAH = low molecular weight PAHs
HMPAH = high molecular weight PAHs

3.1.2 Soil Microorganisms

Population densities for each location are summarized in Table 2. Figure 5 presents the results from enumerations of AHB, IRB, SRB, SRBB and APB in soil samples at the Coke Ovens site. All types of bacteria were present at each sampling location with the exception of SRB grown with sodium benzoate; it had very low population numbers at the Mullin's Bank area (2 MPN/g at 0.25 metres depth).

Table 2: Microbial population densities in soil samples from the Coke Ovens site at surface and at 0.25 metres depth below surface.

Bacteria	Benzol Plant		Coke Storage		Coke Batteries		Domtar		Mullin's Bank	
	S	D	S	D	S	D	S	D	S	D
AHB	9.0×10^6	1.1×10^6	1.3×10^7	5.0×10^6	7.0×10^6	4.5×10^7	1.1×10^7	1.5×10^7	3.0×10^6	8.3×10^5
APB	4.9×10^6	1.1×10^4	3.5×10^5	9.5×10^5	2.8×10^5	4.3×10^5	7.9×10^5	3.3×10^5	2.8×10^4	7.0×10^3
IRB	7.9×10^3	3.3×10^3	1.3×10^4	3.3×10^3	3.3×10^2	3.3×10^2	3.3×10^5	1.3×10^4	3.5×10^3	1.7×10^4
SRB	3.1×10^2	1.4×10^3	1.1×10^3	3.1×10^2	1.8×10^3	7.0×10^2	2.3×10^1	2.3×10^2	4.6×10^2	1.2×10^3
SRBB	4.9×10^2	2.3×10^2	4.9×10^2	2.3×10^2	3.3×10^2	2.3×10^2	4.9×10^2	2.3×10^2	7.9×10^1	2.0×10^0

Notes:
All values expressed as MPN/g, with the exception of AHB values which were expressed as CFU/g wet weight
S = surface sample
D = subsurface sample at 0.25 metres depth

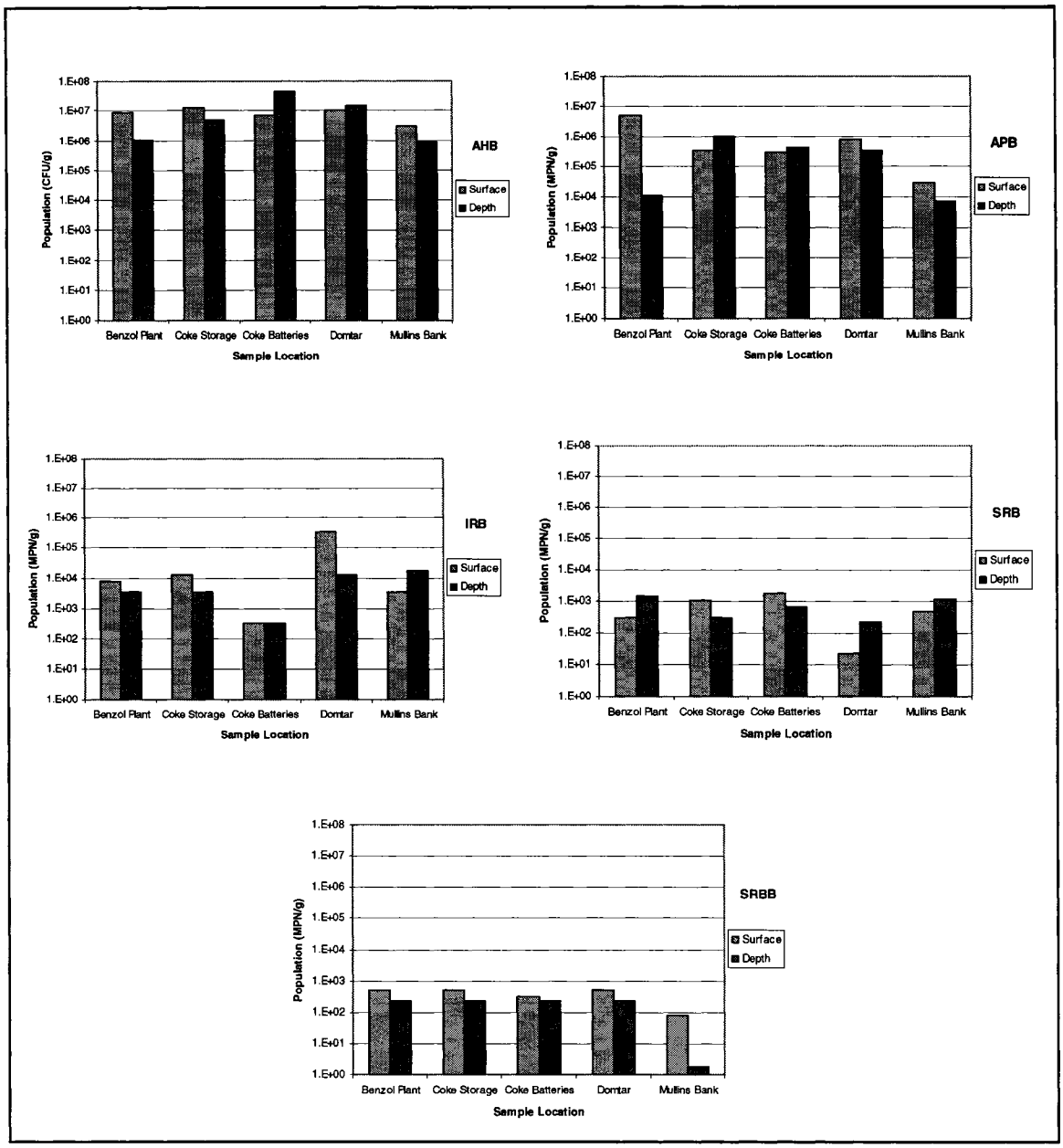

Figure 5: AHB, APB, SRB, IRB and SRBB population densities in soil samples at the Coke Ovens site.

At sampling location 1 (Benzol Plant) the population densities of bacteria were higher at surface when compared to samples at 0.25 metres depth, with the exception of the SRB concentrations, which increased with depth. AHB were the most prevalent bacteria type, followed by APB, IRB, SRB, and SRBB with the lowest population density. The

population of SRB grown with sodium benzoate was similar to the SRB grown on modified Postgate Medium B.

At sampling location 2 (Coke Storage area) the population densities of bacteria were higher at surface when compared to samples at 0.25 metres depth, with the exception of the APB concentrations, which increased with depth. AHB had the highest population density followed by APB, IRB, SRB and SRBB. The population of SRB grown with sodium benzoate was similar to the SRB grown on modified Postgate Medium B.

At sampling location 3 (Coke Batteries Storage area) the population densities of AHB and APB were lower at surface when compared to samples at 0.25 metres depth, while the population densities of SRB and SRBB were higher at surface and IRB populations remained constant at both depths. AHB were the most abundant species. As in sample 1 and 2, APB were the second most abundant bacteria type followed by, SRB, IRB and SRBB. The population densities of SRB and IRB were similar.

At sample location 4 (Domtar area) the population densities of APB, SRBB and IRB were higher at surface when compared to samples at 0.25 metres depth, while the population densities of AHB and SRB increased with depth. The population density of AHB was the highest, followed by APB, IRB, SRBB and SRB. The SRB population density was lower at surface than the SRBB, but their population densities were the same at depth.

At sample location 5 (Mullin's Bank area) the population densities of AHB, APB and SRBB were higher at surface when compared to samples at 0.25 metres depth, while the

population densities of SRB and SRBB increased with depth. The AHB population density was the highest followed by, APB, IRB SRB and SRBB. The population density of SRBB was very low in the Mullin's Bank area compared to all other sample locations.

Overall, the population densities of AHB were the highest followed by the APB population densities. IRB had variable population densities over the site with a range of $3.3x10^2$ to $3.3x10^5$ MPN/g at surface and $3.3x10^2$ to $1.7x10^4$ MPN/g at depth. The SRB population density ranged from 23 to $1.8x10^3$ MPN/g at surface and $2.3x10^2$ to $1.4x10^3$ MPN/g at depth. The SRBB population density was consistent for all sample locations, with the exception of the Mullin's Bank area, with a range of $3.3x10^2$ to $4.9x10^2$ MPN/g at surface and $2.3x10^2$ MPN/g at depth. The Mullin's Bank area had very low population densities with 79 MPN/g at surface and 2 MPN/g at depth.

3.2 Groundwater Samples

3.2.1 Groundwater PAH Analysis

Table 3 presents the results of PAH analyses completed for each groundwater sampling location before purging and after five minutes of consecutive purging of the well water. The Battery Storage area samples exhibited the highest concentrations of PAHs, ranging from non-detectable to 52.8 ppb before purging and from below the laboratory detection limit to 4090 ppb at depth after purging. The Benzol Plant area had concentrations ranging from non-detectable to 6.57 ppb before purging and non-detectable to 2.63 ppb after purging. The background station in Mullin's Bank exhibited lower PAH concentrations, ranging from non-detectable to 0.89 ppb before purging and non-detectable to 0.17 ppb after purging. The Domtar site had relatively low PAH

concentrations before purging with a range from non detectable to 2.08 ppb, while after purging all PAH concentrations were below the detection limit. The Coke Storage area had the lowest PAH concentrations with a range of non detectable to 0.19 ppb before purging and non detectable to 0.06 ppb after purging. Overall there was no dominant PAH at the site. Each location exhibited varying concentrations of the different PAHs. In general the concentrations decreased after purging with the exception of the Coke Batteries area, which significantly increased. The values reported at the Coke Batteries area after purging were the highest of all samples collected, while the Coke Storage, Domtar and Mullin's Bank areas had the lowest concentrations.

Table 3: PAH concentrations (ppb) in groundwater samples from the Coke Ovens site at surface and at 0.25 metres depth below surface.

	Benzol Plant		Coke Storage		Coke Batteries		Domtar		Mullin's Bank	
Parameter (ppm)	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**
Acenaphthene	0.76	0.69	<0.06	0.06	52.8	2820	1.39	<0.07	<0.06	<0.06
Acenaphthylene	0.51	0.26	<0.06	<0.06	25.9	1300	0.24	<0.07	0.14	<0.06
Fluorene	0.99	1	<0.06	<0.06	34.6	1780	0.96	<0.07	0.09	<0.06
Methylnaphthalene,1-	1.2	0.77	<0.06	<0.06	8.74	1940	0.67	<0.07	0.11	<0.06
Methylnaphthalene,2-	0.33	0.1	<0.06	<0.06	<0.6	254	0.1	<0.07	0.12	<0.06
Naphthalene	6.57	0.86	0.08	<0.06	6.8	4090	1.07	<0.07	0.16	0.06
Anthracene	<0.06	<0.06	0.06	<0.06	19.3	578	<0.06	<0.07	0.14	<0.06
Fluoranthene	1.31	0.38	0.14	<0.06	<0.6	833	0.57	<0.07	0.89	0.13
Phenanthrene	5.11	2.63	0.13	<0.06	35.4	3680	2.08	<0.07	0.49	0.12
LMPAH	**16.78**	**6.69**	**0.41**	**0.06**	**183.54**	**17,275**	**7.08**	**--**	**2.14**	**0.31**
Benzo(a)anthracene	0.44	0.16	0.08	<0.06	16.9	301	0.14	<0.07	0.36	0.07
Benzo(b+k)fluoranthene	0.51	0.14	0.19	<0.06	23	231	0.16	<0.07	0.63	0.17
Chrysene	0.48	0.2	0.09	<0.06	25.1	278	0.22	<0.07	0.39	0.1
Pyrene	0.91	0.47	0.09	<0.06	77	995	0.45	<0.07	0.47	0.1
Benzo(a)pyrene	0.39	0.11	0.1	0.04	14.3	185	0.13	<0.01	0.5	0.08
Benzo(g,h,i)perylene	0.24	<0.06	<0.06	<0.06	8.17	<120	<0.06	<0.07	0.26	<0.06
Dibenzo(a,h)anthracene	0.1	<0.06	<0.06	<0.06	<0.6	<100	<0.06	<0.07	<0.06	<0.06
Indeno(1,2,3,-cd)pyrene	0.26	<0.06	<0.06	<0.06	7.83	<120	<0.06	<0.07	0.37	<0.06
HMPAH	**3.33**	**1.08**	**0.55**	**0.04**	**172.3**	**1990**	**1.1**	**--**	**2.98**	**0.52**
TOTAL	**20.11**	**7.77**	**0.96**	**0.1**	**355.84**	**19,265**	**8.18**	**--**	**5.12**	**0.83**

Notes:
B = before purging
A = after purging
LMPAH = low molecular weight PAHs
HMPAH = high molecular weight PAHs

3.2.2 Groundwater Microbiology Analysis

Table 4 presents the results from enumerations of AHB, IRB, SRB and APB in the groundwater samples collected at the five locations of the Coke Ovens site. All types of bacteria were present at the Coke Ovens site; however, population numbers were very low to non-existent at some sample locations. The Mullin's Bank area had the most varied distribution of microbial populations, followed by the Coke Batteries and the Benzol Plant area. The Coke Storage and Domtar areas had low diversity, with the Domtar area only having SRBs present after purging.

Table 4: Microbial population densities in groundwater samples from the Coke Ovens site before purging and after five minutes of continuous purging.

	Benzol Plant		Coke Storage		Coke Batteries		Domtar		Mullin's Bank	
Bacteria	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**
AHB	3.6×10^{6}	1.2×10^{5}	4.3×10^{4}	1.0×10^{5}	1.4×10^{5}	1.0×10^{4}	6.6×10^{3}	0	2.3×10^{5}	4.4×10^{5}
APB	3.3×10^{1}	3.3×10^{1}	2.0	4.9×10^{1}	7.9×10^{4}	3.3×10^{5}	8.0	0	3.3×10^{4}	1.3×10^{4}
IRB	1.7×10^{2}	4.9×10^{1}	0	2.0	2.0	5.0	0	0	4.9×10^{2}	1.1×10^{3}
SRB	3.5×10^{2}	1.7×10^{3}	1.3×10^{2}	2.1×10^{1}	4.9×10^{2}	1.1×10^{3}	1.7×10^{1}	3.1×10^{2}	2.1×10^{3}	4.3×10^{4}
SRBB	8.0	4.9×10^{1}	0	0	2.3×10^{1}	8.0	0	0	2.3×10^{1}	1.7×10^{1}

Notes:
All values expressed as MPN/gmL with the exception of AHB values which are CFU/mL
B = before purging
A = after purging

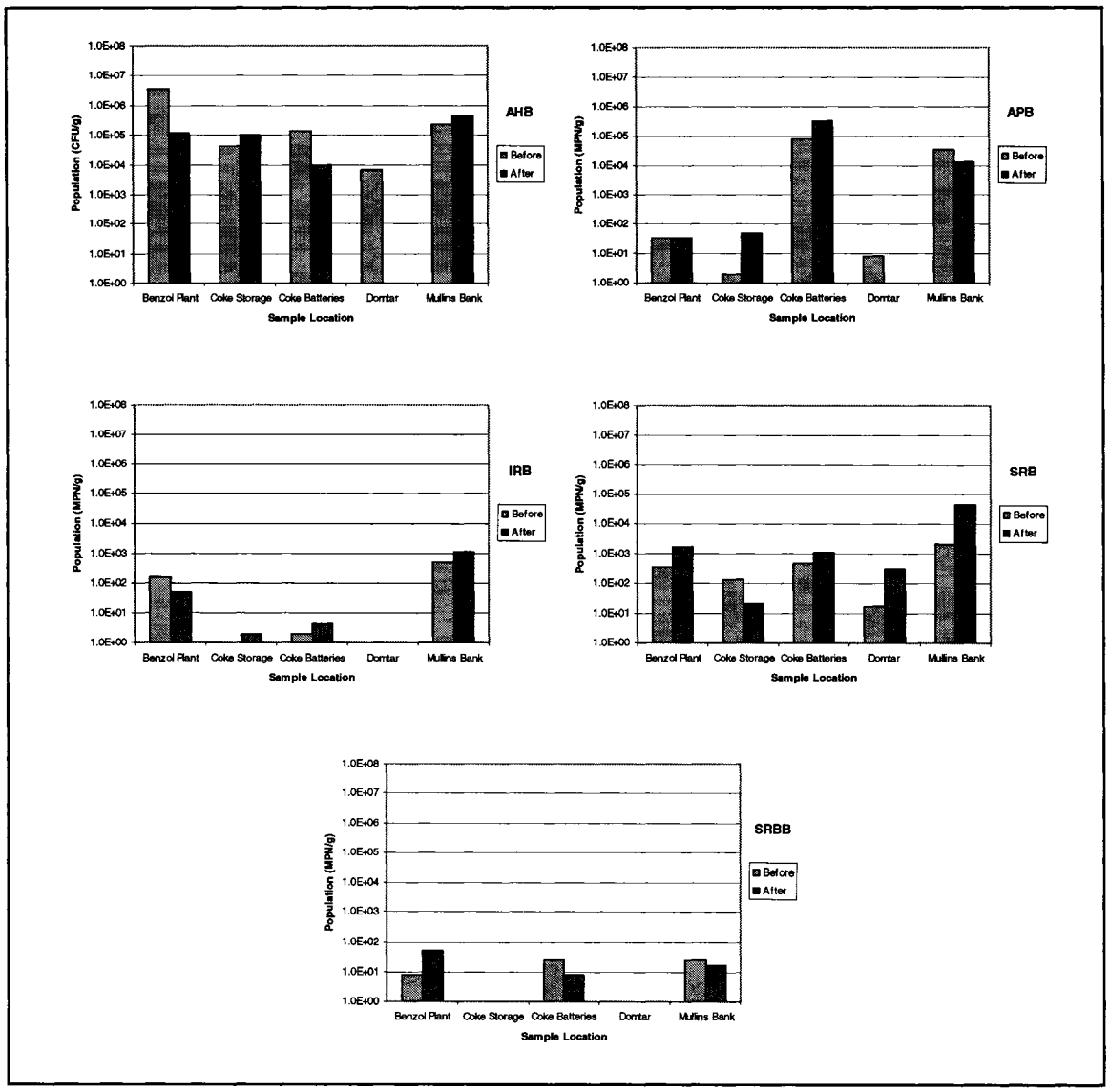

Figure 6: AHB, APB, SRB, IRB and SRBB population densities in groundwater samples at the Coke Ovens site.

At sampling location 1 (Benzol Plant) the population densities of bacteria were low with the exception of the AHB population counts. The concentration of SRB and SRBB were higher after purging of the standing water, but the population numbers of SRBB were still low (<100 MPN/mL). The APB population counts were also very low and remained

unchanged after purging. The IRB population density was higher before purging than after.

At sampling location 2 (Coke Storage area) the population densities of bacteria were very low to non-existent with the exception of AHB populations. There were no IRB present before purging and only 2 MPN/mL after purging. The APB population counts were also low before purging and slightly increased after purging. The SRB populations were slightly higher before purging compared to after purging. There were no SRBB detected at this location.

At sampling location 3 (Coke Batteries Storage area) the population density of AHB in the standing water sample was highest followed by APB and SRB. APB has the highest bacteria population density in the after purging sample followed by AHB and SRB. The IRB and SRBB population counts were very low before (2 and 23 MPN/mL, respectively) and after (5 and 8 MPN/mL, respectively) purging.

At sample location 4 (Domtar area) the population densities were the lowest of all five sites. No IRB or SRBB were detected in sample 4. SRB were present before purging and slightly increased after purging. AHB were present before purging, but were not detected after purging. APB was very low before purging (8 MPN/mL) and was not detected after purging.

At sample location 5 (Mullin's Bank area) the bacteria were more abundant and varied than anywhere else. AHB population numbers were the highest followed by APB, IRB, SRB and SRBB. AHB, SRB and IRB population numbers increased after purging, while

APB and SRBB decreased. The SRBB population numbers were very low (<25 MPN/mL).

Overall, the population density of AHB was the highest with a range of $6.6x10^3$ to $3.6x10^6$ CFU/mL before purging and 0 to $4.43x10^5$ CFU/mL after purging. The population of AHB at the Benzol Plant, Coke Batteries and Domtar areas decreased after purging, while the Coke Storage area and Mullin's Bank area increased. The population densities of APB, SRB and IRB were variable, with some locations having higher concentrations, while others had very low to no bacterial colonies. The SRBB population counts were less than 50 MPN/mL at all sites, with the Coke Storage and Domtar areas having no colonies. The APB population density was the second highest with ranges of 2 to $7.9x10^4$ MPN/mL before purging and 0 to$3.3x10^5$ MPN/mL after purging. IRB had variable population densities over the site as the Benzol Plant, Coke Batteries and Domtar areas had little to no bacteria. The SRB population density ranged from 17 to $2.1x10^3$ MPN/mL before purging and 21 to $4.3x10^4$ MPN/mL after purging.

3.2.3 Groundwater Chemistry Data

The groundwater quality data obtained from the Sydney Tar Ponds Agency are available in Appendix A. Figure 7 shows the distribution of major ion chemistry in the local groundwater. Dissolved ion data were available for only three of the five monitoring wells; therefore, only the Domtar area, Coke Battery area and Benzol Plant areas were plotted. The Benzol Plant groundwater well was screened in the shallow bedrock, while the Domtar and Coke Battery Storage area were screened in the till/fill. All three sample locations have similar chemistry and plot in the calcium bicarbonate (Ca^{2+} - HCO_3^-) field.

The total dissolved solid concentrations from the five sampling sites are provided in Appendix A. The values were generally less than 1,000 ppm, which indicates a fresh water system; however, the data presented for the Mullin's Bank location indicate slightly brackish waters (TDS between 1,000 ppm to 10,000 ppm). The sulphate and chloride concentrations were higher at this location.

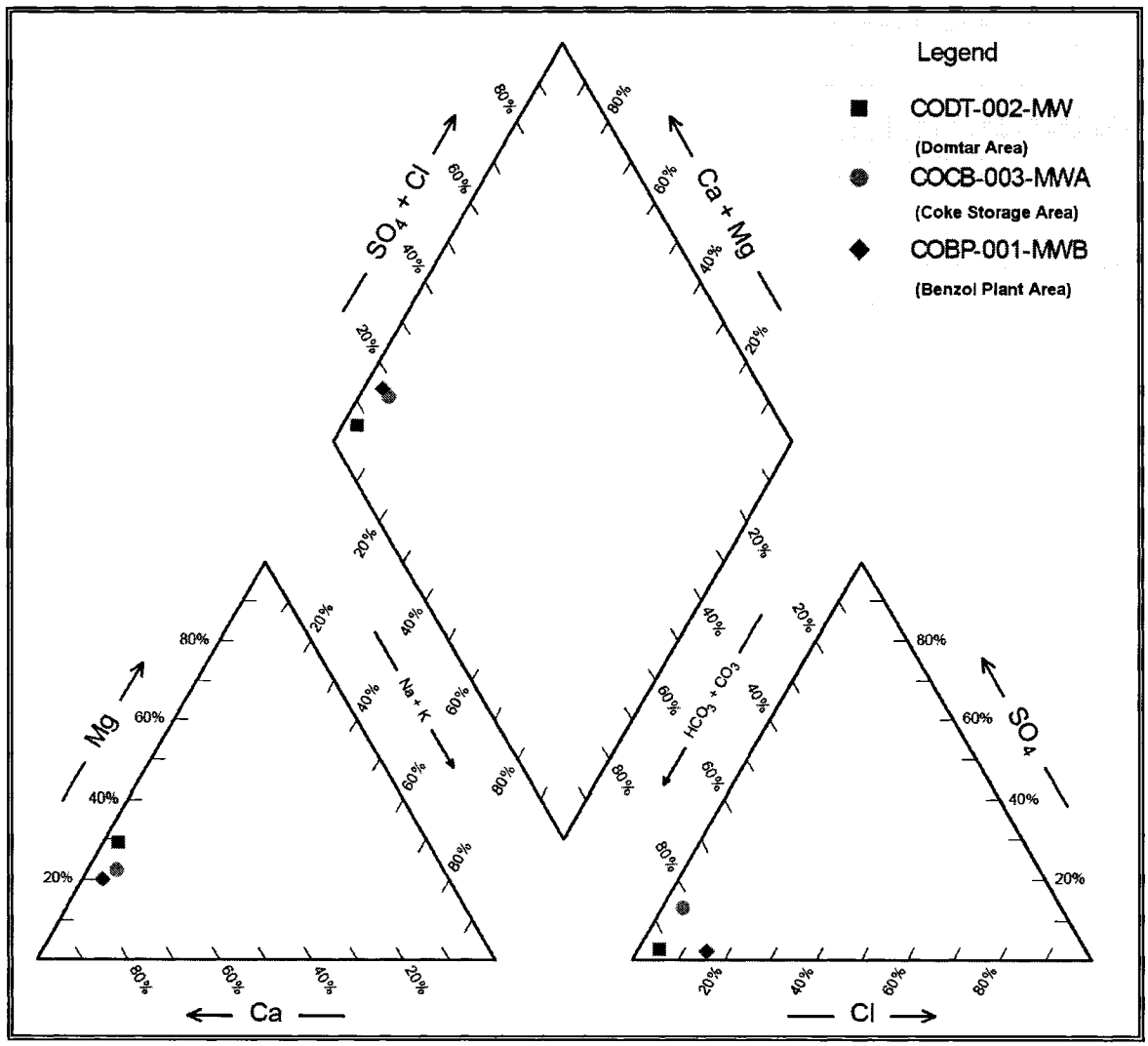

Figure 7: Summary of major ion concentrations for three groundwater monitoring locations, in the STPCO site.

3.3 Effect of Naphthalene on Bacterial Growth

Figure 8 depicts the population numbers of AHB, APB, SRB, IRB and SRBB with varying concentrations of naphthalene under aerobic and anaerobic conditions.

A background sample with no naphthalene showed high population numbers of SRBB under aerobic conditions. AHB, APB and IRB population numbers were also higher aerobically than anaerobically. The SRB population density did not exhibit a significant difference between aerobic and anaerobic conditions.

With a concentration of 100 ppm of naphthalene, the aerobic AHB and SRB population numbers increased, while the APB, IRB and SRBB decreased. Under anaerobic conditions, the AHB population decreased, while APB, IRB, and SRBB population numbers increased and SRB remained unchanged.

The samples with a concentration of 1,000 ppm naphthalene resulted in a decrease in AHB population density under aerobic conditions and increases in APB, SRB and SRBB. IRB populations stayed the same. Under anaerobic conditions, AHB marginally increased, SRB marginally decreased, APB and IRB decreased and SRBB remained unchanged.

The final concentration of 10,000 ppm of naphthalene under aerobic conditions exhibited decreased population numbers of AHB, APB, SRB and SRBB, while IRB populations increased. Anaerobically AHB, SRBB, SRB increased while APB, and IRB decreased.

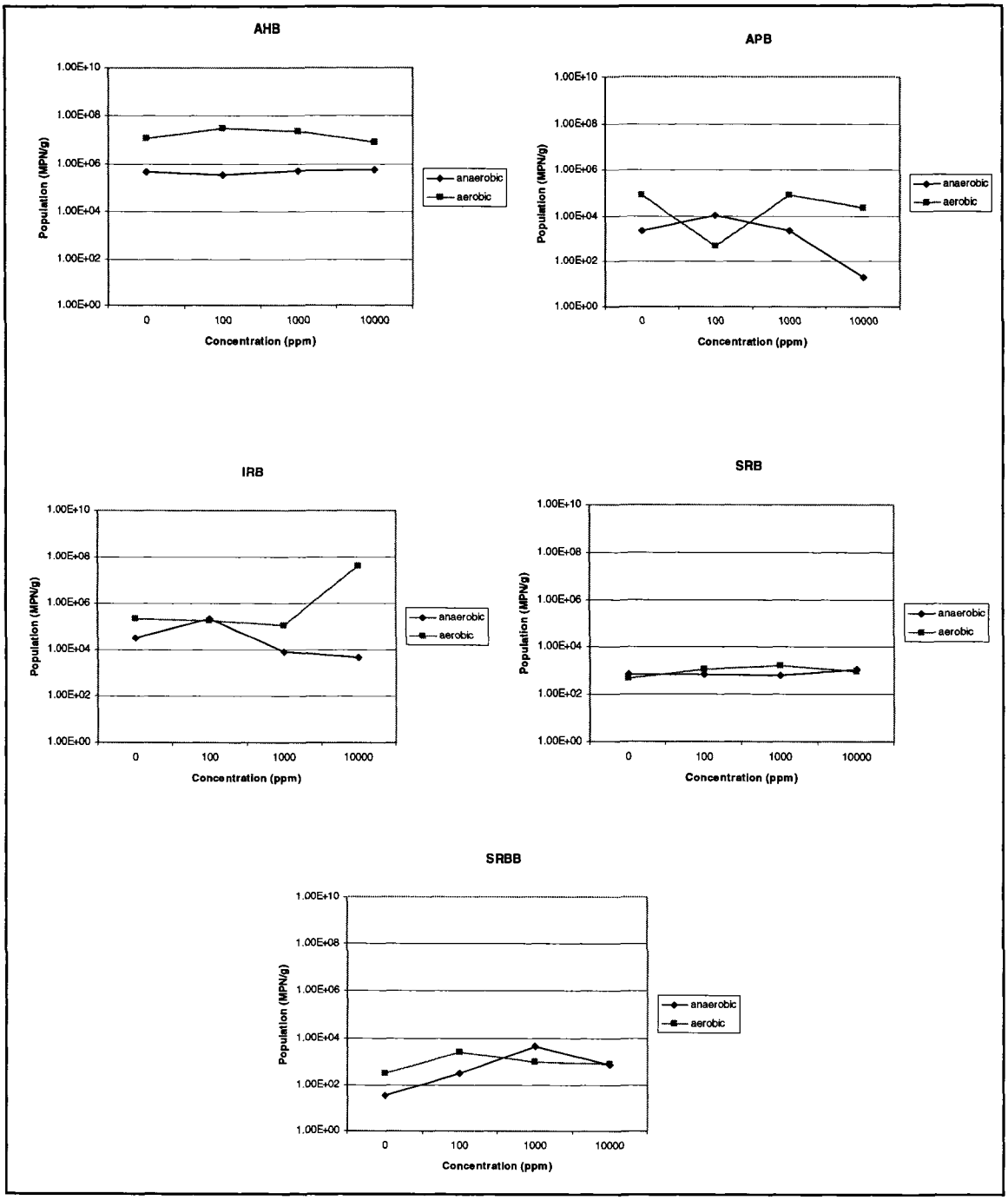

Figure 8: AHB, APB, SRB, IRB and SRBB population densities with varying concentrations of naphthalene under aerobic and anaerobic conditions

4.0 DISCUSSION

4.1 PAH Distribution

PAH analyses were completed on soil and groundwater samples obtained from the Sydney Tar Pond and Coke Oven (STPCO) site. The results presented in Section 3.0 are similar to the results collected at the same locations in 2000, 2001 and 2003 by the STPA (see Appendix A), with a few exceptions. In this study, the highest groundwater PAH concentrations were found at the Coke Battery site while the data provided by the STPA found the highest concentrations to be located at the Domtar site. This may be attributed to the heterogeneity of the contaminants at the sites (King, 2004) or the migration of contaminants.

Soil samples were also collected by the STPA in 2000, 2001 and 2003. These sampling locations were in the vicinity of the locations used in this current study (Figure 3). The results between the two datasets are consistent with a few exceptions. In 2000, the PAH concentrations for samples collected in the vicinity or the Coke Storage area were an order of magnitude higher than in subsequent samples.

The level of contaminants within the five areas of the Coke Ovens site are very heterogeneous. However, based on the results of the PAH analyses completed in this study, the PAH concentrations are generally consistent between the two datasets. In other studies of PAH degradation, the initial concentrations of PAHs were variable. For example, in a study of PAH biodegradation in coal tar contaminated soils at five different manufactured gas plants, the initial concentrations of PAHs ranged from 8 to 1238 ppm (Lee et al., 2001), while in another study by Mendonca (2002) the initial concentrations

ranged from 7 to 192 ppm; similar to the highest concentrations in the Domtar area, which ranged from 2.8 to 108 ppm.

4.2 Characterization of the Microbial Community

The indigenous microbial population composition of the soil and groundwater were investigated by the quantification of total aerobic bacteria and the use of various selective media (sulphate reducers, iron reducers and acid producers). The results show that culturable bacteria are succeeding in the PAH contaminated environment of the Coke Ovens site. AHB had the highest population densities within the soil samples and are within the expected range of typical soil populations at uncontaminated sites (10^3-10^7 cfu/g) (Hardaway et al, 1991).

Aerobic heterotrophic plate counts provide information about the bacterial population as a whole. Higher total AHB population densities were present in the soil compared to the groundwater and bacteria species were overall more abundant and diverse in the soil when compared to groundwater. This result was anticipated because microbes tend to exist in microcolonies on mineral particles, organic matter and roots (Sylvia, 2005). This demonstrates the selective behaviour of bacteria for soil as opposed to groundwater; however, AHB were present in the PAH contaminated and uncontaminated groundwater.

The results presented for selective media bacteria exhibited similar results to the AHB plate counts. It was found that APB, SRB, and IRB were present in all surface and subsurface soil samples, while the groundwater samples had similar groups of bacteria present, but in lower population densities. The population densities probably varied due

to the environmental conditions at each sampling location. It was therefore difficult to find a correlation between the population densities of the different bacterial groups and the individual PAH constituents. For example, in the Domtar groundwater samples, few bacteria were present and the PAH levels were low, while at the Coke Battery site where the PAH levels increased, the bacteria counts also increased. However, the population densities at the Mullin's Bank area were high, while the PAH concentrations were low. Statistical analysis was completed between population densities and PAH constituents and no correlations were present.

The bacteria population density in the groundwater samples at the Domtar site was very low for SRB grown with lactate, acetate and citrate, and non existent for IRB, APB and SRB growth with benzoate. This is similar to the results presented by Saagua et al. (2002), where PAH-degrading bacteria populations were found to be lower in the uncontaminated samples. As discussed in Leahy and Colwell (1990), the increased population counts of microorganisms are a result of their exposure to pollutant compounds and reflect the degree of contamination in the ecosystem.

Benzoate is the most common intermediate compound in the anaerobic degradation of aromatic hydrocarbons (Gibson and Harwood, 2002). SRB from the Coke Ovens site were grown using sodium benzoate as the sole carbon source. The results indicate whether or not the sulphate reducing bacteria present at the site would be capable of degrading aromatic hydrocarbons. SRB were present under the selective conditions with sodium benzoate, however, population densities were less than 100 MPN/g. It is difficult, therefore, to conclude whether or not these bacteria are PAH-degraders or due

to the introduction of bacteria during sample collection and/or analysis. The identification of the bacteria was beyond the scope of this work. Isolation of PAH-degraders could be performed as future work to further identify the strains present and their ability to degrade PAHs. Known naphthalene degrading microorganisms include *Alcaligenes denitrificans, Mycobacterium* sp., *Pseudomonas putida, P.fluorescens, P. paucimobilis, P.vesicularis, P.cepacia, P.testesteroni, Rhodococcus* sp., *Corynebacterium venale, Bacillus cereus, Moraxella* sp. *Streptomyces* sp., *vibrio* sp. *And Cyclotrophicus* sp (Samanta, 2002).

4.3 Potential for Degradation

Previous studies have shown that bacteria are able to degrade potentially harmful environmental pollutants (Sylvia et al., 2005). As described above, the Coke Ovens site contains high levels of PAHs, while still maintaining a diverse microbial community. Various PAHs have been shown to degrade under sulphate reducing conditions (Coates et al., 1996; Langenhoff et al., 1996), nitrate reducing conditions (Bregnard et al., 1996), and iron reducing conditions (Ramsay et al., 2001; Anderson et al., 1998). Little is known about PAH degradation with other groups of bacteria.

The physical properties that result from the ringed structure of PAHs are an environmental concern as their ringed structure affects their physical properties. High molecular weight PAHs (four or more benzene rings) are mutenagenic and carcinogenic, while low molecular weight PAHs (less than four benzene rings) can be acutely toxic (Boonchan et al., 2000). Generally, PAHs have low aqueous solubilities and high solid-water distribution ratios which makes them less available for biological uptake. Johnsen

et al. (2005) suggest that the bioavailability of PAHs decreases almost logarithmically with increasing molecular weight. Therefore, PAHs tend to be recalcitrant and accumulate in the solid phases of the environment. The high molecular weight compounds tend to be more difficult to degrade, but as they breakdown their solubility and mobility increase and toxicity decreases (Johnsen et al., 2000). Johnsen et al. (2000) suggest that the low bioavailability of high molecular weight PAHs may have prevented the evolution of suitable enzymatic pathways in soil bacteria. The degradation of parent compounds to detoxified products, which have increased solubilities and therefore increased bioavailability, reduce the risk of environmental exposure (Boonchan et al., 2000).

It has been shown that naphthalene will degrade under sulphate-reducing conditions (Coates et al 1996a, Langenhoff et al. 1996) and phenanthrene (a three-ringed PAH) will degrade under anaerobic conditions using sulphate-reducing bacteria (Chang et al., 2001). In a study by Chang et al. (2002), the degradation rates were increased under methanogenic and sulphate-reducing conditions compared to nitrate reducing conditions. They used microbial inhibitors to determine the role of specific microbial populations in PAH degradation. It was found that the major microbial component of PAH degradation was sulphate reducing bacteria, but that methanogenic and eubacteria microbial populations were also involved in the process. As discussed in Section 1.0, a proposed degradation pathway of naphthalene under anaerobic conditions occurs through dioxygenase enzymes, while under anaerobic conditions, Zhang and Young (1997) reported that carboxylation is the initial key in the reduction of naphthalene and phenanthrene under sulphate reducing conditions.

It has been shown that anaerobic degradation of two, three and four ringed PAH is possible as a means of remediating contaminated sites (Chang et al., 2002). At the Coke Ovens site there are a range of concentrations of two, three, four and five ringed PAHs present in the different sample locations. Most locations had low concentrations of five ringed PAHs with the exception of the groundwater sample in the Coke Batteries site and the soil sample in the Domtar area, which had very high concentrations of all PAHs.

To test the efficiency of the naturally occurring bacteria to degrade PAHs under sulphate-reducing conditions, SRB were grown with sodium benzoate as the sole carbon source. The population numbers in the soil were similar to the sulphate reducing bacteria grown with lactate, acetate and citrate, while in the groundwater samples the populations were much lower. This indicates that naphthalene does not inhibit SRB growth, but also does not enhance their abundance. Gibson and Subramanian (1984) showed that bacterial, fungal and algal cultures with naphthalene as the substrate were able to oxidize aromatic hydrocarbons. Higher molecular weight PAHs, such as phenanthrene and anthracene, have been shown to have similar degradation routes as naphthalene (McD Francis and Gould, in prep). This indicates that their degradation pathways are similar and if the bacteria present with high concentrations of naphthalene are able to use benzoate as their carbon source, they could potentially remediate PAH contaminated soils. Naphthalene and phenantherene were present in all soil samples and groundwater samples, with the exception of groundwater samples collected after purging at the Coke Storage and

Domtar sites. Anthracene was present in low concentrations at all soil sample locations, but only found in groundwater samples from the Coke Batteries and Mullin's Bank areas.

It was found that the increased concentration of naphthalene did not affect the microbial populations. There was a slight decrease in the anaerobic APB population number compared to the control sample as the naphthalene concentration increased. The other populations remained relatively constant. At known concentrations of naphthalene, it was determined that the various microbes were able to survive and that high concentrations of naphthalene did not adversely affect the AHB, APB, SRB, and IRB populations. However, from these results it is difficult to comment on whether the groups of bacteria were able to degrade PAHs. Further analysis is required to isolate PAH degrading species and perform identifications.

It was found that the population densities for SRB grown with benzoate had higher population numbers under aerobic conditions than anaerobically. The aerobic population densities were similar to the SRB grown with lactate, acetate and citrate. Therefore, it is not possible to conclude whether SRB can degrade naphthalene at the Coke Ovens site. It does, however, show that naphthalene was not toxic to the local AHB, APB, IRB and SRB.

4.4 Remediation of the Coke Ovens site

Based on the results presented in this study, it is difficult to conclude whether bioremediation would be an effective remediation option for the Coke Ovens site.

However, since bacteria are present at the site there is the potential for the use of bioremediation.

The abundance and activity levels of microorganisms are limited by a number of physicochemical parameters such as soil moisture, soil pH, soil temperature, level of inorganic nutrients, level of electron acceptors and types and amount of carbon present (Baker et al., 1994). These amendable parameters are the most important in biodegradation because they can be optimized to breakdown contaminants. The examination of these parameters was beyond the scope of this research but need to be examined at the Coke Ovens site to determine the ideal conditions for the use of indigenous bacteria for bioremediation. The use of landfarming as a bioremediation method provides an environment in which the parameters are idealized for the reduction of contaminants. In order to optimize this process at the Coke Ovens site, the bacteria studied in this research should be applied to test plots with varying concentrations of the parameters.

In order for landfarming to be a plausible approach to the remediation of the Coke Ovens site, time and costs must also be considered. If degradation rates are not optimized to achieve the goal of remediating contaminants in a timely and economical manner, another remediation technique should be applied. Through the development of test plots, parameters can be examined to determine the ideal conditions for optimal degradation rates.

5.0 CONCLUSION

The objectives of this study were to ascertain whether bacteria were naturally occurring in the soil and groundwater, to characterize the natural microbial community at the Coke Ovens site and determine if bioremediation would be a feasible method of remediation. The microbial community within the Coke Ovens site is diverse even though high levels of coal by-products are present throughout the site. In this study, it was found that APB, SRB, IRB, and AHB were present in all surface and subsurface soil samples, while lower population densities were present in groundwater samples. Naphthalene did not have an effect on the indigenous groups of bacteria within the Coke Ovens site; therefore, it is possible that PAH-degrading species are present at the site. However, it was beyond the scope of this research to determine which PAH degrading species were present.

Based on the research presented in this study it is difficult to comment on the potential for bioremediation of PAHs at the Coke Ovens site through landfarming. More research is needed to determine the optimal conditions for sufficient degradation rates. For future studies it is recommended that soil be further characterized in order to proceed with laboratory based experiments where the addition of nutrients and other modifications (based on the soil characterization) can be applied in a controlled environment.

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APPENDIX A

Soil and Groundwater Quality Data

provided by the

Sydney Tar Ponds Agency

Table A.1: Summary of Groundwater PAH concentrations in 2000, 2001, and 2003 supplied by the STPA (ppb)

	Benzol Plant		Coke Storage	Coke Batteries			Domtar Area			Mullin's Bank
	COBP-001-MWB	COBP-001-MWB	COCS-004-MW	COCB-003-MWA	COCB-003-MWA	COCB-003-MWA	CODT-002-MW	CODT-002-MW	CODT-002-MW	COMB-005-MW
Parameter (ppb)	17/10/2001	13/05/2003	18/09/2000	18/09/2000	19/10/2001	12/05/2003	31/10/2001	06/05/2003	06/05/2003	23/09/2000
Acenaphthene	1.2	1.6	0.39	2.2	6.3	13	32	200	190	<0.01
Acenaphthylene	1.3	1.4	0.56	0.16	2.2	4.4	220	1100	980	<0.05
Anthracene	<0.84	1.3	0.03	1	<0.8	0.97	19	360	330	0.02
Benzo(a)anthracene	<0.48	0.48	0.03	0.75	0.54	0.59	2.5	13	16	0.03
Benzo(a)pyrene	0.23	0.28	0.04	0.51	0.19	0.34	0.78	4.4	4.3	0.02
Benzo(b)fluoranthene	0.16	0.25	0.06	0.86	0.14	0.34	0.82	4.3	4.2	0.04
Benzo(ghi)fluoranthene	0.06	0.14	0.03	0.24	0.06	0.17	0.23	1.9	1.4	0.01
Benzo(k)fluoranthene	0.16	0.25			0.14	0.34	0.82	4.3	4.2	
Chrysene	<0.54	0.7	0.05	0.68	<0.5	0.75	1.8	20	19	0.04
Dibenz(a,h)anthracene	<0.01	0.03	<0.01	0.05	0.02	0.04	0.07	0.61	<0.01	<0.01
Fluoranthene	1.2	1.8	0.09	1.3	1.6	3.2	17	220	270	0.07
Fluorene	<1.7	2.4	0.04	0.86	2.1	4.3	81	620	610	0.02
Indeno(1,2,3-cd)pyrene	0.07	0.16	0.02	0.24	0.07	0.16	0.36	2	1.2	0.01
1-Methylnaphthalene	2.2	3.1	0.18	1.3	1.1	4.8	210	870	800	0.09
2-Methylnaphthalene	0.99	0.98	0.14	0.33	0.08	0.49	320	1300	1200	<0.05
Naphthalene	12	21	0.22	2.9	2.7	18	6200	12000	12000	0.94
Perylene	0.04	0.07	<0.01	0.11	<0.02	0.02	0.16	1.4	1.5	<0.01
Phenanthrene	3.4	9.3	0.19	3	1.6	6	72	960	1000	0.17
Pyrene	1.3	2.1	0.1	1.3	1.7	3.3	12	150	190	0.06

Notes:
All values expressed as ppb

Table A.2: Summary of soil PAH concentrations in 2000, 2001, and 2003 supplied by the STPA (ppm)

	Benzol Plant		Coke Storage		Coke Batteries		Domtar Area	Mullin's Bank		
	COL7-202-SS	COM7-220-SS	COCS-001-SS	CON5-235-SS	CON8-2 38-SS	COO8-254-SS	COC2-108-SS	COM12-225-SS	COL12-207-SS	COMB-001-SS
Parameter (ppm)	16/10/2001	16/10/2001	25/09/2000	17/10/2001	17/10/2001	16/10/2001	13/10/2001	19/10/2001	20/10/2001	26/09/2000
Acenaphthene	0.14	<0.05	7.1	0.11	0.12	<0.2	2.6	<0.05	<0.05	<0.05
Acenaphthylene	<0.05	<0.05	52	0.07	<0.05	0.86	0.24	<0.05	<0.05	<0.05
Anthracene	0.5	0.09	81	0.94	0.7	1.9	12	<0.05	<0.05	<0.05
Benzo(a)anthracene	1.2	<0.2	93	1.8	2.2	5.5	20	0.1	<0.05	<0.05
Benzo(a)pyrene	0.76	<0.05	66	0.82	1.4	4.5	16	0.07	<0.05	<0.05
Benzo(b)fluoranthene	0.79	<0.08	56	1	1.6	3.9	13	<0.06	<0.05	<0.05
Benzo(ghi)fluoranthene	0.34	<0.05	21	0.3	0.63	2.4	7.9	<0.05	<0.05	<0.05
Benzo(k)fluoranthene	0.79	<0.08	56	1	1.6	3.9	13	<0.06	<0.05	<0.05
Chrysene	1.2	0.22	78	1.9	2.3	5.7	19	0.11	0.06	<0.05
Dibenz(a,h)anthracene	0.12	<0.05	7.9	0.12	0.22	0.6	2.1	<0.05	<0.05	<0.05
Fluoranthene	2.5	0.41	180	4.4	4.3	14	44	0.19	0.06	<0.05
Fluorene	0.26	<0.2	71	0.39	0.27	0.84	3.8	<0.05	<0.05	<0.05
Indeno(1,2,3-cd)pyrene	0.37	<0.05	32	0.36	0.67	2.7	8.7	<0.05	<0.05	<0.05
1-Methylnaphthalene	0.97	2.4	33	2.2	1.8	1	0.5	0.07	0.67	<0.05
2-Methylnaphthalene	1.3	3.3	38	2.8	2.3	1.3	0.6	0.08	0.95	<0.05
Naphthalene	1.1	2.4	53	2.9	2.3	2.7	0.83	0.1	0.94	<0.05
Perylene	0.19	<0.05	15	0.19	0.35	0.92	3.8	<0.05	<0.05	<0.05
Phenanthrene	2.3	1.3	250	7	4.1	9.2	35	0.19	0.23	<0.05
Pyrene	2	0.4	130	3.3	3.7	11	37	0.17	0.07	<0.05

Notes:
All values expressed as ppm

Table A.3: Summary of the groundwater chemistry concentrations in 2000, 2001, and 2003 supplied by the STPA

		Benzol Plant			Coke Storage	Coke Batteries			Domtar Area		Mullin's Bank
		COBP-001-MWB	COBP-001-MWB	COBP-001-MWB	COCS-004-MW	COCB-003-MWA	COCB-003-MWA	COCB-003-MWA	CODT-002-MW	CODT-002-MW	COMB-005-MW
Parameter	**Units**	22/09/2000	17/10/2001	13/05/2003	18/09/2000	18/09/2000	19/10/2001	12/05/2003	31/10/2001	06/05/2003	23/09/2000
Alkalinity, Total (As CaCO3)	mg/L	303	315	310	249	354	297	280	331	300	227.00
Ammonia	mg/L	0.34	0.18	0.57	1.68	2.12	1.39	2	1.53	0.88	0.66
Bicarbonate (as CaCO3)	mg/L	300.71	313	308	248.70	353.66	297	279	330	299	226.96
Carbonate	mg/L	2.25	2	2	0.29	0.33	<1	<1	<1	1	0.03
Chloride	mg/L	65	61.9	32	27.2	9.5	10.2	8	14.7	8	114
Color	TCU	70	7	10	25	23	24	26	16	18	91
Conductivity	umhos/cm	764	845	665	910	693	710	607	710	570	2150
Cyanide (total)	mg/L				<0.02	0.17					
Cyanide (total)	mg/L	<0.02			<0.02	<0.02					<0.02
Dissolved Organic Carbon (DOC)	mg/L	17.5			10.1	21.8					3.1
Hardness	mg/L	308.40	336	293	381.44	303.91	324	277	345	272	1083.84
Nitrate (as N)	mg/L		0.11				0.14		<0.01		
Nitrite (as N)	mg/L		<0.01				0.01		<0.05		
Nitrite/Nitrate	mg/L		0.11	<0.05			0.15	<0.05	<0.05	<0.05	
Nickel	mg/L	<0.05			<0.05	<0.05					<0.05
Orthophosphate	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.03	<0.01	0.04	<0.01
pH (lab)		7.9	7.8	7.8	7.1	7	7.2	7.3	7.4	7.6	6.3
Silica	mg/L	15	15.7	14	15.8	20.3	18.1	15	21.5	19	2.7
Sulfate	mg/L	1.6	12	6	121	26.7	44	31	7	6	1236
Total Dissolved Solids (TDS)(Calculated)	mg/L	427.65	447	376	486.89	393.87	383	334	383	320	1886.65
Total Organic Carbon (TOC)	mg/L		7.4	7.7			1.7	17.2	13.8	10.2	

		Benzol Plant			Coke Storage	Coke Batteries			Domtar Area		Mullin's Bank
		COBP-001-MWB	COBP-001-MWB	COBP-001-MWB	COCS-004-MW	COCB-003-MWA	COCB-003-MWA	COCB-003-MWA	CODT-002-MW	CODT-002-MW	COMB-005-MW
Parameter	**Units**	22/09/2000	17/10/2001	13/05/2003	18/09/2000	18/09/2000	19/10/2001	12/05/2003	31/10/2001	06/05/2003	23/09/2000
Turbidity	NTU	43	54.5	0.7	30	37	423	194	45.3	45.6	19
Calcium (Dissolved)	mg/L			93				84		76	
Iron (Dissolved)	mg/L			0.15				22		5.7	
Magnesium (Dissolved)	mg/L			15				16		20	
Manganese (Dissolved)	mg/L			1.1				9.7		1.6	
Potassium (Dissolved)	mg/L			5.5				3.1		3.2	
Sodium (Dissolved)	mg/L			24				5.6		5.8	