ECOTOXICOLOGICAL ASSESSMENT OF USING COKE IN AQUATIC RECLAMATION STRATEGIES AT THE ALBERTA OIL SANDS

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ABSTRACT

Oil sands, also known as tar sands or bituminous sands, are sand deposits impregnated with dense, viscous petroleum called bitumen. The two major oil sand mining companies currently producing synthetic crude oil in the province of Alberta are Syncrude Canada Ltd. and Suncor Energy Inc. Coke is a waste product formed during the heavy oil upgrading processes. The amount of coke produced currently at the Syncrude and Suncor operations is significantly more than what can be combusted and/or sold. Therefore, it must be stored on site making coke a necessary component of future reclamation landscapes. It is as yet unclear whether or not coke poses a significant toxicological risk (i.e. through leaching of constituent chemicals and elements) to the aquatic or terrestrial environments if used in a long-term reclamation capacity. The primary objective of this research was to evaluate whether stockpiled Syncrude Canada Ltd. and Suncor Energy Inc. coke can safely and effectively be used as a substrate amendment in an aquatic reclamation option.

Syncrude and Suncor coke were exposed to three different sets of water quality conditions: high and low dissolved oxygen, pH (5, 7.5 and 10) and freeze-thaw cycles. These conditions have the potential to affect the leaching of constituents from coke once placed in an aquatic environment in northern Alberta. Metals were observed to leach from both coke types under all treatments. Some of these metals (cobalt, copper, manganese, molybdenum, nickel, vanadium and zinc) reached levels of toxicological interest by exceeding published LC_{50} values for the aquatic macroinvertebrate *Chironomus* sp. and/or established Canadian Water Quality Guidelines for the protection of aquatic life.

To determine the source of metals observed to leach in the leaching experiments, an accelerated weathering experiment was conducted. Coke from both Syncrude and Suncor were pre-treated by rinsing with water to remove any natural soil or sediment particles that become associated with the coke during storage, and with peroxide to remove any metals bound to the surface of the coke. It was concluded that the metals leaching into the overlying water and pore water of the coke were from either the natural soil/sediment particles, and/or were weakly bound to the surface of the coke. Rinsing coke with water before adding it as a substrate amendment in an aquatic

reclamation strategy may decrease its potential toxicity to aquatic organisms by removing the soil/sediment debris and metals loosely bound to the surface of the coke, reducing initial amounts of metals available to the organisms in the pore and overlying waters.

As part of these leaching experiments, coke from both Syncrude and Suncor were further characterized with elemental analysis and qualitative analysis with polarized light microscopy and scanning electron microscopy. These analyses showed distinct differences in the physical properties (i.e. particle size and structure) of Syncrude and Suncor coke. However there appeared to be little variation in the elemental and structural composition among the different weathering treatments within each coke type.

Following leaching, coke from Syncrude and Suncor was used as a substrate in 10-d toxicity tests with *Chironomus tentans*. These experiments evaluated whether the leachate generated from coke, or the coke itself, caused of an adverse effect on the survival and/or growth of this aquatic invertebrate. Decreased survival and growth of *C. tentans* was observed when Suncor coke was used as a substrate. However, further experimentation showed that these effects were due to the physical properties of Suncor coke, rather than any constituents that leached from the coke.

In a separate experiment, combinations of fresh oil sands waste materials were added to experimental enclosures constructed at Syncrude Canada Ltd in May 2002. Core samples of these waste materials were collected after aging *in situ* for periods of 2 and 14 months. The aged samples along with fresh (0 month) samples, were used as substrate material in 10-d toxicity tests with *C. tentans* to assess the potential toxicity of both fresh and field-aged combinations of waste materials. These experiments found that there is a potential for greater initial stress or toxicity to aquatic organisms when the substrates are freshly added to the reclaimed wetlands. However, this initial potential toxicity of oil sands waste materials can decrease with aging in an aquatic environment.

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DEDICATION

To my family: Jim, Gail, Victoria and Kimberly.
Thank you for being the home base from which I draw my motivation.

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LIST OF ABBREVIATIONS

α = alpha

λ = lambda

$>$ = greater than

$<$ = less than

$\geq$ = greater than or equal to

$\mu g/g$ = micrograms per gram

$\mu g/L$ = micrograms per litre

$\mu g/mL$ = micrograms per millilitre

μm = micrometre

AEUB = Alberta Energy and Utilities Board

ANOVA = analysis of variance

BDL = below detection limit

BOD = biochemical oxygen demand

^{o}C = centigrade

$CaCO_3$ = calcium carbonate

C/H = carbon per hydrogen

cm = centimetre

cm/s = centimetres per second

Co = cobalt

CT = composite or consolidated tailings

Cu = copper

CWQG = Canadian Water Quality Guideline

d = day

DO = dissolved oxygen

DOC = dissolved organic carbon

DOM = dissolved organic matter

g/cm^3 = grams per cubic centimetre

GC-MS = Gas Chromatography-Mass Spectrometry

h = hour

H^+ = hydrogen ion

H_2O_2 = hydrogen peroxide

H_2SO_4 = sulphuric acid

ICP-ES = Inductively Coupled Plasma-Emission Spectroscopy

ICP-MS = Inductive Coupled Plasma-Mass Spectrometry

kg = kilogram

L = litre

LC_{50} = median lethal concentration

M = molar

m^2/g = square metres per gram

m^3 = cubic metre

MFT = mature fine tailings

mg = milligram

mg/L = milligrams per litre

mg/m^3 = milligram per cubic metre

min = minute

mL = millilitre

mm = millimetre

Mn = manganese

Mo = molybdenum

mPas = millipascal second

mV = millivolt

n = number of samples

NaOH = sodium hydroxide

Ni = nickel

nm = nanometre

PAH = Polycyclic aromatic hydrocarbon

Pas = pascal second

psi = pounds per square inch

rpm = revolutions per minute

SE = standard error

sec = seconds

SEM = Scanning Electron Microscopy

Syn or Syncrude = Syncrude Canada Ltd.

Sun or Suncor = Suncor Energy Inc.

V = vanadium

VO_2^+ = vanadium IV

VO_4^{3-} = vanadium V

w/w = by weight of the total substance, solution or mixture

Zn = zinc

CHAPTER 1. INTRODUCTION

1.1 The Oil Sands

Oil sands, also known as tar sands or bituminous sands, are sand deposits impregnated with dense, viscous petroleum called bitumen. They are found throughout the world, often in the same geographical areas as conventional petroleum. The largest oil sand deposits are in Canada and Venezuela. Oil sand deposits in northwestern China (Zinjiang Autonomous Region) are also large and at some locations around Karamay, the bitumen appears directly on the land surface (Speight, 1999). Smaller oil sand deposits occur in the United States (mainly in Utah), Peru, Trinidad, Madagascar, the former Soviet Union, the Balkan States, and the Philippines (Speight, 1999).

In Canada, one of the major industries in the province of Alberta is the oil sand industry. There are four major deposits of oil sands in this province; the Athabasca, Peace River, Cold Lake, and Wabasca. The largest of these, and the only one currently amenable to surface mining, is the Athabasca deposit, which covers a total area of approximately 31,000 km^2 (Barton and Wallace, 1979). The Alberta Energy and Utilities Board (AEUB) estimates that Alberta's oil sands contain between 1.7 trillion and 2.5 trillion barrels of bitumen, although most of this is not accessible using current mining technique (Scott and Fedorak, 2004).

The predominant theory for the origin of these oil sands is that they evolved in highly organic Cretaceous shales in the southern portion of the Alberta Sedimentary Basin. Underground pressure forced the oil to soak into the existing silt grade sediments and localized sand bodies of the McMurray formation. Consequently, there are wide variations in the viscosity and saturation of the bitumen (0-18 % (w/w) bitumen), even within a particular deposit of oil sands (Speight, 1999).

The two major oil sand mining companies currently producing synthetic crude oil on this site are Syncrude Canada Ltd. and Suncor Energy Inc. These two companies produced a combined total of over 150 million barrels of crude oil in 2002, and both are projecting major increases in their annual production during the next decade. Some estimates suggest that at least 300 billion barrels of bitumen can be recovered using current methods (Scott and Fedorak, 2004). Bitumen from the Athabasca region currently accounts for over 20% of Canada's petroleum, with projections approaching 50% in a few years (Leung *et al.,* 2001).

1.1.1 Industry History

Early explorers had observed oil sands bitumen and speculated that the surface seeps arose from underground pools. The Canadian government took the first scientific interest in tar sands in 1890, however, it was still unknown at this time how best to exploit this resource profitably. In 1916, Sidney C. Ells started the industry of using unrefined oil sands bitumen in road paving around the province of Alberta, but this had to be abandoned when it could not compete with traditional asphalt sources.

It is much more expensive to produce a synthetic crude oil from oil sands than it is from conventional oil reserves. This is because oil sands projects require long lead times from initial planning to inception, and then longer still until a profit is made (de Malherbe *et al.*, 1983). Therefore, with the domestic availability of conventional sources there has been no incentive to develop the oil sands until very recently.

The most important progression in the oil sands industry occurred in the 1920s when Dr. Carl Clark developed a hot water extraction method that effectively separated the oil from the sand (Scott and Fedorak, 2004). From this discovery up until 1960, many small-scale commercial enterprises were attempted but not sustained. Between 1957 and 1967, three extensive pilot-plant operations were conducted in the Athabasca region. Syncrude took over operation of the Cities Service Athabasca Inc. project in 1965, and Suncor formed from the amalgamation of Sun Company Inc. (Canada) and Great Canadian Oil Sands Ltd. in 1979 (Scott and Fedorak, 2004). In order to accomplish these ventures, the concentration of the resource (measured as percent bitumen saturation) and its accessibility (measured as overburden thickness) had to be considered (Speight, 1999).

1.1.2 Mining

Most of the Athabasca oil sands are currently being mined using conventional surface mining techniques. In surface mining, the overburden layer that includes vegetation as well as a layer of sand, gravel, clay and silt must be removed. After this layer is cleared, the oil sands are removed using a combination of shovels, conveyor belts and large trucks. The oil sands are then sent to the extraction plant via pipelines for further processing.

However, these techniques are only economically feasible on deposits that lie under 76 metres or less of overburden. This accounts for just over seven percent of the total area of the Athabasca oil sand deposits. The majority of the remaining oil sands lies under 198 metres or more of overburden. These deposits are only recoverable using *in situ* techniques, such as the application of heat and pressure to separate the bitumen from the sand in place (Rogers, 2003). Any deposits located between 76 and 198 metres are considered too deep for surface mining, but not deep enough for in situ methods since the shallow cover makes high pressure steam injection impractical. Therefore, with current technology, these deposits are considered unrecoverable. Because Athabasca oil sands have a maximum thickness of 90 metres and an average thickness of 45 metres, there are indications that no more than 10% of the in-place deposit is mineable within 1990s concepts of the economics and technology of open-pit mining (Speight, 1999)

1.1.3 Extraction

Most mined oil sand has the average composition of 10% bitumen, 5% water and 85% solids, such as sand (Stubblefield, 1989). Before the bitumen can be processed into a useable synthetic crude oil, it must first be separated from the solids. This is accomplished through a hot water flotation method that mixes the mined sand with hot water to produce a slurry. A caustic soda is also added to act as a surfactant

(Rogers, 2003). This slurry is transported onto vibrating screens where large materials such as rocks and lumps of clay are rejected (Syncrude Facts, 1997). From there, the oil sand slurry is transported to primary separation vessels where the sand settles to the bottom and the bitumen floats to the surface as froth. Hot water extraction of bitumen from the oil sands is approximately 90% efficient (Madill et al., 2001). Syncrude-produced bitumen is a very heavy oil. It has a density of 1.01 X 10^3 kg/m^3 and a viscosity of at least 105 mPas at 15.6 °C. It contains ca. 5 % (w/w) sulfur and ca. 0.45 % (w/w) nitrogen, as well as smaller amounts of the metals nickel, vanadium and iron (Stubblefield, 1989).

1.1.4 Upgrading

After bitumen is extracted from the sand, it is upgraded, converting it from viscous, tar-like oil to a more useable, light oil product. The general principal behind this process is to decrease the carbon to hydrogen ratio of the oil. As the C/H ratio is decreased, more energy is “packed” into the synthesized product and the product becomes “lighter”, lowering the boiling point of the synthesized fuel (Singh, 1985).

Processing of bitumen yields the product called synthetic crude oil. Syncrude’s synthetic crude oil is known as Syncrude Sweet Blend (SSB), and is characteristically low in sulfur (Scott and Fedorak, 2004). This contributes greatly to the North American refinery goal to produce a more environmentally friendly, lower sulfur petroleum product. Suncor produces two blends of synthetic crude oil that differ in their sulfur content. One is a sweet blend not unlike SSB, while the other is a sour blend containing higher amounts of sulfur to allow Suncor to better meet the specific needs of different consumers (Scott and Fedorak, 2004).

1.1.5 Waste Products

Sand: Sand from the extraction process at Syncrude Canada Ltd. is stored in the Southwest Sand Storage area pit. Here the sand and clay settle out and the water containing clay fines is returned to the Mildred Lake Settling Basin for further clarification (Syncrude Facts, 1997). Sand from the Suncor Energy Inc. operations is also similarly stored on site.

Fluid Tailings: The caustic soda hot water floatation process used during the extraction of bitumen from the oil sands deposits requires large volumes of water (about 0.65 m^3 wastewater for each ton of oil sands processed) and produces a waste product called mature fine tailings (MFT) (Matthews *et al.*, 2000). Tailings are a mixture of solids, water and non-extractable bitumen (50:50:1) (Herman *et al.*, 1994). The major components of tailings ponds include water (clarified water in the surface zone and water in the sludge), mineral solids (sand, silt, clays), dissolved solids (inorganic and organic components, process chemicals and leachates), and bitumen (unrecovered during extraction) (MacKinnon, 1989).

A second type of tailings is composite tailings (CT), which are a mixture of MFT and different coagulants. These coagulants solidify the MFT, thereby reducing the overall fluidity of the tailings deposit. This type of tailings allows for more reclamation alternatives since they can now be stored as a soil matrix (Matthews *et al.*, 2000).

Tailings have been shown to contain a number of contaminants of concern, including a variety of trace metals and organic compounds such as polycyclic aromatic hydrocarbons (Madeill *et al.*, 2001). The concentrations of these elements in the tailing ponds are ultimately dependent on the concentrations present in the oil sands. However, the concentrations of these metals are being maintained at low and fairly constant levels through interactions with the high-suspended solids fraction in the tailing slurries and in the sludge (MacKinnon, 1989). Most of the constituents of the wastewater retained in the tailing ponds are found in surrounding natural surface waters even though their concentrations and relative distributions are different (MacKinnon and Boerger, 1986).

Biodegradation studies conducted in the 1990s indicated that the presence of toxic compounds in oil sands tailings did not inhibit microbial activity. It has also been shown that microbes indigenous to oil sand tailings can degrade carboxylated cycloalkanes (Lai et al., 1996 and Herman *et al.*, 1994). Bacteria have been found to be present in fairly high numbers (106 to 108 cells/mL) in tailing ponds where they are capable of degrading bitumen (Foght *et al.*, 1985).

Water from Syncrude tailings waste has been shown to be acutely toxic to aquatic organisms. The amounts of cadmium, zinc, lead and vanadium present in the tailings were shown by Barton and Wallace (1979) to be well above levels which have been shown to elicit a toxic response in aquatic invertebrates and other taxa. These responses have been observed using aquatic toxicity tests with *Selenastrum capricornutum* (Chlorophyceae), Microtox®, *Daphnia magna*, *Hyalella azteca,* and *Onchorhynchus mykiss* using waters freshly derived from MFT (mature fine tailings) and CT (composite or consolidated tailings) processes (Herman *et al*., 1994; Leung *et al.*, 2001). Storage and disposal of the vast amounts of high moisture content fine tailings continues to be one of the major problems associated with the current oil sands mining and processing technology (Dawson *et al.*, 1999).

Coke: The waste product coke is produced during the heavy oil upgrading processes at the Alberta oil sands. However, Syncrude Canada Ltd. and Suncor Energy Inc. produce coke through two different coking processes-fluid and delayed coking (see section 1.3.1). Most of the coke is stored directly onsite at the oil sands operations, although some of the coke produced via delayed coking is sold and shipped off site (Scott and Fedorak, 2004). Coke contains a number of different contaminants such as metals and polycyclic aromatic hydrocarbons (PAHs). The production, composition and end uses of coke are discussed in detail throughout the rest of this chapter.

1.2 History of Coke Production

Some of the first recorded observations of coke formation in Canada occurred in the late 1800s by a refinery industry in Alberta experimenting with distillation of crude oil to obtain kerosene (Scott and Fedorak, 2004). Coke occurred because their method of heating the oil involved wood or coal. This provided a very uneven temperature distribution, causing the oil at the bottom of the stills to overheat, forming coke. The stills had to be shut down periodically to remove the coke until measures were developed to reduce its formation, such as better temperature regulation (Scott and Fedorak, 2004). However, with the need for gasoline increasing, the development of a catalytic cracking process in 1937, involving the use of catalysts to break down hydrocarbons, gave the industry a new way to produce desirable products without the delays of cokers. However, after 1960 there was a reemergence of coking and several new methods, such as fluid coking (see section 1.3.1), were developed.

1.3 Coke production at the Athabasca Oil Sands

Coking is an essential part of the upgrading system at the Athabasca oil sands because it enables mining companies to convert less profitable heavy oil fractions into the more valuable light fractions. Coke formation is characterized by an overall increase in the ratio of carbon to hydrogen atoms and, therefore, coking can be viewed as a carbon rejection method.

Coke is primarily classified based on the degree of large scale ordering present in the deposit. The two major classifications of coke are anisotropic and isotropic. Anisotropic includes both liquid phase derived and vapor phase derived coke. These cokes have a highly ordered, layered macroscopic structure. Isotropic coke, however, is characterized primarily by a lack of large-scale order. This coke type is typically formed from non-fluid precursors that inhibit the molecules from aligning (Syncrude Canada Ltd., 2003).

1.3.1 Methods of Coke Production

Syncrude Canada Ltd. uses an unconventional continuous fluid coking system, which involves the use of both a reactor and a burner (Figure 1.1). In the burner, heat is generated for the thermal cracking process by burning coke in the fluidized bed of the burner. Heat from the burner is transferred to the reactor via solids circulating between the two units in transfer lines. Heated coke from the burner moves to the reactor, to form a bed of hot particles at 500 °C. Preheated bitumen is sprayed onto this hot coke bed, which causes the heavy molecules to crack, producing light molecules and more fluid coke.

The light molecules produced are in the form of vapor. These vapors are condensed in the upper portion of the reactor in the scrubber and are cleaned of coke and heavy hydrocarbons when they leave the coker to be separated in the fractionation facilities (Mankowski, 1989). The vapors from this process are separated by distillation into four main components: light process gas, naphtha (which is further upgraded into gasoline), kerosene (to produce jet fuel), and gas-oil (the heaviest component used as a heating fuel).

The main areas of a fluid coking system are characterized as chunky withdrawal, bed coke, stripper sheds, upper dense phase wall, dilute phase, horn chamber, cyclone inlets, cyclone barrel, cyclone gas outlet tube, cyclone snout and scrubber grid. Due to the different precursors and temperatures as well as the length of time which coke is retained in the different sections, different classifications or types of coke can be found at each of these areas (Syncrude Canada Ltd., 2003).

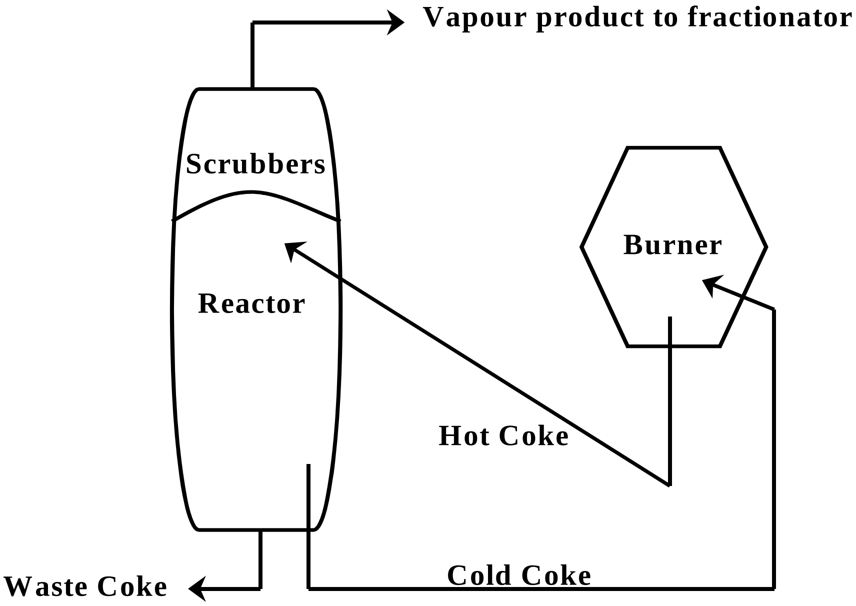

Figure 1.1. A simplified diagram of a fluidized coke system. Adapted from Mankowski (1989) and Syncrude Canada Ltd. (2003).

Suncor Inc. uses a delayed coking process, which is a 'batch by batch' procedure with each coker unit containing a heater and a pair of drums (Figure 1.2). Bitumen is introduced into the drums and is progressively heated to above 490 °C. The heat cracks the molecules into vapors and solid coke. The coke is then deposited in a drum, along with most of the sulfur and virtually all of the metals. The stock leaving the furnace usually consists of hot liquid and vapors mixed with a small amount of steam (Scott and Fedorak, 2004). As in Syncrude, they are fractionated and separated by distillation for consumption.

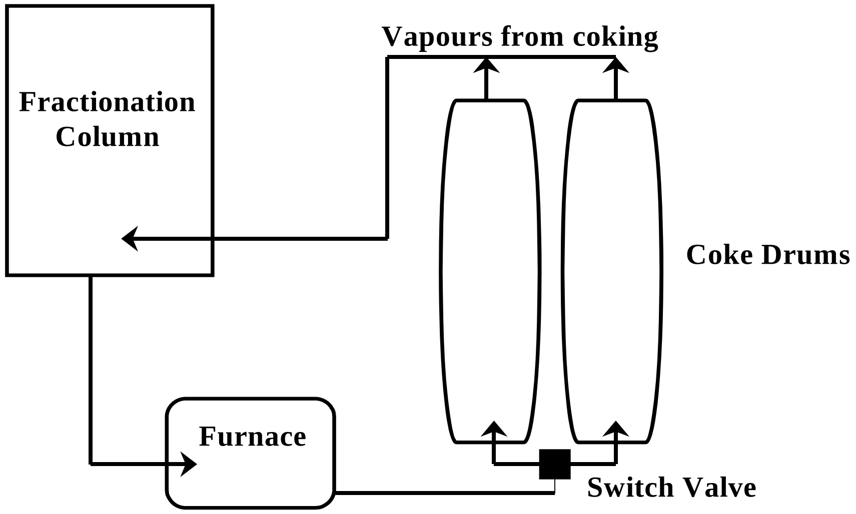

Figure 1.2. A Simplified diagram of a delayed coker system. Adapted from Scott and Fedorak (2004).

1.3.2 Current Disposal Methods for Coke

Syncrude: There are several options being developed for the petroleum coke produced during the coking processes at Syncrude Canada Ltd. There is considerable potential, despite the presence of sulfur, that Syncrude coke can be gasified and used as an energy source. However, the commercial gasification of oil sands coke is delayed due to the availability of natural gas on the site of the upgrading plants (Furimsky 1998). It has also been demonstrated that activated carbons with surface areas and micropore volumes comparable to existing commercial activated carbons can be produced from Syncrude fluid coke (DiPanfilo and Egiebor 1996).

The main problem with these options is that the amount of coke produced at the Syncrude Canada Ltd. operations (over 2,000 tonnes per day) is significantly more than can be combusted and/or sold. Therefore, it must be stored on site in "coke cells" and these then become a necessary component of the reclamation landscapes.

Coke cells are located in mined out areas, or more recently, in tailings holding ponds (Scott and Fedorak, 2004). The coke is transported there as a slurry with recycled water, and transported using a network of pipelines. The coke cells extend to the base of a mined out pit, and are surrounded by earth dikes constructed of "extraction rejects". These are clay lumps that were rejected when the oil sand was initially processed during extraction (Komex International Ltd., 1998). Currently, land on the reclaimed surface areas of coke cells are used primarily as wildlife habitat (Golder Associates Ltd., 2000).

Suncor: Prior to the recent expansions at the mine sites north of Fort McMurray, coke production at Suncor Energy Inc. was low enough that most of it was utilized in the steam and power production for on-site energy services (Scott and Fedorak, 2004). However, with the new expansions, the amount of coke is increasing, and new strategies are being developed to compensate. Approximately 10% of Suncor coke is sold to Japanese ammonia plants. The majority, however, is stored in large piles on site.

1.3.3 Physical and Chemical Properties of Coke

Coke produced by fluid cokers is termed fluid coke. This coke is formed almost instantaneously as feed (bitumen) is sprayed onto the hot coke particles in the reactor. This produces a layered type of coke since new layers of coke are added as cracking occurs on each particle. Therefore, fluid coke can resemble the structure of small onions with an average diameter of between 100 and 150 μm (Scott and Fedorak, 2004). In contrast, three different types of coke can be produced from delayed cokers. These are termed sponge coke, needle coke and shot coke (Scott and Fedorak, 2004). Some of the physical and chemical characteristics of coke from Syncrude Canada Ltd. and Suncor Energy Inc. are included in Table 1.1.

1.3.4 Coke Toxicity and Leachability

Due to the different upgrading methods used at Syncrude Canada Ltd. and Suncor Energy Inc., the toxicological properties of the coke produced by these two companies should, theoretically, be different. However, there have been no studies conducted that fully characterizes the toxicological properties of coke for either Syncrude Canada Ltd. or Suncor Energy Inc., but some leaching work has been done.

A study looking at the short-term metal leaching rates of Syncrude Canada Ltd. coke was conducted in 1996. This study looked at the amounts of various trace metals found in the coke before and after leaching. In these short-term (18 hr) leachate tests, no organic substances (such as polycyclic aromatic hydrocarbons) could be detected in the leachate (Chung *et al.*, 1996). Therefore, it is now believed that metal-containing compounds in the coke are buried in the carbon matrix in such a way that they are not accessible by water (Chung *et al.*, 1996). Proximate and ultimate analyses indicated that the composition of the samples exhibited little change over several years of coke production. A rather low oxygen content, in spite of prolonged weathering, indicated a resistance of the coke to oxidation (Chung *et al.*, 1996).

Leaching experiments using different acids and with a range of pH showed that little material is leached from Syncrude Canada Ltd. coke. The only metals removed were nickel and vanadium (Komex International Ltd., 1998). Molybdenum removal was not detected in the leaching tests, but was found to be concentrated in water associated with coke storage (Komex International Ltd., 1998).

Table 1.1. Physical and chemical characteristics of Syncrude Canada Ltd. and Suncor Energy Inc. cokes. Adapted from Komex International Ltd. (1998) and Scott and Fedorak (2004).

Characteristic	**Syncrude**	**Suncor**
Size	Medium to fine sand size (uniform)	Well-graded sandy gravel to large chunks (non-uniform)
Shape	Spheres	Irregular lumps
Structure	Onion-like layering	Highly porous, sponge-like
Water[a]	0.25 to 0.69%	0.24 to 0.66%
Non-Combustible Ash[a]	4.8 to 7.5%	3.3 to 6.5%
Volatile Matter[a,b]	4.9 to 6.2%	8.3 to 11.0%
Surface Area	10.7 to 12.2 m^2/g	Highly variable
Specific Gravity	1.55 to 1.65 g/cm^3	1.2 to 1.37 g/cm^3 (highly dependent on particle size)
Density in Coke Cells	~1.0 mg/m^3	Coke cells not used
Permeability	4 to 6 x 10^{-4} cm/s at density ~0.94 mg/m^3	Highly variable depending on density (an inverse relationship)
Sulphur	6.2 to 6.8%	5.86 to 6.15%
Carbon	80.7 to 83.7%	81.54 to 84.35%

[a] Proximate analysis (typical).

[b] Volatile matter is weight lost upon heating at 925°C for 7 min in an oxygen-free atmosphere.

It has been shown previously that nickel (<0.05 to 0.068 mg/L) and vanadium (0.04 to 7.0 mg/L) are more mobile under slow, long-term leaching conditions. Molybdenum is also considered to have long-term leaching potential since it was found in coke storage water (0.3 to 0.8 mg/L) (Komex International Ltd., 1998). These findings conflict with the previously held conclusion, that coke will not leach significant amounts of toxic constituents, and suggest that a thorough evaluation program involving long-term leaching tests is required in order to fully understand the risks associated with using coke as part of a reclamation program (Komex International Ltd., 1998).

1.4 Reclamation Strategies at the Alberta Oil Sands

The goal of reclamation at the oil sands is to achieve maintenance-free, self-sustaining ecosystems with capabilities equivalent to or better than pre-disturbance conditions (Golder Associates Ltd., 2000). Indigenous biota living in wetlands created on mined out oil sands leases will be exposed to complex effluent containing a number of potentially toxic compounds. Therefore, characterizing the toxic effects of one chemical alone cannot assess the suitability of the wetlands as a habitat (Pollet and Bendell-Young, 2000). Organisms also differ in their route of exposure to stressors (e.g. water, sediment, or food) and, therefore, they may not be exposed to the same amounts or types of contaminants (Bendell-Young *et al.*, 2000).

The main sources of toxicity from the oil sand mining process to the surrounding ecosystem have been identified as tailings (fine and coarse), process water, sulfur, and coke. Both Suncor and Syncrude maintain a no discharge policy in regard to these contaminants. Therefore, these waste products are stored on site until reclamation occurs. One strategy for utilizing this coke is as a substrate layer in an aquatic reclamation program (Figure 1.3). Coke is proposed to be added between a tailings and peat layer in reclaimed wetlands (Golder Associates Ltd., 2000). This is because coke has the potential to act as a “buffer” for any contaminants which may leach from the tailings layer into the overlying clean water cap.

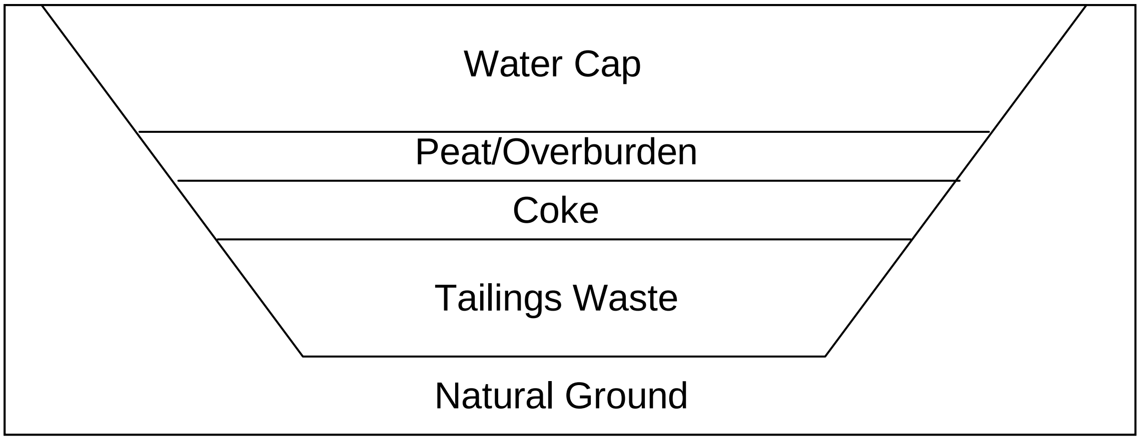

Figure 1.3. Possible layering of oil sand waste materials in a wetland reclamation strategy on mined oil sand leases (Adapted from Golder Associates Ltd., 2000 and MacKinnon, 2002).

1.4.1 Coke in an Aquatic Reclamation Program

Today, Syncrude Canada Ltd. produces approximately 23 kg of coke per barrel of Syncrude Sweet Blend (SSB) oil. This totals approximately 2 million tonnes of coke per year, with planned expansions in the next few years increasing this number to 3 million tonnes per year (Komex International Ltd., 1998; Scott and Fedorak, 2004). As part of the Syncrude Canada Ltd. operation, about 2,000 tonnes per day of this coke is being stockpiled in proximity to the plant (Chung *et al.*, 1996). Suncor produces 39.6 kg of coke per barrel of bitumen processed, amounting to the production of over 3 million tonnes of coke per year (Scott and Fedorak, 2004).

Coke contains a high amount of organic carbon. Using coke as a substrate layer in an aquatic reclamation strategy would therefore allow for immediate additional input of organic carbon into a wetland. This could be useful for the timely development of sustainable wetlands on old oil sands leases where natural organic matter is not very abundant. In wetlands dissolved organic matter (DOM) plays an important role in the biogeochemistry of carbon (Kalbitz *et al.*, 2000). Dissolved oraganic matter in established wetlands originates from plant litter, soil humus, microbial biomass, algal exudates, decomposing biota or from root exudates.

A diverse benthic invertebrate community could not develop successfully without the presence of organic carbon. The invertebrate community establishes early in any freshwater ecosystem and is an integral part of the aquatic food web. Thus, the benthic macroinvertebrate community structure in wetlands receiving industrial effluent is relevant to the overall biotic structure of such a wetland (Bendell-Young *et al.*, 2000). As a result, the abundance of coke, and its high percentage of organic carbon, makes it a very attractive option for use in the aquatic reclamation process.

An evaluation program looking at the possible long-term effects of adding coke to an aquatic environment should be representative of the environment encountered in the oil sands region, including some of the more extreme environmental conditions. This will help determine under what conditions coke could potentially release the most toxic constituents, thus posing the greatest risk to the surrounding aquatic environment. One such variable is the level of dissolved oxygen in the overlying water cap. Some metals have been shown to speciate differently under different redox conditions, potentially becoming more toxic (Meng *et al.,* 2001).

Another water quality condition to consider is pH. There is a potential for coke to be exposed to various pH levels in a reclaimed environment due to layering with other waste products (such as tailings) in the reconstructed wetlands. It is known that under lower pH conditions, metals can be released (ionized) into water from sediment more easily (Wren and Stephenson, 1991). It has also been shown in previously conducted short-term work that coke may produce acutely toxic seepage water under more acidic conditions (Lane *et al.* 1984).

It is also important to take into account significant climate variables, such as the freeze-thaw cycle. In previous studies it was discovered that negative pore water pressures develop when water-saturated oil sands fine tails are subjected to below freezing temperatures (Dawson *et al.,* 1999). These negative pore water pressures can cause water to migrate to ice crystals already growing in the pores, forming an ice-soil structure similar to that seen in permafrost soils. This ice-soil structure has been demonstrated to cause substantial dewatering of fine tails in both the laboratory and the field (Dawson *et al.,* 1999). Since the oil sands region in northern Alberta undergos a considerable drop in temperature during the winter season, the possibility exists for coke to undergo this same process, thus releasing pore water that is potentially more toxic into the overlying water.

1.5 *Chironomus tentans* as a Test Organism

Chemical analysis alone is not enough to assess the toxicological risk in an aquatic environment. It is impossible to analyze for all of the chemicals that may contribute towards toxicity (Juvonen *et al*., 2000). Bioassays integrate the combined effects of all chemicals present at a polluted site, including their bioavailability (van Gestel *et al*., 2001). Because of the key position that larvae of members of the family Chironomidae hold among the invertebrates in freshwater ecosystems, they have received increased attention in ecotoxicological studies (de Bisthoven *et al*., 2004). Among freshwater macroinvertebrates, chironomid larvae are considered a good indicator of water quality because of their abundance in aquatic ecosystems (Mousavi *et al*., 2003). The species, *Chironomus tentans*, comprises a large percentage of the invertebrate biomass in the wetlands of Northern Alberta, making it a good representative of aquatic organisms that may come into contact with oil sands waste material (Baker, 2004).

Chironomus tentans are easy to culture and handle in the laboratory. They have a relatively short life cycle (approximately 30 days at 24 ± 1 C°) making them an ideal candidate for both acute and chronic toxicity studies (Pery *et al*., 2003). They have several life stages consisting of an egg mass, larvae (which also has four instars), pupae and adult (mature fly). The adult stage can cause *C. tentans* to transport trace metals and other contaminants from the aquatic to the terrestrial environment (Timmermans and Walker, 1989).

Chironomus sp. have been shown to be sensitive to a broad range of contaminants in both water and sediments and therefore are commonly used as part of metal sediment toxicity studies (Besser and Rabeni, 1987; Ingersoll *et al*., 1996; Leppanen *et al*., 1998; Liber *et al*., 1996; Peeters *et al*., 2001). Timmermans *et al*. (1992) found that exposure to both zinc and copper caused delayed development and reduced growth of *Chironomus riparius* larvae. A study conducted by Powlesland and George (1986) found that nickel can also bring about reduced growth and development as well as mortality in the sensitive 1st instar larvae of *C. riparius* at concentrations of 79.5 mg/L. The most obvious impact that metal toxicity can have on *C. tentans* is the death of the organism. However, there are more subtle impacts such as growth, emergence and reproduction that can also be observed (Reynoldson, 1987).

2. RESEARCH GOAL AND OBJECTIVES

2.1. Goal

The overall goal of this research was to evaluate whether stockpiled Syncrude Canada Ltd. and Suncor Energy Inc. coke can safely and effectively be used as a capping material for consolidated and/or mature fine tailings in aquatic reclamation. It is as yet unclear whether or not coke poses a significant toxicological risk (i.e. through leaching of constituent chemicals and elements) to the aquatic or terrestrial environments if used in a long-term reclamation capacity.

2.2. Objectives

The specific research objectives were to:

I) Determine if the coke generated by Syncrude Canada Ltd. and Suncor Energy Inc. display different physical properties (porosity, texture) and/or contain different types or concentrations of toxic constituents (both inorganic and organic), that could potentially be liberated and affect their suitability for use as substrate amendments in wetland reclamation options.

II) Determine whether aging under different water quality conditions (e.g. pH, DO and freeze-thaw) could influence the degree to which toxicants are released from the coke and become available to aquatic organisms; identify what conditions are most important in such processes; and determine the acute and sublethal toxicity of both Syncrude and Suncor coke and their leachates to a representative benthic invertebrate, *Chironomus tentans,* after weathering under different overlying water conditions for 30-90 days.

III) Evaluate if different mixture combinations of coke, soft tailings and reclamation soil influence the degree to which potential toxicants are released and become available to aquatic organisms *in-situ* over time.

3. THE EFEECTS OF DISSOLVED OXYGEN, pH, AND FREEZE-THAW CYCLES ON THE POTENTIAL LONG-TERM TOXICITY OF OIL SANDS COKE AND THEIR LEACHATES TO CHIRONOMUS TENTANS

3.1 Introduction

Oil sands are sand deposits impregnated with dense, viscous petroleum called bitumen. The two major oil sand mining companies currently producing synthetic crude oil in Alberta are Syncrude Canada Ltd. and Suncor Energy Inc.

One waste product produced during the upgrading processes at the Alberta oil sands is called coke. Currently, Syncrude produces approximately 2 million tonnes of coke per year, with planned expansions in the next few years increasing this number to 3 million tonnes per year (Komex International Ltd., 1998; Scott and Fedorak, 2004). Suncor already produces over 3 million tonnes of coke per year (Scott and Fedorak, 2004). Syncrude and Suncor produce coke through different coking processes, called fluid and delayed coking. Most of the coke is stored directly on-site at the oil sands operations, although some of the coke produced via delayed coking is sold and shipped off site.

Coke contains a high amount of organic carbon. Using coke as a substrate layer in an aquatic reclamation strategy therefore allows for immediate, additional input of organic carbon into a constructed wetland. This could be useful for the timely development of sustainable wetlands on old oil sands leases where natural organic matter is not very abundant. An evaluation program looking at the long-term effects of adding coke to an aquatic reclamation strategy should be representative of the environmental conditions encountered in the oil sands region. This will help to determine under what circumstances coke could potentially release the greatest amount of toxic constituents, thereby posing the greatest risk to the surrounding aquatic environment. An important environmental variable to consider is the level of dissolved oxygen in the overlying water cap. Some metals may speciate differently under different redox conditions, potentially becoming more toxic (Meng *et al*., 2001).

There is also the potential for coke to be exposed to various pH levels in a reclaimed environment due to layering with other waste products (such as tailings) in reconstructed wetlands. It is known that under lower pH conditions, most metals tend to be released (ionized) into water from sediment more easily (Wren and Stephenson, 1991). It has also been shown in previously conducted short-term work that coke may produce acutely toxic seepage water under more acidic conditions (Lane *et al*., 1984).

It is also important to take into account any significant climate changes encountered in the northern regions of Alberta, such as freeze-thaw cycles. In previous studies conducted at the Alberta oil sands, it was discovered that negative pore water pressures develop when water-saturated oil sands fine tailings are subjected to below freezing temperatures (Dawson *et al*., 1999). These negative pore water pressures can cause water to migrate to ice crystals already growing in the pores, forming an ice-soil structure similar to that seen in permafrost soils. This ice-soil structure has been demonstrated to cause substantial dewatering of fine tailings under both laboratory and field conditions (Dawson *et al*., 1999). Since the oil sands region undergoes a considerable drop in temperature during the winter season, the possibility of coke undergoing this same process, and releasing pore water that is potentially more toxic into the environment is significant.

The objective of the following experiments was to determine the effects of environmental factors such as the dissolved oxygen and pH levels of the overlying water, and the freeze-thaw cycles experienced in Northern Alberta, on the long-term toxicity of Syncrude and Suncor coke and their leachates if coke is incorporated into an aquatic reclamation landscape.

3.2 Materials and Methods

3.2.1 Study Design

A static test protocol was chosen because this would provide a “worst-case” scenario resulting in more concentrated overlying water and pore water. Leaching, as used in this thesis, refers to the inherent movement of toxic constituents (i.e. metals) from the waste product coke into the overlying water and pore water. It is assumed that any seepage to groundwater from coke if used in reclamation landscapes would be minimal due to the assumed presence of fine and/or consolidated tailings underneath the coke layer. Depths of water and coke used in these laboratory experiments are based on the ratio of the proposed coke and water depths of the constructed wetlands, approximately 0.5 - 0.75 and 1.0 - 2.0 metres, respectively. This creates, at a minimum, a 1:4 ratio of coke to water (MacKinnon, 2002).

The test vessels for all experiments were 2 L glass jars with screw caps. This size was chosen because it provided enough water for sampling, and the caps provide a sealed environment ideal for the easy maintenance of specific DO and pH levels.

Each test vessel contained a 400 mL layer of coke or sand covered with a 1600 mL layer of reconstituted water, the characteristics of which are listed in Table 3.1. This water was prepared using laboratory deionized water the day before the start of the experiment. On day 0 of each leaching experiment, the reconstituted water was thoroughly mixed before being added to the substrate (coke or sand) in each test jar.

For each leaching experiment, the coke was obtained directly from Syncrude Canada Ltd. and Suncor Energy Inc. on-site storage piles in May 2002. The sand used in the control vessels was pure quartz (250-425 μm) sand obtained from Brock White Canada in Saskatoon, SK, and was rinsed several times with deionized water before being used in each experiment.

Table 3.1. Characteristics (means ± SE) of reconstituted water used in laboratory leaching experiments, and surface water sampled from the Deep Wetland field site located at Syncrude Canada Ltd.

Characteristic	Deep Wetland Water[1]	Reconstituted Water
pH	8.4 ± 0.003	8.4 ± 0.03
Hardness (mg/L $CaCO_3$)	198.7 ± 1.8	204.0 ± 3.4
Alkalinity (mg/L $CaCO_3$)	215.3 ± 3.5	194.7 ± 10.1

[1] Samples were collected in May 2002 (*n* = 4).

3.2.1.1 Dissolved Oxygen

The dissolved oxygen leaching experiment was 30 days in duration, and consisted of a low and high dissolved oxygen treatment. Prior to adding the reconstituted water to the substrate in each jar, the water was pre-aerated overnight with nitrogen for the low oxygen and air for the high oxygen treatments. Afterwards, the jars were continuously aerated by introducing their respective gases as close to the surface of the coke/sand layer as possible, without disturbing the surface. This was done using a hollow glass rod attached to aquarium tubing outside of the test vessel so as to prevent any contact between the plastic tubing and the water. The dissolved oxygen levels (mg/L) in each test vessel were measured every second day. Overlying water and pore water was sampled on days 0, 10, 20 and 30 for analysis of trace metals and standard water quality variables (see section 3.2.2.1).

3.2.1.2 pH

The pH experiment was 90 days in duration with water sampling occurring on days 0, 45, and 90 (see section 3.2.2.1). The three pH treatments used in this experiment were 5, 7.5 and 10, selected to encompass the range of values that each coke type may be exposed to during the duration of an aquatic reclamation program. Prior to adding the reconstituted water to the substrate in each jar, it was adjusted to the desired pH level with concentrated (1M) H_2SO_4 or NaOH. Random checks on each of the test vessels were made twice per week and, if necessary, the pH was adjusted using H_2SO_4 or NaOH to keep it within the acceptable range of ± 0.5 pH units. There was no aeration of the test vessels during this experiment, since it was conducted in an airtight system to better maintain stable pH levels. Dissolved oxygen was monitored every one to two weeks to ensure that levels in the overlying water were not below 3 mg/L, the lowest level required for the proper growth of the aquatic invertebrate, *Chironomus tentans* (Irving *et al*., 2004).

3.2.1.3 Freeze-thaw

In the freeze-thaw experiment, coke and its overlying waters were frozen in 2-L plastic jars with enough headspace so as to prevent any possibility of cracking the jars due to expansion of the overlying water during freezing. Six freeze-thaw cycles were conducted with sampling of the overlying and interstitial waters prior to the first cycle and after cycles 1, 3 and 6 (see section 3.2.2.1). Each cycle consisted of 2 days of freezing at –20°C, and 4 days of thawing in an environmental chamber at 23 ± 1°C.

3.2.2 Sampling and Analysis

3.2.2.1 Water

At each sampling time, three replicates (jars) from each treatment for each coke type and control were removed. The overlying water was carefully decanted off the coke layer and then filtered using a 3.1-µm pore-size glass fiber filter (Pall Life Sciences, Mississauga, ON) to remove any coke particles which may have been present. The overlying water was analyzed for standard water quality variables (ammonia, conductivity, pH, hardness and alkalinity) at the Toxicology Centre, University of Saskatchewan, Saskatoon, SK. Sub-samples of overlying water were further filtered using 0.45-µm Nalgene® membrane filters before being transferred into pre-cleaned 15-mL Nalgene® bottles (Nalge Nunc International, Rochester, NY, USA) for trace metal analysis. These samples were acidified with double distilled (ultra-pure) nitric acid

(1N) to pH 2 and stored at 4 ºC until they were analyzed. Trace metal analysis was performed in the Department of Geological Sciences at the University of Saskatchewan using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Polycyclic aromatic hydrocarbon (PAH) analysis was conducted on two replicate samples of each dissolved oxygen treatment (high and low) for each coke type on Day 30 of the leaching period. Filtered overlying water was transferred into sterile amber glass jars with no head-space. PAH analysis was performed by Enviro-Test Laboratories (Saskatoon, SK) using Gas Chromatography-Mass Spectrometry (GC-MS).

After the overlying water was decanted from the leaching jar, coke was transferred from the jar into a small, plastic sample container. Pore water was then extracted from the coke by vacuum filtration with a 0.45-µm membrane filter (Pall Life Sciences, Mississauga, ON). Pore water was analyzed for trace metals and the same standard water quality variables as described previously for overlying water.

3.2.2.2 Coke

The coke used in these experiments was also analyzed for elemental composition. A sub-sample of each coke type used for each treatment in the dissolved oxygen and pH experiments (Table 3.2) was dried in an oven at 60 ºC for 48 hrs. These samples were then sent to Acme Analytical Laboratories Ltd. (Vancouver, BC) for analysis using ICP-MS and Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) techniques.

Table 3.2. Origin of Syncrude Canada Ltd. and Suncor Energy Inc. coke samples chosen for elemental analysis[1].

Syncrude Canada Ltd. Coke	Suncor Energy Inc. Coke
Unweathered Syncrude coke, from the coke piles (starting material)	Unweathered Suncor coke, from the coke piles (starting material)
Weathered Syncrude coke, exposed to water with low dissolved oxygen (~ 1 mg/L) for 30 days	Weathered Suncor coke, exposed to water with low dissolved oxygen (~ 1 mg/L) for 30 days
Weathered Syncrude coke, exposed to water with high dissolved oxygen (~ 8 mg/L) for 30 days	Weathered Suncor coke, exposed to water with high dissolved oxygen (~ 8 mg/L) for 30 days
Weathered Syncrude coke, exposed to water at pH 5 for 45 days	Weathered Suncor coke, exposed to water at pH 5 for 45 days
Weathered Syncrude coke, exposed to water at pH 7.5 for 45 days	Weathered Suncor coke, exposed to water at pH 7.5 for 45 days
Weathered Syncrude coke, exposed to water at pH 10 for 45 days	Weathered Suncor coke, exposed to water at pH 10 for 45 days

[1] Coke was originally obtained from Syncrude coke piles 4 and 5, and the most current Suncor coke piles in May 2002.

3.2.3 Toxicity Tests

On the last day of the dissolved oxygen and freeze-thaw experiments, and on days 45 and 90 of the pH experiment, a toxicity test using the macroinvertebrate, *Chironomus tentans*, was conducted following the protocol outlined by Environment Canada (1997). These tests were 10-d experiments measuring the growth and survival of *C. tentans*. For each treatment, the combination of the coke + leachate and leachate independently were tested to allow for the effects of the leachate and the coke to be assessed separately.

Chironomus tentans were obtained from a laboratory culture maintained at the Toxicology Centre, University of Saskatchewan. Organisms were cultured in an environmental chamber at a photoperiod of 16:8 h light:dark and a temperature of 23 ± 1 °C. The culture was maintained using performance-based techniques according to culturing protocol outlined by Environment Canada (1997). Organisms were fed three times per week with a Tetramin® fish food slurry (Tetra Werke, Melle, Germany). The culture water was carbon-filtered, Saskatoon municipal water.

Test animals were obtained by aspirating fully emerged adults from the main colony into a 500-mL Erlenmeyer flask. The adults were then transferred to a glass breeding jar containing a piece of Parafilm® floating on a layer of culture of water and two strips of plastic netting, thus providing ample surface area for mating. Each morning, the breeding jar was checked for egg masses, which, if present, were transferred to 10-L glass aquaria (2-3 egg masses per aquaria) containing a thin layer of rinsed culture sand (particle size 250-425 μm) and aerated culture water. After the first 24 hours, animals were fed three times per week with 2.5 mL of a 6 mg/L Tetramin® fish food slurry. After 8-10 d, larvae (second instar) were transferred from these tanks to glass pans where they were separated from their cases using plastic pipettes before being added to test beakers.

All tests were carried out in 250-mL beakers containing 200 mL of leachate water and 50 mL of substrate. Substrates consisted of culture sand (particle size 250-425 μm) for the leachate only exposures and leached coke for the coke + leachate exposures. Ten *C. tentans* larvae (8-10 d old) were added to each test vessel at the start of the test and fed a minimum of 5 mg/L of Tetramin® slurry daily throughout the test period. Tests were conducted in an environmental chamber at the Toxicology Centre, University of Saskatchewan, at a photoperiod of 16:8 h light:dark and an ambient temperature of 23 ± 1 °C.

These were static tests with constant aeration of the overlying water. Dissolved oxygen (mg/L) and temperature (ºC) of the overlying water were checked on a daily basis in all test vessels. At the end of all tests, each beaker was assessed for changes in survival and growth (measured as dry weight after 48 h at 60ºC) of *C. tentans* larvae. Overlying water was sampled (10 mL) on days 5 and 10 and analyzed for ammonia to ensure that these levels were not so high as to cause toxicity, thereby confounding results. Separate samples of the overlying water (10 mL) were collected and analyzed for alkalinity, hardness, conductivity and pH at the end of the 10 d test to ensure that these variables were within the acceptable range for proper *C. tentans* survival and growth.

3.2.4 Data Analysis

Mass balance calculations were performed for metals identified to be of concern in the dissolved oxygen and pH leaching experiments. These calculations used the peak concentrations of the identified metals of concern in both overlying water and pore water, and compared them to their respective concentration in the untreated coke (i.e. coke that had not undergone any leaching). If the concentration in the corresponding leached coke was greater than the concentration in the untreated coke, the leached coke value was used. Peak values were utilized in these calculations in order to simulate the worst case scenario of using coke as a substrate in an aquatic reclamation strategy.

Statistical analyses were performed using the computer program SigmaStat®, version 2.03 (SPSS Inc., Chicago, IL, USA) at a 95% ($\alpha = 0.05$) level of confidence. A two-way ANOVA was conducted on ranked metals data from the DO, pH and freeze-thaw experiments since these data failed the test and transformations for homogeneity of variance. These tests identified statistical differences between the overlying water and pore water, and among the treatments within these waters for each experiment. If statistical differences were found, a Holm-Sidak multiple comparison test was run for all ANOVA tests.

For the toxicity data, a two-way ANOVA was conducted on *C. tentans* survival and growth (measured as dry weight after 48 h at 60ºC) to identify statistical differences among substrate types and treatments (DO, pH and freeze-thaw) within the leachate water alone and within the coke plus leachate water treatment. The test used for normality was Kolmogorov-Smirnov and the test for homogeneity of variance was the Levene median test. If the data failed the test and transformations for homogeneity of variance, the data were ranked, and a two-way ANOVA was run on the ranked data. If statistical differences were found, a Holm-Sidak multiple comparison test was run for all ANOVA tests.

3.3 Results

3.3.1 Chemical Endpoints

3.3.1.1 Water

Some trace elements reached concentrations in the overlying water and pore water during the leaching period that were toxicologically relevant. These concentrations either exceeded the Canadian Water Quality Guidelines for aquatic life (CCME, 2003), or exceeded published LC_{50} values for *Chironomus* species (Figure 3.1 and 3.2).

Some metal leaching observations were common among each experiment (i.e. DO, pH and freeze-thaw). First, metal concentrations generally increased in overlying waters, while decreasing in pore waters. Even though these rates of loss and accumulation were not similar, in most cases the amount of element lost from the pore water was close to the amount which accumulated in the overlying water. It was also observed that there was a rapid release of metals at the beginning (i.e. within the first few hours) of the experiments, slowing to a lesser rate of release during the remainder of the leaching period.

There were no detectable levels of any of the PAHs measured in any of the analyzed Syncrude coke leachate waters (Table 3.3). Some minute levels of phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene and benzo(b)fluoranthene were detected in the Suncor coke leachate waters.

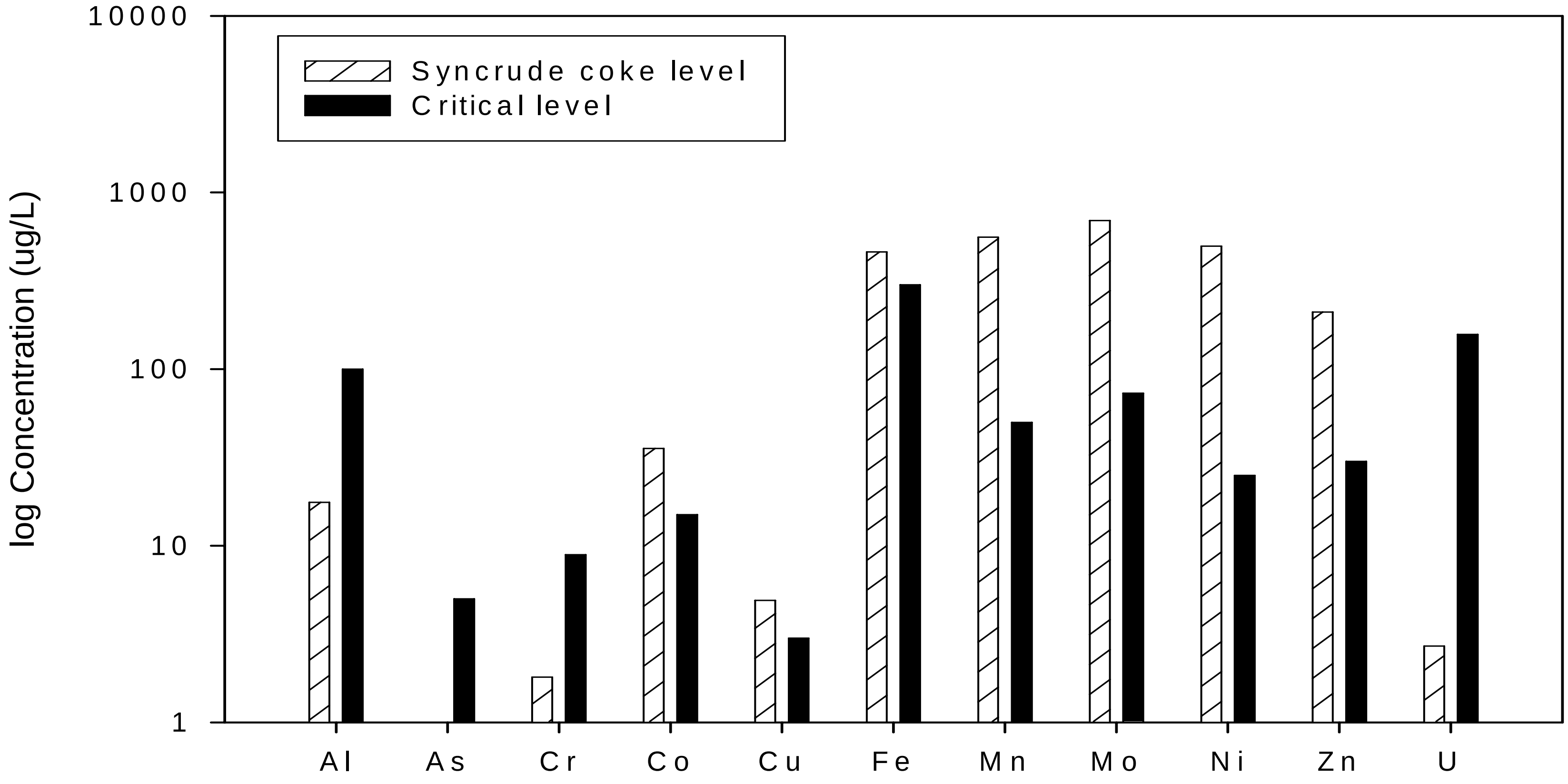

Figure 3.1: Metal concentrations from Syncrude (Syn) coke versus critical metal concentrations for selected metals analyzed during the dissolved oxygen, pH and freeze-thaw leaching experiments. Metals were not included if they were below the detection limit, or if no critical level could be identified (Ag, Li, Mg, P, Ca, Ti, Ga, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Hg, Tl, Th, V). All critical concentrations are from the Canadian Water Quality Guidelines (CCME, 2003), except for Co (Marr *et al*., 1998) and U (Muscatello, 2004).

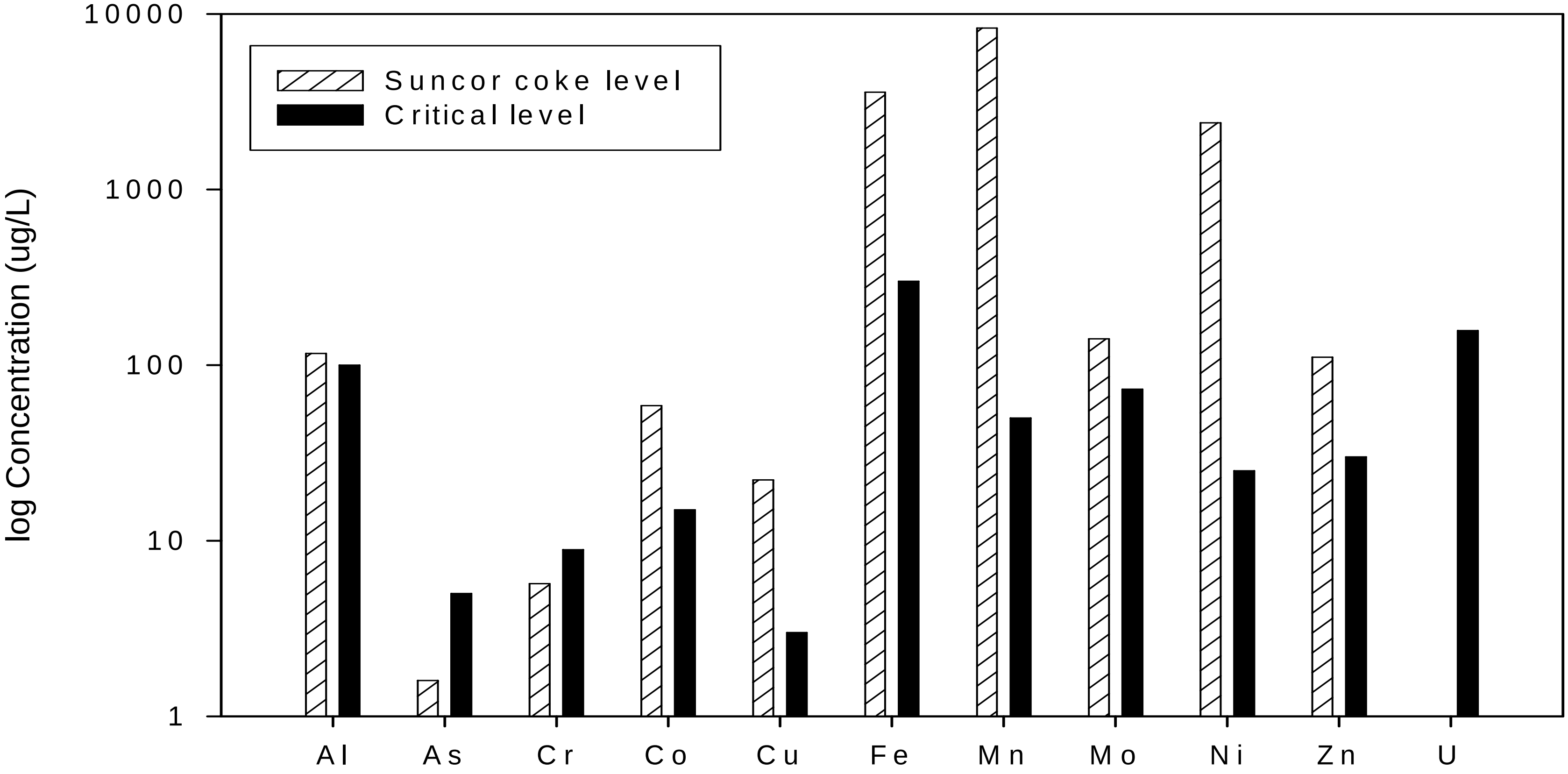

Figure 3.2: Metal concentrations from Suncor (Sun) coke versus critical metal concentrations for selected metals analyzed during the dissolved oxygen, pH and freeze-thaw leaching experiments. Metals were not included if they were below the detection limit, or if no critical level could be identified (Ag, Li, Mg, P, Ca, Ti, Ga, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Hg, Tl, Th, V). All critical concentrations are from the Canadian Water Quality Guidelines (CCME, 2003), except for Co (Marr *et al*., 1998) and U (Muscatello, 2004).

Table 3.3. Mean levels of polycyclic aromatic hydrocarbons (PAHs) in filtered overlying waters obtained during a dissolved oxygen leaching experiment using coke from Syncrude Canada Ltd. and Suncor Energy Inc. (μg/L).

PAH	Syncrude High DO	Syncrude Low DO[1]	Suncor High DO[1]	Suncor Low DO
Naphthalene	<0.01	<0.01	<0.01	<0.01
Methyl naphthalenes	<0.01	<0.01	<0.01	<0.01
Acenaphthylene	<0.01	<0.01	<0.01	<0.01
Acenaphthene	<0.01	<0.01	<0.01	<0.01
Fluorene	<0.01	<0.01	<0.01	<0.01
Phenanthrene	<0.01	<0.01	<0.01	0.06 ± 0.06
Anthracene	<0.01	<0.01	<0.01	0.01 ± 0.001
Fluoranthene	<0.01	<0.01	<0.01	0.05 ± 0.06
Pyrene	<0.01	<0.01	0.24	0.52 ± 0.02
Benzo(a)anthracene	<0.01	<0.01	<0.01	0.07 ± 0.06
Chrysene	<0.01	<0.01	0.05	0.07 ± 0.06
Benzo(b)fluoranthene	<0.01	<0.01	<0.01	0.01 ± 0.003
Benzo(k)fluoranthene	<0.01	<0.01	<0.01	<0.01
Benzo(a)pyrene	<0.01	<0.01	<0.01	<0.01
Indeno(1,2,3-cd)pyrene	<0.01	<0.01	<0.01	<0.01
Dibenzo(a,h)anthracene	<0.01	<0.01	<0.01	<0.01
Benzo(g,h,i)perylene	<0.01	<0.01	<0.01	<0.01

[1] These samples are not presented as means due to replicate samples being destroyed during transport to Enviro-Test Laboratories.

3.3.1.1.1 Dissolved Oxygen

The average level of dissolved oxygen in the overlying water in the dissolved oxygen experiment was 7.94 ± 0.04 mg/L for the high and 0.92 ± 0.08 mg/L for the low DO treatments. Overlying water in the low dissolved oxygen treatment tended to have slightly higher metal levels than overlying water in the high dissolved oxygen treatment, especially when Suncor coke was used as a substrate (Table 3.4). However, this difference between the high and low dissolved oxygen treatments was significant for less than 12% of the samples when evaluated over all time points for both Syncrude and Suncor coke combined (Figure 3.3 and 3.4).

Some of the metals identified to be of particular concern (i.e. present at levels that were toxicologically relevant) during this experiment were cobalt, copper, manganese, molybdenum, vanadium and zinc. Table 3.4 lists the peak overlying and pore water levels measured for these metals during the experiment. All metal values for the overlying and pore waters obtained during this experiment can be found in Appendix I. Figures 3.3 and 3.4 show the mean values of these metals for Syncrude and Suncor coke, respectively, over the course of the leaching experiment.

These figures show that metal levels in the pore water from Syncrude coke generally decreased over time (with the exception of Mn), while the overlying water metal levels generally increased, the most obvious case being vanadium (Figure 3.3). This often caused the metals to reach similar concentrations in the pore water and overlying water by day 30. This trend was not apparent for Suncor coke (Figure 3.4). Instead, metal concentrations here seemed to decrease in both the overlying water and pore water over the 30-d experiment, with the exception of V and Mo in overlying water, which showed an increase by day 30.

Table 3.4. Peak concentrations (µg/L) of several metals that reached levels of concern in the overlying water (leachate) and coke pore water during the dissolved oxygen leaching experiment: (a) Syncrude coke, (b) Suncor coke.

(a)

		Overlying Water		**Pore water**			
Element	**Detection Limit**	**High Oxygen**	**Low Oxygen**	**High Oxygen**	**Low Oxygen**	**CWQG [1] (µg/L)**	**LC$_{50}$ for *Chironomus* sp. (µg/L)**
Cobalt	0.2	0.3	0.2	0.5	0.4	--[2]	n/a
Copper	0.9	> 0.9	1.1	4.9	4.0	3	54[3]
Manganese	0.3	8.4	6.5	4.2	8.6	50	55[4]
Molybdenum	0.1	76.6	85.9	559.9	693.9	73	360[4]
Vanadium	0.1	607.5	757.0	1276.0	2360.5	--[2]	240[4]
Zinc	0.3	7.3	4.9	210.5	57.6	30	1125[3]

(b)

		Overlying Water		**Pore water**			
Element	**Detection Limit**	**High Oxygen**	**Low Oxygen**	**High Oxygen**	**Low Oxygen**	**CWQG [1] (µg/L)**	**LC$_{50}$ for *Chironomus* sp. (µg/L)**
Cobalt	0.2	3.6	3.8	14.2	33.9	--[2]	n/a
Copper	0.9	0.6	22.2	1.6	1.7	3	54[3]
Manganese	0.3	144.6	161.4	958.0	1555.6	50	55[4]
Molybdenum	0.1	36.8	27.1	88.5	97.1	73	360[4]
Vanadium	0.1	40.2	68.5	18.7	21.4	--[2]	240[4]
Zinc	0.3	4.8	19.9	13.4	23.7	30	1125[3]

[1] Canadian Water Quality Guidelines (CCME, 2003); [2] No Canadian Guideline available; [3] (Phipps *et al*., 1995); [4] (Fargašová, 1997)

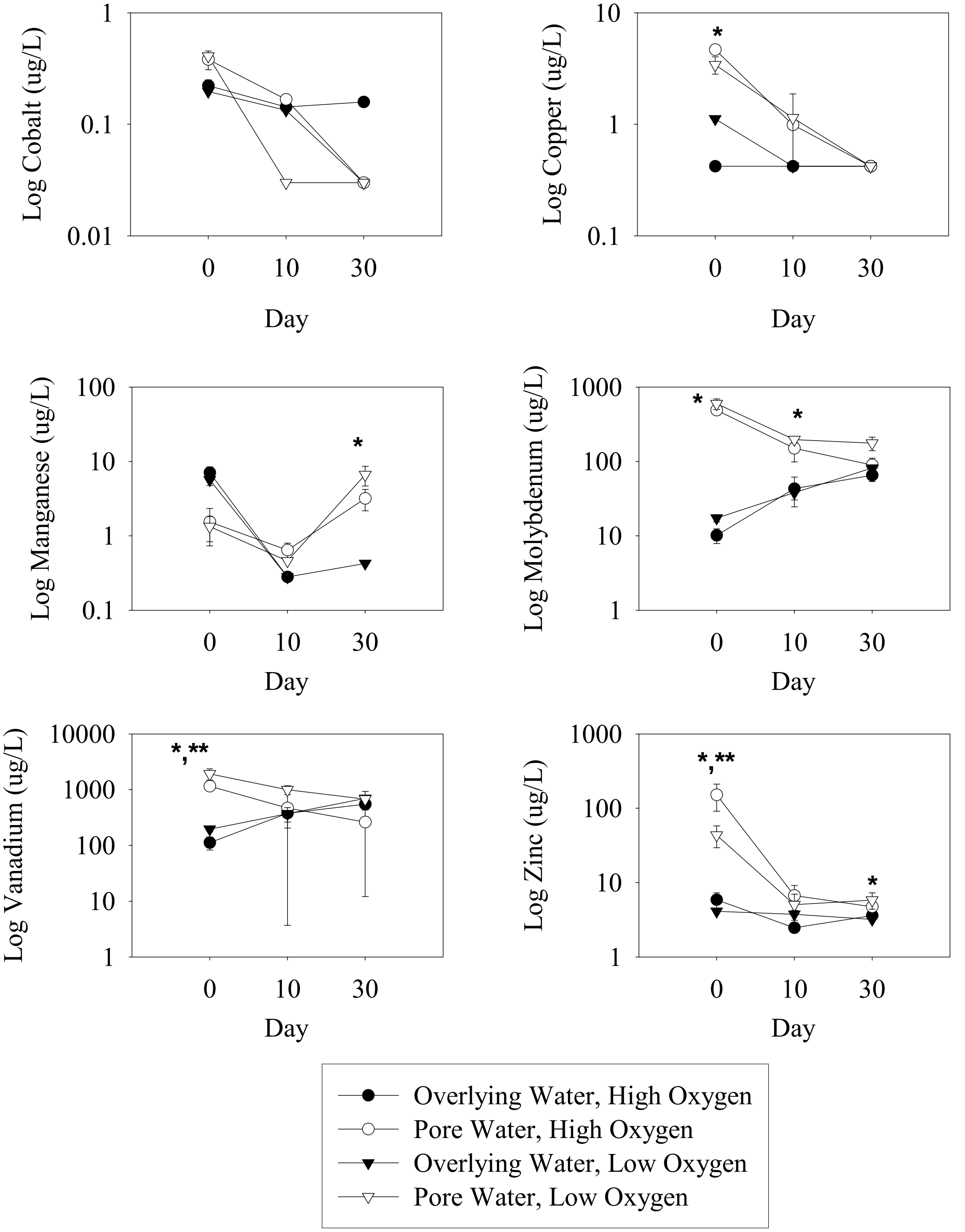

Figure 3.3. Log mean values ± standard error for selected metals of concern in overlying water and pore water for Syncrude coke during a 30-day dissolved oxygen leaching experiment. (* denotes significant differences between overlying water and pore water, ** denotes significant differences between high and low dissolved oxygen levels).

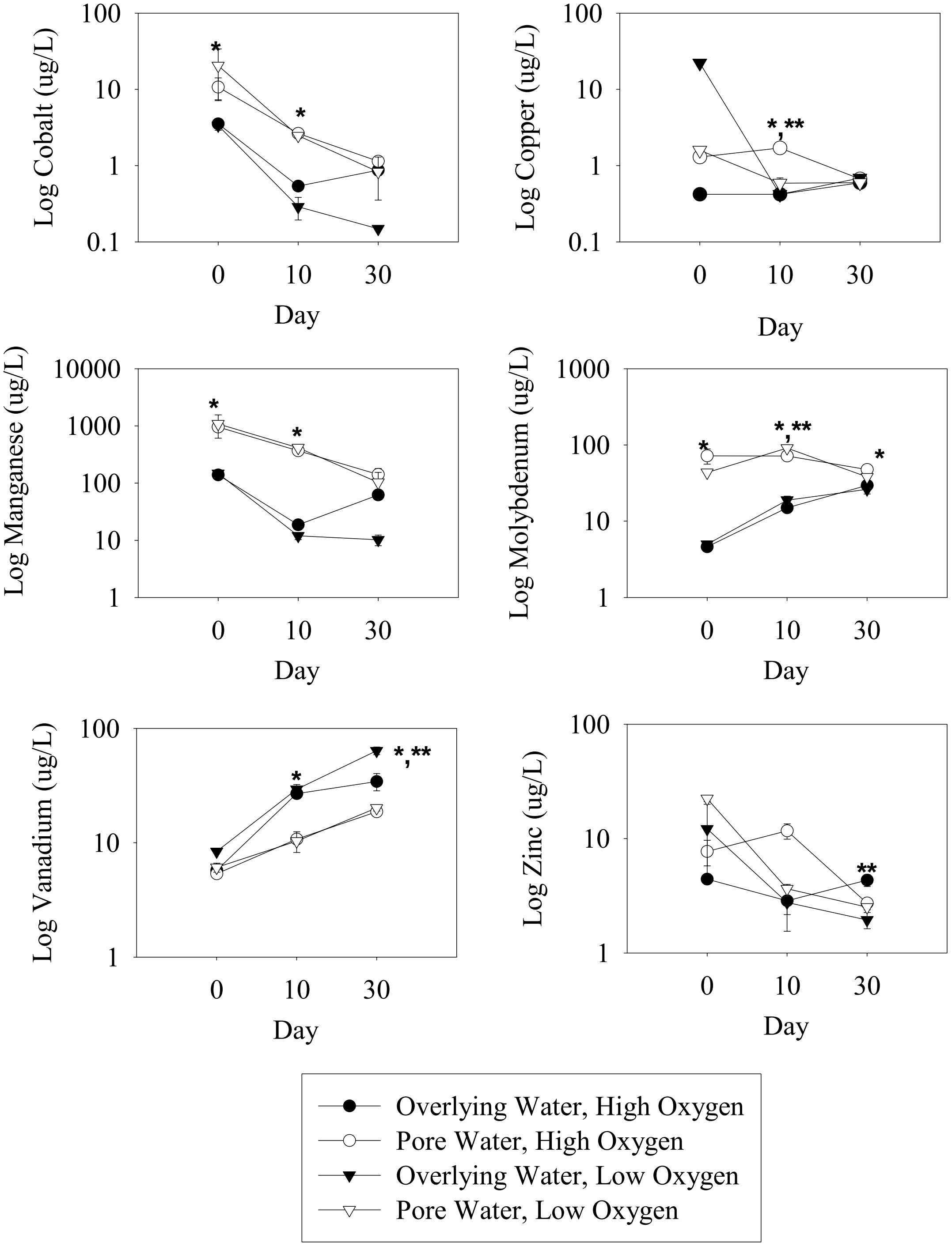

Figure 3.4. Log mean values ± standard error for selected metals of concern in overlying water and pore water for Suncor coke during a 30-day dissolved oxygen leaching experiment. (* denotes significant differences between overlying water and pore water, ** denotes significant differences between high and low dissolved oxygen levels).

3.3.1.1.2 pH

The pH level in the overlying water in the pH experiment were 4.88 ± 0.14 for the pH 5, 7.95 ± 0.15 for the pH 7.5, and 9.37 ± 0.12 for the pH 10 treatment. Metal leaching was observed at all pH levels; with the lowest pH treatment (pH 5) appearing to have the highest concentration of metals leaching into the overlying water and pore water when compared to the pH 7.5 and 10 treatments (Table 3.5). However, this difference among treatments was significant for only 19% of the time with Syncrude coke and 33% of the time with Suncor coke over the course of the 90-d experiment (Figures 3.5 and 3.6). The exceptions to this are molybdenum and vanadium, which leached at significantly higher concentrations in the pH 10 treatment.

The metals identified to be of particular concern during this experiment were cobalt, copper, manganese, molybdenum, nickel, vanadium and zinc. Table 3.5 lists the peak overlying and pore water levels measured for these metals during this experiment. All metal concentrations measured during this experiment can be found in Appendix II. Figures 3.5 and 3.6 show the mean values of these metals for Syncrude and Suncor coke, respectively, over the time of the leaching experiment.

Overlying waters generally had lower concentrations of metals than the pore waters for both Syncrude and Suncor coke. However, the metal levels in pore waters for Suncor coke generally decreased over time, while the overlying water metal levels tended to increase, thereby causing the metals to reach similar levels in the pore water and overlying water by day 90 (Figure 3.6). This trend was less often observed for Syncrude coke. Instead, the metal levels often increased and/or decreased at the same time and rate in both the overlying and pore waters (i.e. they mimicked each other) within the three treatments over the 90-d leaching experiment (Figure 3.5).

Table 3.5. Peak concentrations (µg/L) of several metals that reached levels of concern in the overlying water (leachate) and coke pore water during the pH leaching experiment: (a) Syncrude coke, (b) Suncor coke.

(a)

		Overlying Water			**Pore water**				
Element	**Detection Limit**	**pH 5**	**pH 7.5**	**pH 10**	**pH 5**	**pH 7.5**	**pH 10**	**CWQG [1] (µg/L)**	**LC_{50} for *Chironomus* sp. (µg/L)**
Cobalt	0.01	13.1	0.6	0.2	35.5	1.1	2.8	--[2]	n/a
Copper	0.1	2.5	2.4	1.6	1.9	1.7	2.5	3	54[3]
Manganese	0.4	281.2	9.0	1.0	559.0	14.0	63.0	50	55[4]
Molybdenum	0.1	33.6	35.7	79.1	72.1	151.6	169.5	73	360[4]
Nickel	1.1	258.5	19.2	7.3	497.9	37.5	55.8	25-150	250[4]
Vanadium	0.1	90.8	269.0	546.0	113.6	292.4	730.8	--[2]	240[4]
Zinc	0.3	65.7	19.3	5.6	65.9	4.8	8.5	30	1125[3]

(b)

		Overlying Water			**Pore water**				
Element	**Detection Limit**	**pH 5**	**pH 7.5**	**pH 10**	**pH 5**	**pH 7.5**	**pH 10**	**CWQG [1] (µg/L)**	**LC_{50} for C*hironomus* sp. (µg/L)**
Cobalt	0.01	22.6	3.6	2.0	121.3	103.7	634.0	--[2]	n/a
Copper	0.1	7.0	6.8	1.1	32.2	4.7	29.8	3	54[3]
Manganese	0.4	424.2	301.0	118.7	2343.0	3143.0	20150.0	50	55[4]
Molybdenum	0.1	2.5	46.8	57.7	15.3	47.6	344.7	73	360[4]
Nickel	1.1	176.0	26.4	24.0	1025.6	923.2	5867.8	25-150	250[4]
Vanadium	0.1	47.0	41.0	162.9	292.6	42.1	130.1	--[2]	240[4]
Zinc	0.3	53.0	6.8	5.7	154.3	69.1	263.1	30	1125[3]

[1] Canadian Water Quality Guidelines (CCME, 2003); [2] No Canadian Guideline available; [3] (Phipps *et al*., 1995); [4] (Fargašová, 1997)

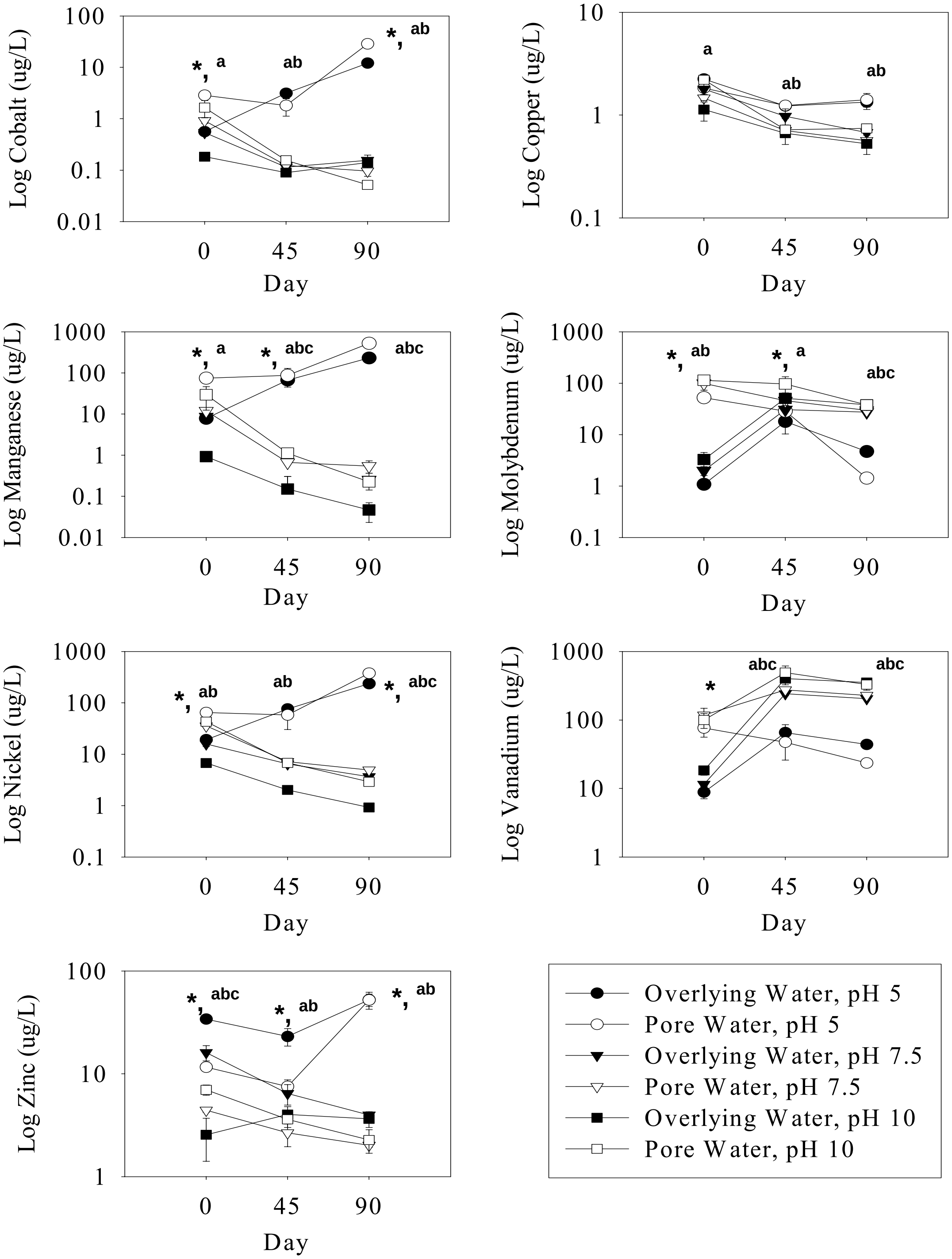

Figure 3.5. Log mean values ± standard error for selected metals of concern in overlying water and pore water for Syncrude coke during a 90-day pH leaching experiment. (* denotes significant differences between overlying water and pore water, [a] denotes significant differences between pH 5 and pH 10, [b] between pH 7.5 and pH 10 and [c] between pH 5 and pH 7.5 treatments).

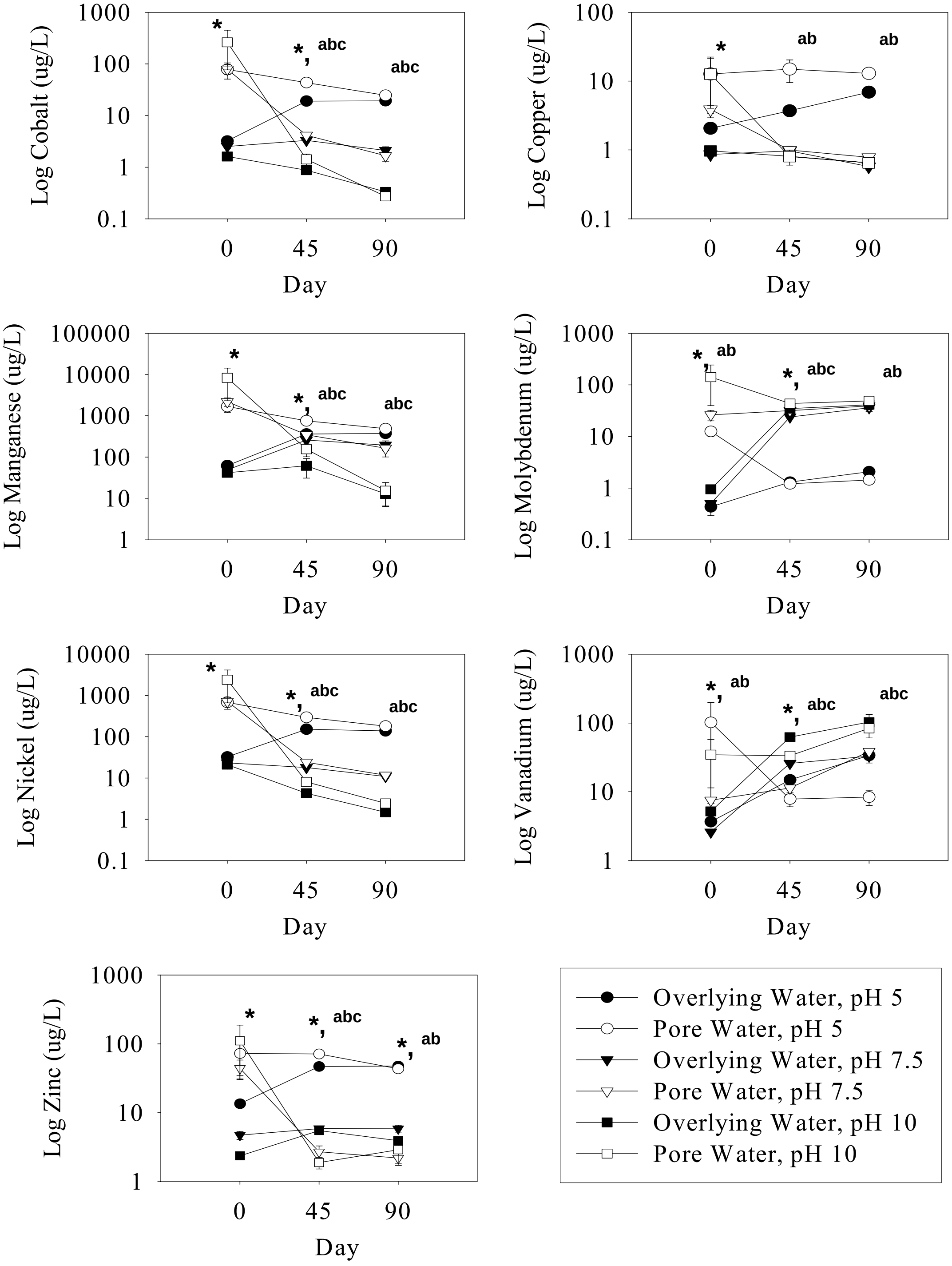

Figure 3.6. Log mean values ± standard error for selected metals of concern in overlying water and pore water for Suncor coke during a 90-day pH leaching experiment. (* denotes significant differences between overlying water and pore water, ^{a} denotes significant differences between pH 5 and pH 10, ^{b} between pH 7.5 and pH 10 and ^{c} between pH 5 and pH 7.5 treatments).

3.3.1.1.3 Freeze-thaw

Some of the metals that reached levels of concern in this experiment were cobalt, copper, manganese, molybdenum, nickel, vanadium and zinc. Table 3.6 lists the peak concentrations of these metals measured during the experiment in both the overlying water and pore water. All metal concentrations recorded during this experiment can be found in Appendix III. Figures 3.7 and 3.8 show the mean values of these metals for Syncrude and Suncor coke, respectively, over the course of the leaching experiment. Treatments which underwent the six freeze-thaw cycles showed significantly higher metal concentrations than those which underwent no freezing less than 25% of the time for both Syncrude and Suncor coke (Figures 3.7 and 3.8).

These figures show that overlying water in this experiment had, with few exceptions, much lower concentrations of metals than pore water for both Syncrude and Suncor coke. However, the metal levels in the pore water from Suncor coke mostly decreased over time, while increasing in the overlying water, thereby causing the metals to reach similar concentrations in the pore water and overlying waters by cycle 6. There was no clear general trend for Syncrude coke. Instead, some metal levels generally decreased in both the overlying water and pore water over the six freeze-thaw cycles (Co, Ni), while others followed the same trends as was seen in Suncor coke (Cu, Mo).

Table 3.6. Peak concentrations (µg/L) of several metals that reached levels of concern in the overlying water (leachate) and coke pore water during the freeze-thaw leaching experiment: (a) Syncrude coke, (b) Suncor coke.

(a)		**Overlying Water**		**Pore water**			
Element	**Detection Limit**	**Control**	**Frozen**	**Control**	**Frozen**	**CWQG** [1] **(µg/L)**	**LC_{50} for *Chironomus* sp. (µg/L)**
Cobalt	0.1	0.3	5.1	0.7	1.1	--[2]	n/a
Copper	0.03	1.1	0.9	2.7	2.7	3	54[3]
Manganese	0.1	3.1	5.9	13.4	10.2	50	55[4]
Molybdenum	0.2	70.6	42.7	144.9	225.1	73	360[4]
Nickel	0.2	9.1	8.3	16.9	11.2	25-150	250[4]
Vanadium	0.03	97.8	92.7	152.9	185.8	--[2]	240[4]
Zinc	5.2	5.3	5.1	10.1	9.3	30	1125[3]

(b)		**Overlying Water**		**Pore water**			
Element	**Detection Limit**	**Control**	**Frozen**	**Control**	**Frozen**	**CWQG** [1] **(µg/L)**	**LC_{50} for *Chironomus* sp. (µg/L)**
Cobalt	0.1	13.9	3.5	61.9	65.0	--[2]	n/a
Copper	0.03	1.6	1.1	4.5	13.8	3	54[3]
Manganese	0.1	497.4	174.3	2130.3	1823.7	50	55[4]
Molybdenum	0.2	24.03	23.34	44.98	64.8	73	360[4]
Nickel	0.2	63.5	16.2	308.6	331.8	25-150	250[4]
Vanadium	0.03	38.5	28.8	45.7	63.4	--[2]	240[4]
Zinc	5.2	8.1	4.4	15.3	23.1	30	1125[3]

[1] Canadian Water Quality Guidelines (CCME, 2003); [2] No Canadian Guideline available; [3] (Phipps *et al*., 1995); [4] (Fargašová, 1997)

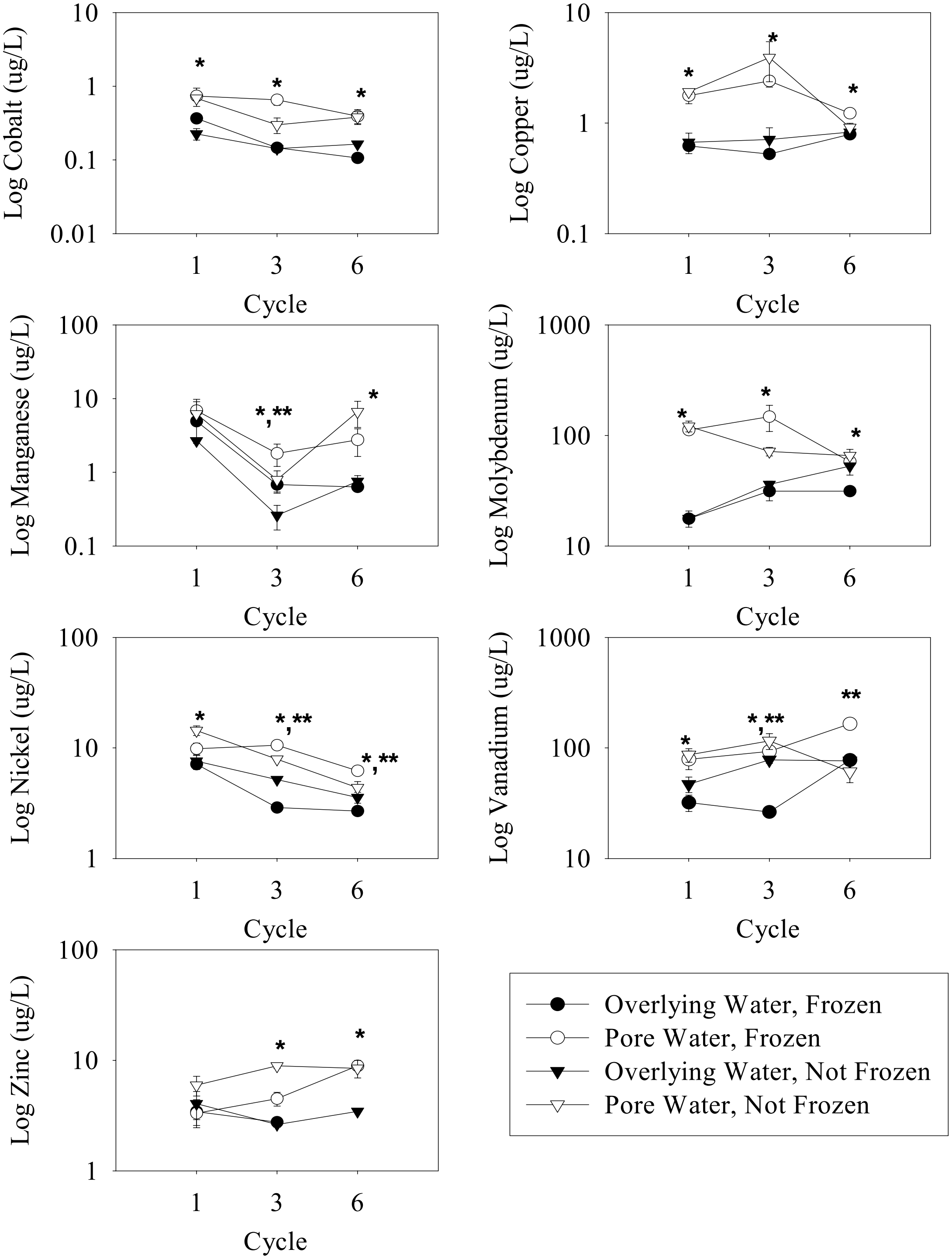

Figure 3.7. Log mean values ± standard error for selected metals of concern in overlying water and pore water for Syncrude coke during a six-cycle freeze-thaw leaching experiment. (* denotes significant differences between overlying water and pore water, ** denotes significant differences between frozen and not frozen treatments).

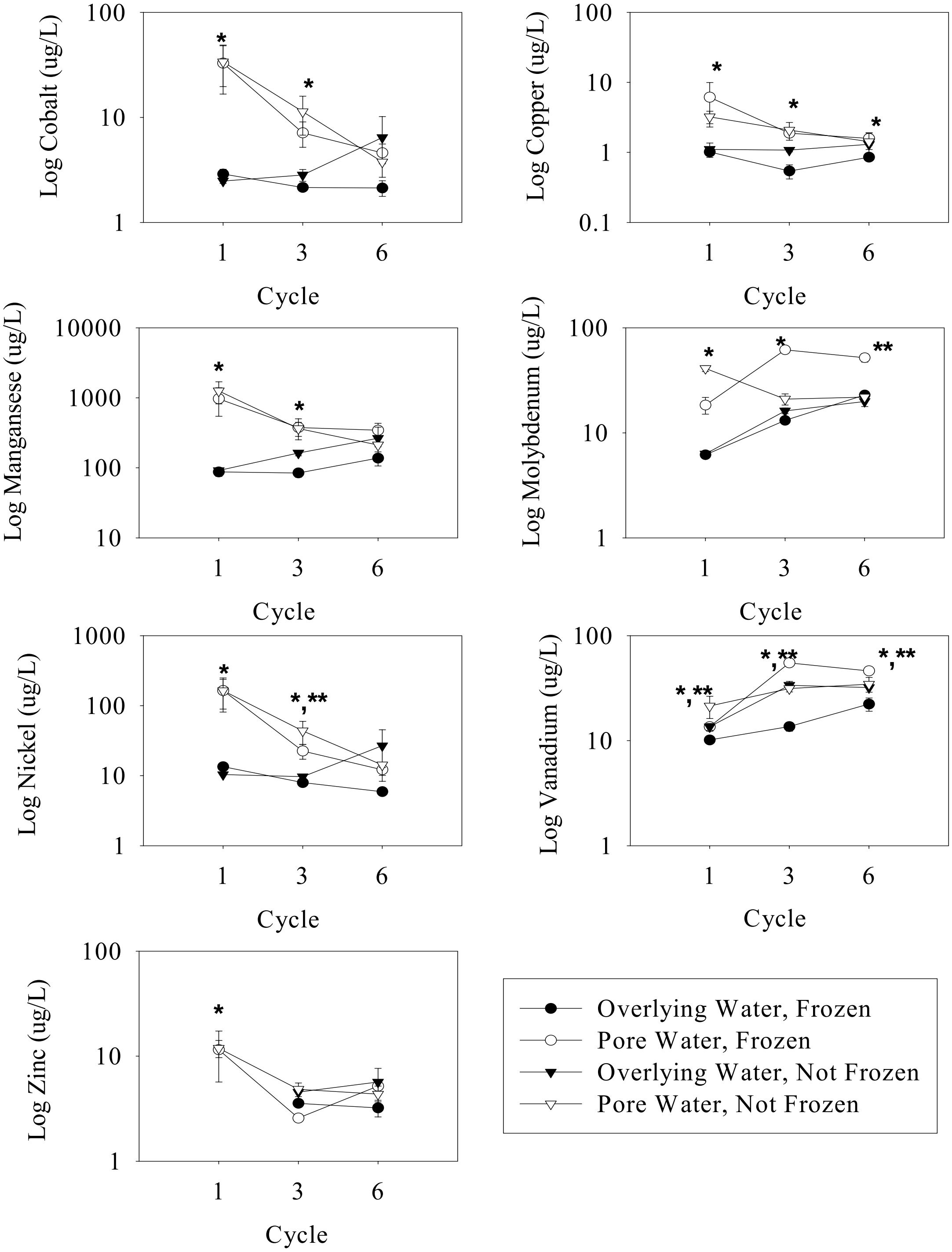

Figure 3.8. Log mean values ± standard error for selected metals of concern in overlying water and pore water for Suncor coke during a six-cycle freeze-thaw leaching experiment. (* denotes significant differences between overlying water and pore water, ** denotes significant differences between frozen and not frozen treatments).

3.3.1.2 Coke

Concentrations of metals of concern (as identified previously in the overlying water and pore water) in Syncrude and Suncor coke can be found in Table 3.7. The concentrations of these metals were similar between untreated coke and coke which had been weathered during the dissolved oxygen and pH leaching experiments.

Using the values for unweathered and weathered coke from Table 3.7, mass balance calculations were performed to assess the percentage of total metal in the coke that had leached into the overlying water and pore water. These percentages are listed in Table 3.8. Overall, these percentages are very small, with the majority being less than 1%. The largest percentage (33.05%) occurred with molybdenum in Syncrude coke weathered under pH 10 conditions.

Table 3.7. Peak concentrations of selected metals in untreated and weathered Syncrude (a) and Suncor (b) coke that also reached levels of concern in overlying water and pore water during the dissolved oxygen (low and high oxygen levels) and pH (5, 7.5 and 10) experiments (μg/g).

(a)

Element	**Untreated[1]**	**Low Oxygen**	**High Oxygen**	**pH 5**	**pH 7.5**	**pH 10**
Cobalt	8.3	7.5	9.0	9.1	11.2	8.7
Copper	1.4	0.8	1.0	1.1	0.7	0.9
Molybdenum	1.5	1.9	1.6	1.5	1.4	1.3
Nickel	376	462	438	438	462	446
Vanadium	1247	1297	1228	1256	1351	1280
Zinc	4	2	2	3	2	2

(b)

Element	**Untreated[1]**	**Low Oxygen**	**High Oxygen**	**pH 5**	**pH 7.5**	**pH 10**
Cobalt	7.1	8.4	7.3	6.9	7.3	7.8
Copper	3.3	2.9	2.6	2.9	2.9	2.5
Molybdenum	12.7	11.5	10.6	12.1	11.3	10.2
Nickel	315	283	291	270	297	299
Vanadium	830	863	864	812	798	890
Zinc	4	4	4	4	4	3

[1] Untreated coke is defined as coke that has not undergone any leaching.

Table 3.8. Percentages of selected metals in Syncrude (a) and Suncor (b) coke that leached into the overlying water and pore water during the dissolved oxygen (low and high oxygen levels) and pH (5, 7.5 and 10) experiments.

(a)

Element	**Low Oxygen**	**High Oxygen**	**pH 5**	**pH 7.5**	**pH 10**
Cobalt	0.01	0.02	0.79	0.03	0.02
Copper	0.42	0.00	0.95	0.90	0.63
Molybdenum	26.77	28.05	12.17	14.30	33.05
Nickel	0.00	0.00	0.32	0.02	0.01
Vanadium	0.32	0.26	0.04	0.11	0.23
Zinc	5.48	2.14	11.69	5.08	1.5

(b)

Element	**Low Oxygen**	**High Oxygen**	**pH 5**	**pH 7.5**	**pH 10**
Cobalt	0.25	0.25	1.70	0.35	0.75
Copper	3.31	0.09	1.12	1.03	0.23
Molybdenum	1.11	1.46	0.10	1.84	2.45
Nickel	0.00	0.00	0.30	0.06	0.18
Vanadium	0.04	0.02	0.03	0.02	0.09
Zinc	2.50	0.62	6.83	0.97	1.20

3.3.2 Biological Endpoints

3.3.2.1 Dissolved Oxygen

There was no significant difference in either survival or growth of *Chironomus tentans* larvae between the high and low dissolved oxygen treatments in the substrate + leachate water or the leachate water only tests (Figures 3.9a and b) for either coke type. There was a significant decrease ($p < 0.005$) in survival of *C. tentans* in the treatment containing leached Suncor coke with its overlying leachate water, compared to both the Syncrude coke and the leached control sand treatments with their respective overlying waters (Figure 3.9a). There were no significant differences in survival of *C. tentans* with Syncrude coke and its overlying water compared to the control sand treatment ($p = 0.914$). Suncor coke and its overlying leachate water resulted in a significant decrease ($p < 0.05$) in *C. tentans* growth when compared to both the Syncrude coke and control sand treatments (Figure 3.9b). In contrast, growth of *C. tentans* was significantly greater ($p < 0.05$) in the treatment containing Syncrude coke and its overlying leachate water than in both the leached control sand and the Suncor coke treatment (Figure 3.9b).

3.3.2.2 pH

There were no significant differences in C. *tentans* survival or growth for either Suncor or Syncrude coke among any of the pH treatments containing leachate water with new culture sand as a substrate from either days 45 or 90 of this leaching experiment (Figures 3.10 and 3.11).

In the toxicity test conducted using the substrates and leachate waters from Day 45 of the leaching experiment there were no significant differences in survival of *C. tentans*. There was a significant decrease ($p < 0.05$) in *C. tentans* growth in the treatment with Suncor coke as a substrate, and a significant increase ($p < 0.05$) in growth in the treatment with Syncrude coke as a substrate, when compared to the control (Figure 3.10b). Within the Suncor coke substrate treatment, there was a significant increase in growth in the pH 10 treatment, while within the Syncrude coke substrate treatment there was a significant decrease in growth in the pH 10 treatment when compared with the pH 5 and 7.5 treatments.

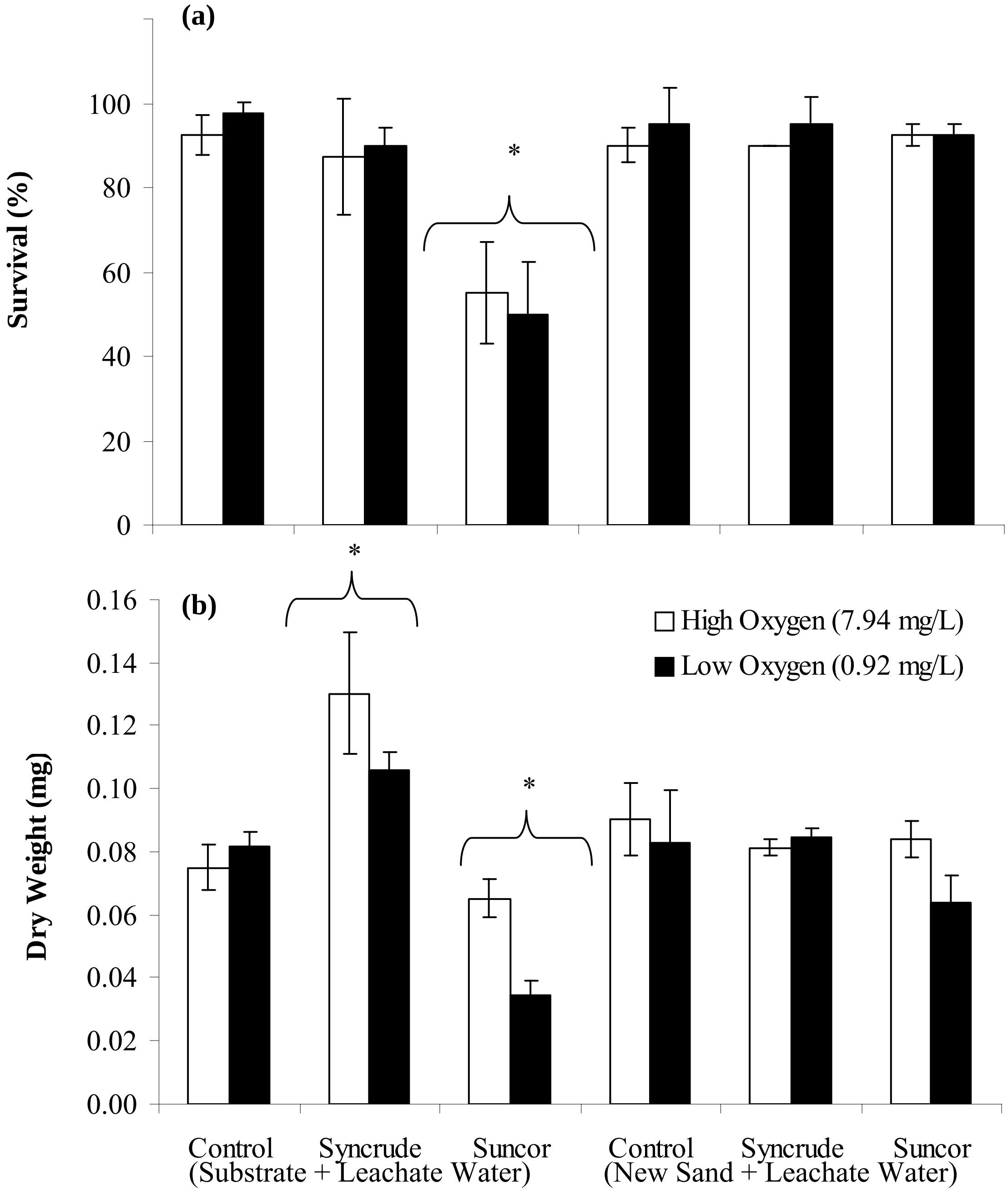

Figure 3.9. Survival (a) and growth (b) of *Chironomus tentans* (mean ± SE) larvae after a 10-day toxicity test with coke from Syncrude Canada Ltd. and Suncor Energy Inc. and their overlying leachate waters leached under high and low dissolved oxygen conditions for 30 days. (* denotes significant differences between each coke type and the control sand).

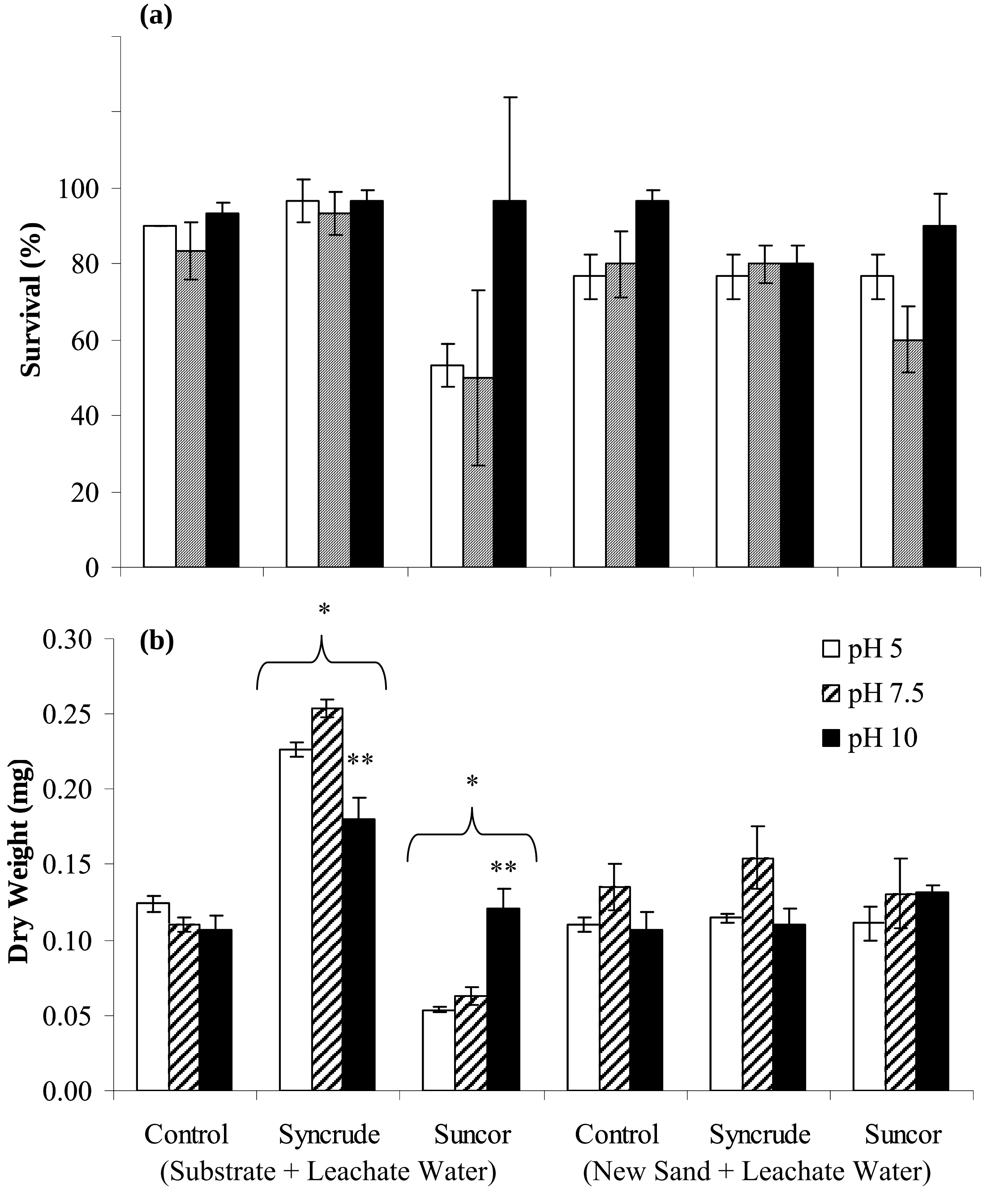

Figure 3.10. Survival (a) and growth (b) of *Chironomus tentans* larvae (mean ± SE) after a 10-day toxicity test with coke from Syncrude Canada Ltd. and Suncor Energy Inc. and their overlying leachate waters leached under pH 5, 7.5 and 10 for 45 days. (* denotes significant differences between each coke type and the control sand, ** denotes significant differences among pH within each substrate treatment).

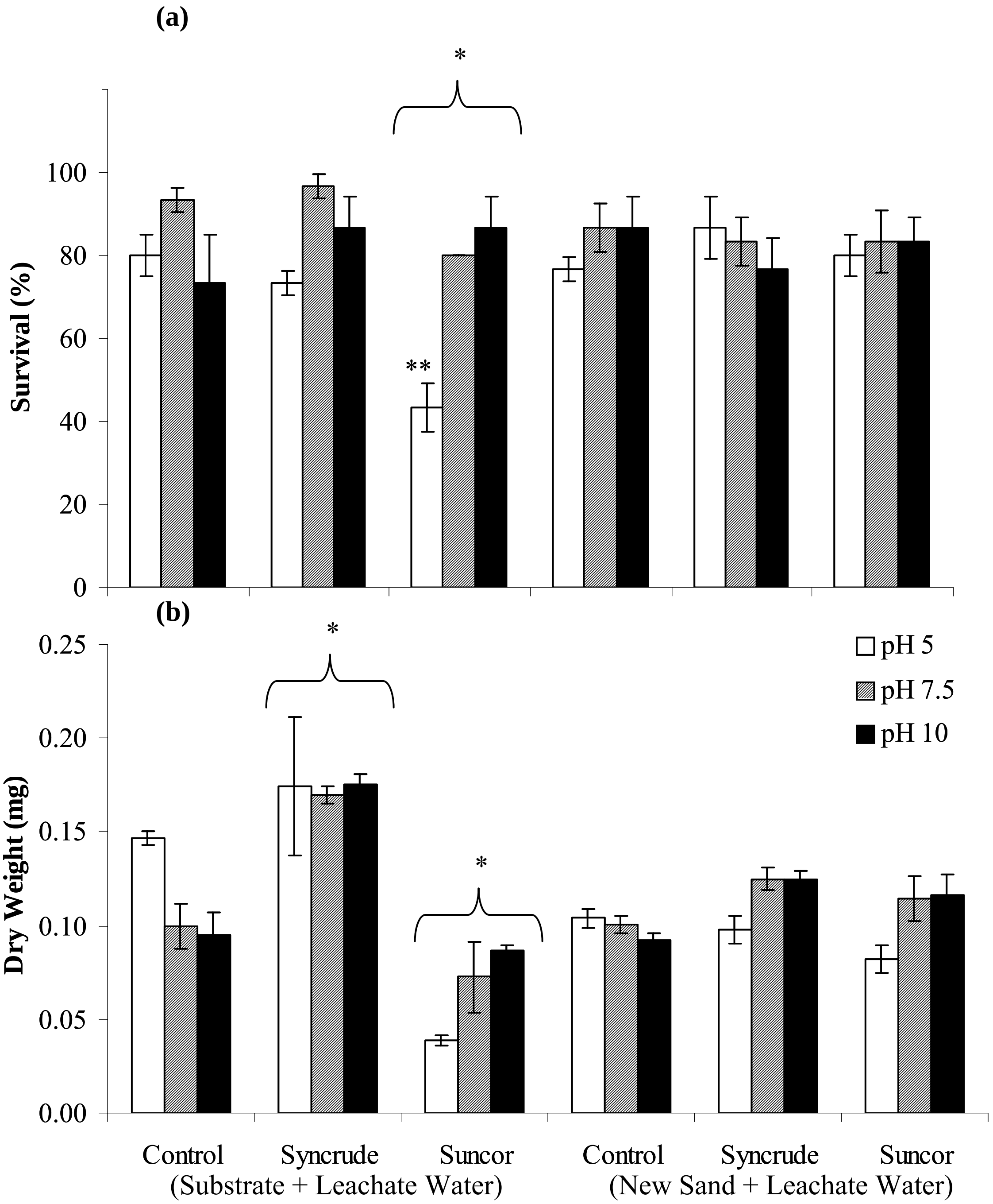

Figure 3.11. Survival (a) and growth (b) of *Chironomus tentans* larvae (mean ± SE) after a 10-day toxicity test with coke from Syncrude Canada Ltd. and Suncor Energy Inc. and their overlying leachate waters leached under pH 5, 7.5 and 10 for 90 days. (* denotes significant differences between each coke type and the control sand, ** denotes significant differences among pH within each substrate treatment).

There was a significant decrease ($p < 0.005$) in survival of *C. tentans* in the treatment with Suncor coke as a substrate compared to both the control sand and Syncrude coke in the toxicity test conducted using coke and overlying waters obtained from day 90 of the leaching experiment (Figure 3.11a). For Suncor coke, there was a significant decrease in *C. tentans* survival in the pH 5 treatment when compared with the pH 7.5 and 10 treatments. There were no significant differences in *C. tentans* survival with Syncrude coke as a substrate ($p = 0.568$). There was a significant decrease ($p < 0.05$) in *C. tentans* growth in the treatment with Suncor coke as a substrate and a significant increase ($p < 0.05$) in growth in the treatment with Syncrude coke as a substrate, when compared to the control (Figure 3.11b).

3.3.2.3 Freeze-thaw

There were no significant differences in survival or growth of *C. tentans* between the treatments which underwent six freeze-thaw cycles, and those that did not, for any of the substrate types. There were also no significant differences in survival or growth of *C. tentans* among any of the three treatments containing only leachate water with new culture sand (Figures 3.12a and b).

There were no significant differences in survival of *C. tentans* between frozen and unfrozen samples for both coke types compared to the control sand ($p = 1.00$) (Figure 3.12a). However, treatments with Suncor coke and its overlying leachate water caused a significant decrease ($p < 0.05$) in *C. tentans* growth when compared to the control sand treatment (Figure 3.12b). In contrast, growth of *C. tentans* larvae was significantly greater ($p < 0.05$) in the treatments containing Syncrude coke and its overlying leachate water when compared to the leached control sand (Figure 3.12b).

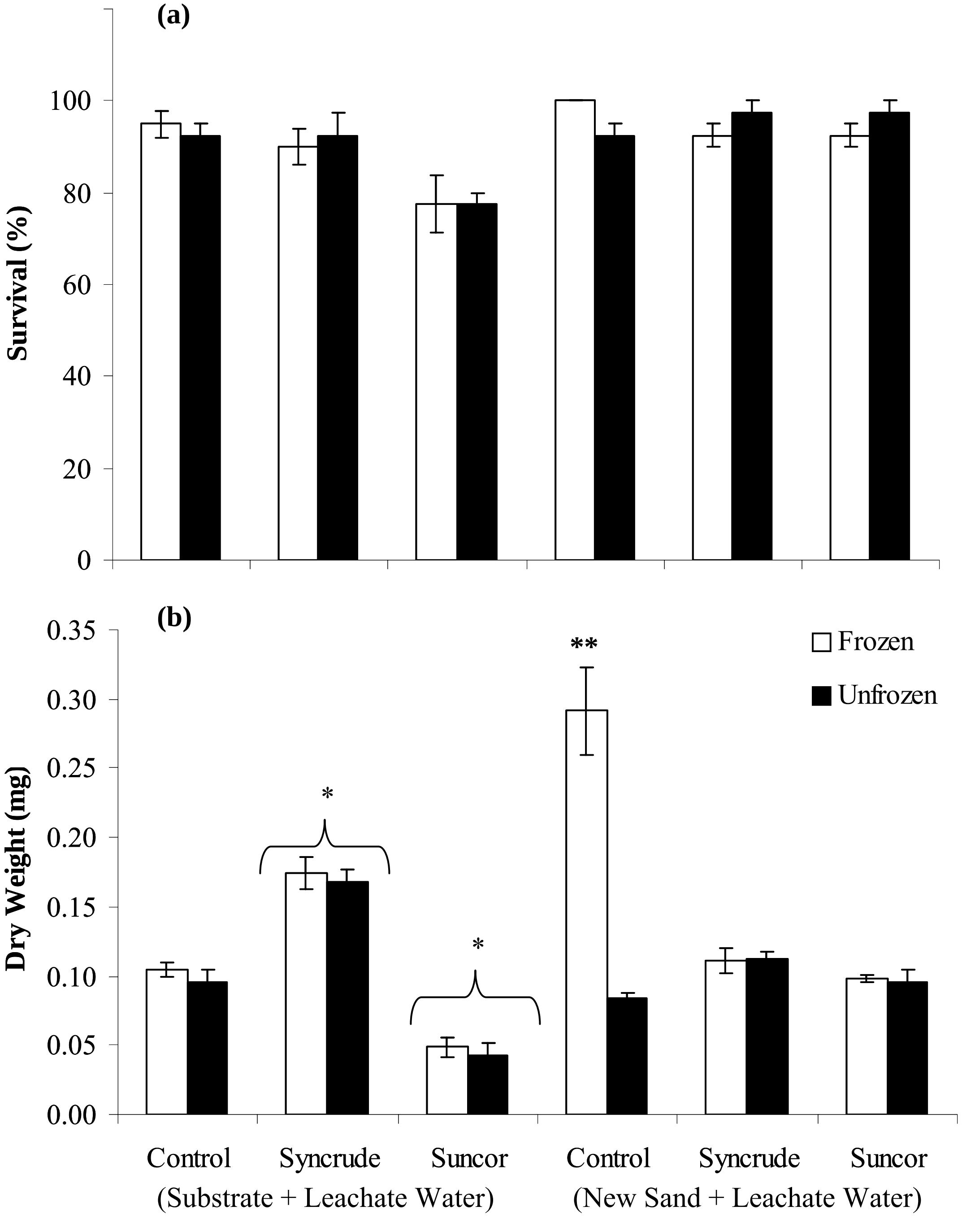

Figure 3.12. Survival (a) and growth (b) of *Chironomus tentans* (mean ± SE) after a 10-day toxicity test with coke from Syncrude Canada Ltd. and Suncor Energy Inc. and their overlying leachate waters leached for six consecutive freeze-thaw cycles. (* denotes significant differences between each coke type and the control sand, ** denotes significant differences between each treatment).

3.4 Discussion

3.4.1 Metal Chemistry

3.4.1.1 Water

Coke from the Syncrude Canada Ltd. operations generally released higher concentrations of metals than coke from the Suncor Energy Inc. operations during the three leaching experiments described here. One possible explanation for this is the difference in particle size between the two coke types. Syncrude coke has a much smaller particle size than Suncor coke. Therefore, there is more surface area available for leaching to take place than for the same volume of Suncor coke.

For each leaching experiment, there was a general trend of increasing metal concentrations in overlying water, and decreasing metal concentrations in pore water, over time. As a result of the static test system used, this reflected the tendency towards the establishment of equilibrium conditions between the two water phases. It is well known that as metals are released into pore waters, they can diffuse into the less concentrated overlying waters (Barna *et al.*, 2005). This allows for further metal leaching from the coke particles into the now less concentrated pore water.

It was also observed that a rapid release of metals generally occurred at the beginning (i.e. within the first few hours) of each experiment, slowing to a lesser rate of release during the remainder of the leaching period. This may reflect the way the metals are bound to the coke particles. A rapid release of metals at the beginning of the leaching period suggests that the metals are either loosely bound to the surface of the coke particles, or they are bound within the clay particles which can contaminate the coke after storage in the field. As soon as the coke comes in contact with water, these loosely bound metals are released, causing a spike in water metal concentrations, as seen in the leaching experiments described here.

Well-aerated soils are characterized by redox potentials of +400 mV or greater, whereas waterlogged stagnant soils have redox potentials as negative as -300 mV (Carbonell *et al.*, 1999). Some metals leached to reach higher mean concentrations in the treatment with low dissolved oxygen in the dissolved oxygen leaching experiment. In previously conducted research looking at the distribution of dissolved metals in contaminated sediments, Mn and Zn were shown to be released to the water column under oxygen reduced conditions (Sokolowski *et al.*, 2001; Charlatchka and Cambier, 2000). Soil oxidation conditions also influence soil pH, a major factor influencing metal chemistry. As oxidized soils are flooded and become anaerobic or reducing, the pH tends to converge toward 7 (neutrality), favoring metal immobilization (Gambrell, 1994).

Sulphuric acid as chosen to adjust pH in this study because it is commonly found in acid mine drainage, due to the oxidation of sulphides, and it is a main acid present in acid rain, due to the oxidation of SO_2 (Ribeiro *et al.*, 2000). Like hardness ions, H^+ ions compete with trace metals at binding sites. Therefore, at low pH more protons are available for binding and fewer metal ions will be bound to sites on cell surfaces. An increase in pH not only reduces the proton concentration, but also alters metal speciation distribution leading to a decrease in free metal ion concentration. This metal fraction is generally considered to be the most bioavailable form for most metals (Heijerick *et al.*, 2003).

Trace metal solubility as a function of pH is directly related to pH-controlled dissolution and desorption processes causing a shift to the free metal ion. These can involve initially present sediment phases and/or phases formed during subsequent drainage and oxidation of the sediment (Singh *et al.*, 2000). Previous studies have shown that the water solubility of metals increases sharply when the pH decreases from pH 6-7 to pH 1-5 (Dudka and Adriano, 1997). It has been suggested that the dissolution of $CaCO_3$ contributes the metal release from the sediments under these acidic conditions (Zhang *et al.*, 2002).

It has been reported that the best estimate of the potential leachability of Co, Mn, Ni and Zn can be found in acid-extractable fractions (pH 4) (Singh *et al.*, 2000). While decreasing media pH will dramatically increase the concentrations of some metals in leachates, it has not been shown to strongly affect Cu concentrations (Sukreeyapongse *et al.*, 2002; Singh *et al.*, 2000; Sawhney *et al.*, 1995). This is possibility due to the formation of soluble Cu complexes with dissolved organic matter (Sawhney *et al*., 1995). Copper, and to a lesser extent lead, are capable of forming complexes with organic matter and these complexes remain stable even below pH 3 (Singh *et al*., 2000).

In the pH leaching experiment, the majority of metals (except for V and Mo) leached to a greater extent under low pH conditions (i.e. pH 5). This correlates with previous findings where lower pH levels in overlying waters have been shown to increase leaching and therefore availability of trace metals in an aqueous environment (Chirenje and Ma, 1999; Horne and Dunson, 1995). A study conducted by Wickham *et al.* (1987) found that the soluble concentrations of Cu, Mn and Zn were all significantly higher in overlying water of an acidic pond when compared to the overlying water of a similar alkaline pond. It is possible that in an oil sands reclamation situation the overlying waters will have pH levels as low as 6 (Golder Associates Ltd., 2000). Therefore, the implications of releasing coke into waters with an acidic pH present a legitimate concern for possible reclamation programs at the Alberta oil sands.

Two of the exceptions to these observations are molybdenum and vanadium, which leached to higher concentrations at pH 10 instead of at pH 5. Influenced by pH, molybdenum, an essential trace element, will remain in solution at pH > 5, but forms complexes with Fe and Al at pH < 5, thereby promoting the bioavailable fraction in alkaline solutions (CCME, 2003). Solutions with moderate to weak acidity (pH 2-5) have also been shown to extract very little vanadium (Jack *et al*., 1979; Tyler, 1978). In a strong aqueous alkali solution, vanadium is in the form VO_4^{3-} (vanadium V), while in an acidic solution, it is in the form VO_2^+ (vanadium IV) (Greenwood and Earnshaw, 1997). Vanadium IV is a hard Lewis acid and has a strong tendency to coordinate with oxygen donor atoms. It is therefore capable of both forming strong complexes with soluble organic chelates and becoming specifically adsorbed to particles, thereby reducing its solubility and consequent availability in water at low pH levels (Wehrli and Strumm, 1989).

Frozen treatments were shown to leach a greater concentration of metals than not frozen treatments less than 25% of the time for both Syncrude and Suncor coke. It is known that contaminants in a large volume of dilute waste water can be concentrated into a smaller volume by freezing. When water freezes, ice crystals grow from pure water and impurities (or contaminants) are rejected from the ice structure and become concentrated in the remaining liquid phase which can be separated and subsequently treated or disposed of. (Gao *et al.*, 2004). Although no clear conclusion can be reached on the effects of freezing on the leachability of coke from this study, the possibility of overlying water and pore water containing toxicologically relevant metal concentrations is still pertinent.

3.4.1.2 Coke Elemental Chemistry

The concentrations of trace metals found in the coke itself did not appear to change substantially with any of the weathering treatments (i.e. DO, pH and freeze-thaw). Some of the minute changes which did occur could likely be attributed to natural variation in the coke which reflects the natural variations in the starting oil sand material. Mass balance calculations conducted on the overlying water and pore water from the dissolved oxygen and pH weathering experiments showed that only a very small amount (~1%) of the overall metal in the coke actually leached into the overlying water and pore water. These metal leaching percentages are too small to show up as changes in the coke itself. Therefore, the majority of the metals are either bound tightly within the coke matrix, or they are attached to the coke surface in such a way as to be unavailable using the weathering techniques and durations employed in these experiments.

3.4.2 Toxicity of Coke and its Leachates

There were no significant differences in survival and growth of *C. tentans* for any of the treatments containing only leachate water with new culture sand for any of the three leaching experiments. This shows that the leachate water itself was not toxic to *C. tentans*. Therefore, the amount of metals leaching into the overlying and pore waters in these experiments had no measurable detrimental effects on *C. tentans* over 10-d exposures.

Some effects on the survival and growth of *C. tentans* larvae were expected since the peak levels of copper, manganese, molybdenum, nickel, vanadium and zinc in the overlying water and/or pore water of the leaching experiments conducted in this chapter exceeded either published LC_{50} data for *Chironomus* sp., or the Canadian Water Quality Guidelines (CWQG) for the protection of aquatic life. However, the CWQGs are meant to protect all forms and stages of aquatic life, and are based on the most sensitive species at its most sensitive life stage (CCME, 2003). Organisms which are commonly used in the derivation of these guidelines are crustaceans, such as *Daphnia magna* and *Hyallea azteca*, and algae. Consequently, these guidelines are not necessarily representative of threshold values for *C. tentans*. In addition, these guidelines also employ a safety factor to account for differences among species and environments. For example, the guideline for molybdenum was derived by multiplying the lowest chronic toxicity value (for *Oncorhynchus mykiss*) by a safety factor of 0.1 (CCME, 2003).

There were several differences between the studies conducted to generate the referenced LC_{50} data, and the toxicity experiments described in this thesis, which may account for this discrepancy in toxicity. In the study conducted by Phipps *et al.* (1995), sample size was not constant since some of the replicates contained only five *C. tentans* for each exposure. The present study consistently used ten animals per replicate. Using fewer animals per replicate can decrease the reliability of test results since a lower statistical power is associated with a smaller sample size (Zar, 1999).

The study conducted by Fargašová (1997) used a different species (*C. plumosus*) which were acquired from the field. Although the author kept a constant length (2.5 cm) among the animals, there is no guarantee that each animal was the same age, as was possible in the present study where the animals are raised directly from hatch. The experiments conducted by Fargašová (1997) were also 96 h exposures, and the solutions were not aerated or fed throughout the test. These factors should also be considered when comparing this study to the present one where the exposures were 10 d in length, with constant aeration and feeding once per day as per the Environment Canada (1997) protocol. It is possibly that the toxicity observed in the Fargašová (1997) study was compounded with effects of decreased food availability and dissolved oxygen (not measured).

Differences in toxicity to *C. tentans* between the studies conducted by Fargašová (1997), Phipps *et al.,* (1995), and the present one may also reflect differences in the bioavailability of the metals in the test waters. The leachate waters in the present study were adjusted to mimic the higher hardness and alkalinity of the surface water found in the oil sands area, before being added to the coke leaching jars (hardness 204.0 ± 3.4 mg/L $CaCO_3$, and alkalinity 194.7± 10.1 mg/L $CaCO_3$). Increased hardness and alkalinity can reduce the bioavailability, uptake and toxicity of metals to *C. tentans* through two mechanisms: (a) competitive inhibition between calcium, magnesium and other metals at the metal binding and transport sites on cell surfaces, and/or (b) complexation of metals with carbonate, resulting in a decrease of the free hydrated metal ion activity (Barata *et al*., 1998). These mechanisms may increase the potential for coke to be used as an aquatic reclamation amendment at the oil sands operations, since the presence of naturally higher hardness in this area may help reduce the bioavailability and consequent potential toxicity of some metals to aquatic organisms.

A study conducted assessing the LC_{50} values for *H. azteca* in both soft and hard water for a variety of metals found that cobalt, copper and nickel were four, three and two times less toxic, respectively, in hard water (Borgmann *et al*., 2005). Vanadium and zinc have also been previously shown to be less lethal in harder water (Holdway and Sprague, 1979; De Schamphelaere and Janssen, 2004b; Heigerick *et al*., 2003). Since the potential toxicity of the metals identified to be of concern in this study can be affected by water hardness, this factor should be taken into consideration when assessing the potential for coke to act as a substrate amendment in an aquatic reclamation strategy in areas with naturally occurring higher hardness, such as the oil sands.

No significant differences in survival and growth of *C. tentans* were found among treatments for any of the substrate types (control sand, Syncrude coke and Suncor coke) in either the dissolved oxygen or freeze-thaw experiment. However, there were some significant decreases in survival and growth among treatments in the pH leaching experiment. Using leachate water and substrates from Day 45 of the pH leaching experiment, there was a significant decrease in *C. tentans* growth in the Syncrude coke substrate treatment. *Chironomus* larvae have been documented to accumulate more metals and other elements when the acidity of the water is higher (de Bisthoven *et al*., 2004). Changes in pH have also been shown to influence the metabolism of daphnids, as well as affecting both the speciation of the metals in an aqueous medium and their solubility (Seco *et al*., 2003). Therefore, out of the three weathering treatments tested here (dissolved oxygen, pH and freeze-thaw), pH seemed to have the greatest potential to influence the toxicity of coke in an aquatic reclamation program.

Significant decreases in *C. tentans* survival and growth were found in treatments containing leached Suncor coke with its corresponding overlying water in all of the three leaching experiments. It is unlikely that this result is due to the release of metals or other potential toxicants into the overlying and pore waters since corresponding effects were not seen in treatments with Syncrude coke as a substrate, or in corresponding leachate only treatments. Instead, this result may be due to differences in the physical properties of Syncrude and Suncor cokes.

Macroinvertebrates such as *C. tentans* need to build tubes/burrows in or on the sediment/substrate in order to successfully feed, breathe and protect themselves from predation (Pinder, 1995; Hare *et al*., 2001). They do this by pumping water through their burrows, thus increasing the levels of dissolved oxygen and moving edible particulate matter. In treatments containing Suncor coke as the substrate, *C. tentans* may have had difficultly building their tubes due to the larger particle size of Suncor coke. Therefore, the general stress created by a deficiency in oxygen and/or food due to their inability to construct proper tubes may have caused a significant decrease in both survival and growth of *C. tentans* in the Suncor treatments.

3.5 Conclusions

There were few differences in the leaching capabilities of coke under different water quality conditions (dissolved oxygen, pH and freeze-thaw cycles). However, the treatment which showed the greatest influence on metal leaching from coke was pH. In the pH leaching experiment, the majority of metals considered here leached to a greater extent at low pH levels. This, in turn, may increase the availability of trace metals once coke is placed in an acidic, aqueous environment. It is recommended that this variable be monitored in future studies to better assess its potential impact on the leachability of coke in an aquatic reclamation wetland.

The observed leaching rates for some elements from the pore water to the overlying water showed that Syncrude and Suncor cokes have the potential to present a certain degree of toxicological hazard to the environment they come in contact with. However, it is unknown at this point whether the metals leaching into the pore and overlying waters are coming from inside the coke matrix, from the coke surface, or even from debris that contaminate the coke as a result of storage in the field (e.g. clay or detrital particles). Further leaching studies should focus on determining the origin of the metals leaching from the coke in order to better assess the potential leaching hazard of coke as a sediment amendment in an aquatic reclamation project.

The results from the leaching experiments described here showed that Syncrude coke has the potential to pose a toxicological hazard through the leaching of toxic constituents once placed in an aquatic environment. However, despite this greater potential for toxicity, no significant toxic effects were seen in any of the bioassay tests. Instead, a significant positive effect on growth was seen in the treatments containing Syncrude coke as a substrate. Therefore, either the compounds released into the leachate waters from Syncrude coke are not in a biologically active form, or the test animals used in these experiments were able to tolerate the observed exposure concentrations.

In these experiments, Suncor coke had a significant negative effect on *C. tentans* survival and growth. However, since these reductions were not seen in treatments containing leachate without the presence of Suncor coke as a substrate, it can be concluded that these effects were due to the presence and physical properties of the coke itself, rather than any toxic constituents leaching from the coke into the overlying water. Since Suncor coke has a much larger particle size than Syncrude coke, it is possible that this inhibited the growth and survival of *C. tentans* during the bioassays. Therefore, it is necessary to conduct experiments which will address this difference in coke particle size in order to draw a conclusion on the potential risk of using Suncor coke in an aquatic reclamation strategy.

Differences in species behaviour, lifestyle, and physiology can contribute to different sensitivities to contaminants among species (Milani *et al.*, 2003). *Hyallea azteca* has been found to be more sensitive to metals than *C. tentans* in water-only exposures (Phipps *et al.*, 1995). Organism physiology plays an important role in their sensitivities to metals. Chironomid larvae have been shown to regulate the accumulation of copper, nickel and zinc in their tissues through the utilization of metal-binding proteins such as metallothioneins (Suedel *et al.*, 1996). Therefore, knowledge of the sensitivities of different species is imperative when evaluating the possible sources(s) and potential for sediment toxicity (Milani *et al.*, 2003).

The discrepancies between conclusions drawn from the chemical data (i.e. metal leaching) and the biological data (i.e. growth and survival of *C. tentans*) limit our ability to draw definite conclusions about the risk of using oil sands coke as a substrate amendment in an aquatic reclamation strategy. Therefore, it is recommended that a test species, such as a crustacean, which has been shown to be more sensitive to metals than *C. tentans*, be used to better asses the impacts of placing coke in an aquatic environment. To further increase the significance of this test, a more sensitive endpoint (i.e. reproduction) should be evaluated rather than growth and survival as was used in the present study.

It is also recommended that longer term weathering/leaching studies be conducted simulating the greater amount of waste material that would be used in the construction of an aquatic reclamation wetland. The increased volume of waste material could change the dynamics of the leachability of coke and long-term leaching studies will provide a clearer picture on the chronic leaching rates of metals found in Syncrude and Suncor coke into overlying water and pore water

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4. USE OF MICROSCOPY TECHNIQUES TO EVALUATE PHYSICAL DIFFERENCES IN WEATHERED VERSUS NON-WEATHERED COKE

4.1 Introduction

Oil sands, also known as tar sands or bituminous sands, are sand deposits impregnated with dense, viscous petroleum called bitumen. The two major companies currently mining oil sands in Northern Alberta, Canada, are Suncor Energy Inc. and Syncrude Canada Ltd. A major waste product produced during the process of upgrading bitumen to crude oil is coke. Over 2,000 tonnes of coke are produced per day per oil sands operation (Chung *et al*., 1996).

Suncor Inc. uses a delayed coking process, which is a 'batch by batch' procedure with each coker unit containing a heater and a pair of drums. Bitumen is introduced into the drums and is progressively heated, cracking the molecules into vapors and solid coke. The coke is deposited in the drum with the lighter molecules, produced in the form of vapor, condensing to be separated and processed in fractionation facilities. Syncrude Canada Ltd. uses an unconventional continuous fluid coking system, which involves the use of both a reactor and burner. Preheated bitumen is sprayed onto a preheated hot coke bed in the reactor, which causes the heavy molecules to crack, producing light molecules and more fluid coke. As at Suncor, the vapors are fractionated and separated by distillation for consumption.

The structure of petroleum coke is a direct result of how it is formed and how it behaves during the coking process, and is fundamental to the understanding of its fate and behaviour when it is released into the environment for storage and/or reclamation purposes. Coke by nature contains a high amount of organic carbon. The additional input of organic carbon is useful for the timely development of sustainable wetlands on old oil sands leases where organic matter is not very abundant. The abundance of coke, and its high percentage of organic carbon, makes it an attractive option for use as a substrate amendment in aquatic reclamation processes at the Alberta oil sands.

Coke is essentially a heterogeneous substance for which the chemical structure has not yet been clearly established. Its structure is also largely dependent on the starting material (i.e. bitumen) (Scott and Fedorak, 2004). Therefore, due to the natural variations present in unprocessed, mined oil sands, the structure of coke is not identical between batches and over time.

As an unwanted by-product, coke contains many different potentially toxic constituents. The concentrations and types of these constituents depend on what is present in the starting material, bitumen. They typically include many heavy metals which tend to be concentrated in the coke waste product during the coking process (Scott and Fedorak, 2004). Currently, coke is stored in large cells dug during the initial mining process, or stored on site in large piles. These practices cause the coke to become "contaminated" with particles (such as clay and silica) from the surrounding environment during storage. These particles have the potential to influence the weathering of coke or the release of toxic constituents in an aquatic reclamation strategy.

Presently, it is poorly known how the environmental weathering of coke changes its physical structure. The primary objective of the work described here was to determine if the physical structure and/or surface appearance of both Syncrude and Suncor coke change over time when weathered (for 30 to 90 d) under an overlying layer of water. If changes were observed, the secondary objective was to consider whether these changes could have the potential to affect the toxicity of coke and coke leachates when placed in a long-term aquatic reclamation strategy.

4.1.1 What is Polarized Light Microscopy?

Polarized light microscopy can be used to analyze both the texture and morphology of any layered structure at the micron range. From this, information on the thermal history and mechanism of formation of a coke sample can be obtained (Skoog *et al.*, 1998). In this technique, a beam of unpolarized light moving in the x direction has an electric field associated with it that comprises the entire y-z plane. Through cross polarization, a light source can be generated that gives rise to an electric field in only one dimension. When a coke sample is irradiated with polarized light, some of the incident beam will be reflected (Syncrude Canada Ltd., 2003). The amount of light reflected is related to the order or configuration of the molecules in the solid sample. Since polarized light is used, areas of the coke that have a different ordered microstructure would rotate (or refract) the light to a different degree. The amount of light reflected off the sample is related to the order of the molecules within the solid sample. Therefore, regions of different order can be differentiated based on apparent brightness. When the sample is rotated perpendicular to the light beam, the brightness of an ordered region will change, while a region with no order will remain dark (Syncrude Canada Ltd., 2003). A full wave retardation plate (λ) was used in the following experiments, which accounts for the pink color associated with the photographs taken using this method.

4.1.2 What is Scanning Electron Microscopy?

The classical method used to obtain detailed knowledge of the physical nature of the surfaces of solids is optical microscopy, such as the polarized light microscope technique described above (Skoog *et al*., 1998). However, the resolution of optical microscopy is very limited due to diffraction effects from the beam of light. Surface information at considerably higher resolution can be obtained through scanning electron microscopy (SEM). Therefore, SEM provides both morphologic and topographic information about the surfaces of solids that is necessary to understand the behavior of substances (Skoog *et al*., 1998). Scanning electron microscopy produces an image by bombarding the sample with a beam of electrons in a raster pattern (such as that used in a conventional television set) (Syncrude Canada Ltd., 2003). Since this technique gives no information on the crystal ordering of a sample, it provides a complementary technique to polarized light optical microscopy. By using this technique where the resolution is on the order of 0.05 microns, information on the sub-micron structure of a sample can be obtained.

4.2 Materials and Methods

4.2.1 Sample Selection

The samples analyzed under both polarized light and scanning electron microscopy were selected from previously conducted dissolved oxygen and pH weathering experiments (see Chapter 3). Samples were chosen to represent different amounts and types of weathering, in order to generate a structural comparison between unweathered and weathered coke types. The types of samples chosen for these analyses are described in Table 4.1.

Prior to analysis, the coke pore water was removed by vacuum filtration and each sample was dried in an air oven at 60 ºC overnight to ensure that no water remained, which would cause interference with the sample preparation for the polarized light microscope method. Each sample underwent further preparation at the Syncrude Canada Ltd. Research Centre located in Edmonton, AB, Canada, before analysis using polarized light and scanning electron microscopy techniques.

Table 4.1. Origin of chosen Syncrude Canada Ltd. and Suncor Energy Inc. coke samples analyzed under polarized light and scanning electron microscopy techniques.

Syncrude Canada Ltd. Coke	**Suncor Energy Inc. Coke**
Unweathered Syncrude coke, from the coke piles (starting material)	Unweathered Suncor coke, from the coke piles (starting material)
Weathered Syncrude coke, exposed to water with a low dissolved oxygen level (~ 1 mg/L) for 30 days	Weathered Suncor coke, exposed to water with a low dissolved oxygen level (~ 1 mg/L) for 30 days
Weathered Syncrude coke, exposed to water with a high dissolved oxygen level (~ 8 mg/L) for 30 days	Weathered Suncor coke, exposed to water with a high dissolved oxygen level (~ 8 mg/L) for 30 days
Weathered Syncrude coke, exposed to water at pH 5 for 45 days	Weathered Suncor coke, exposed to water at pH 5 for 45 days
Weathered Syncrude coke, exposed to water at pH 7.5 for 45 days	Weathered Suncor coke, exposed to water at pH 7.5 for 45 days
Weathered Syncrude coke, exposed to water at pH 10 for 45 days	Weathered Suncor coke, exposed to water at pH 10 for 45 days

4.2.2 Polarized Light Microscopy Analysis

4.2.2.1 Procedure for the preparation of coke samples in epoxy

The apparatus used for imbedding the coke samples in epoxy is shown in Figure 4.1a. It consisted of an Edwards #2 two-stage vacuum pump (BOC Edwards, Wilmington, MA, USA) with a filtering flask and a Buehler vacuum impregnation unit (Buehler Canada, Markham, ON). Buehler Sampl-kups (3.18 cm ID) (Buehler Canada), reusable plastic cold mounting cups (Buehler Canada), were used to hold the coke in epoxy during the vacuum process. Crown-ready release silicone (Buehler Canada) was used to release the epoxy samples from the sample cups after the epoxy set.

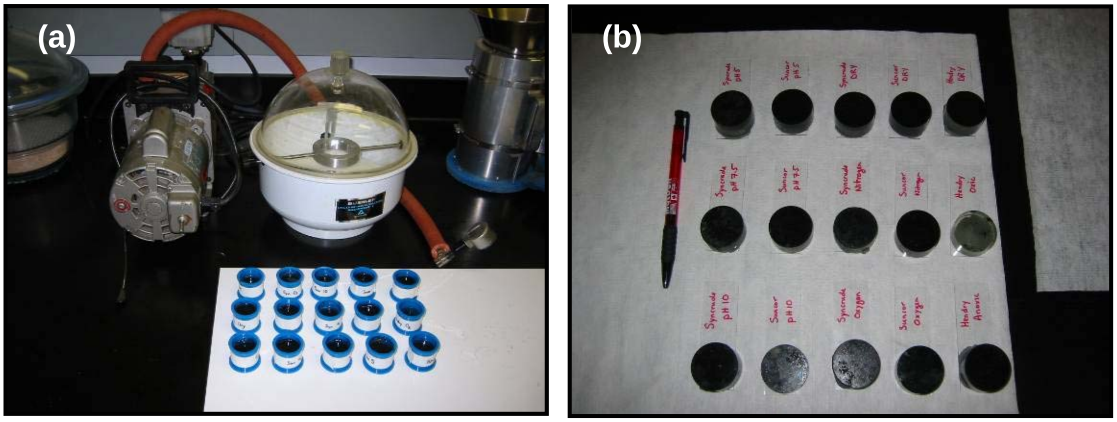

Figure 4.1. (a) Vacuum apparatus used for the preparation of coke samples in epoxy. (b) Finished samples prepared for polarized light microscopy analysis.

A light coat of release silicon was sprayed on the inside of each sample cup before the coke sample was added. The samples were added with the side of the sample that was to be examined by the microscope facing the bottom of the cup. Small samples were weighted down with pieces of metal to keep them from overturning during the degassing procedure. The epoxy mixture was prepared by mixing epoxide resin with epoxide hardener in a 5:1 ratio for approximately 2 min. The cups containing coke samples were filled with epoxy to approximately 0.32 cm from the top and placed into the vacuum impregnator.

The vacuum impregnator was placed under full vacuum in order to draw out any air bubbles in the epoxy that could interfere with the microscopy analysis. Air was leaked into the system only if the air bubbles began to spill over the edge of the cups. The cups were kept under full vacuum for approximately 5 min after the bubbling had stopped to ensure that all voids in the coke samples were filled with epoxy. The samples were allowed to sit overnight to dry at room temperature. After drying, each of the samples were removed from the cups one at a time and the sample identification number was marked on the side of the epoxy mount using an engraver.

4.2.2.2 Procedure for the polishing of coke samples

Any surface irregularities on the topside of the epoxy-impregnated samples were ground off using a Buehler Automet #2 power head with an Ecomet #3 variable speed grinder-polisher and a 80-grit belt surfacer (Buehler Canada, Markham, ON). This was done to make mounting of the sample for the microscopical work easier and to remove any sharp edges. The samples were then polished following the sequence listed in Table 4.2, with the power head rotated clockwise and the polisher/grinder rotated counter clockwise. Once the samples were removed, clean dry air was blown across the face of each of the samples to thoroughly remove any water that may have been present in the pores or openings of the sample. This also eliminated any water spots, which may have hindered the microscopical examination. Each coke sample was mounted by attaching plasticine to the back of each sample, before attaching it to one end of a microscope slide. The samples were then pressed onto the slide with a press, and any excess plasticine was removed. Polished samples are shown in Figure 4.1b.

4.2.2.3 Procedure for microscopic analysis of coke samples

The microscope used in the polarized light analysis was a Zeiss Axioplan (Carl Zeiss Canada Ltd., Toronto, ON) cross-polarized, λ plate, 50X-oil immersion microscope. The associated computer was set up and calibrated before immersion oil was placed on the sample surface. The entire sample was first examined to determine if it was consistent, and then a representative area was selected and photographed.

Table 4.2. Sample-polishing sequence used to prepare coke samples for analysis using polarized light microscopy[1].

Abrasive disc	Polishing cloth	Time/Comments	Water	Pressure (psi)	Speed (rpm)
120 grit	None	2 min 30 sec, until samples are flat and can be seen in the mount.	On	15	120
240 grit	None	2 min 30 sec.	On	15	120
320 grit	None	30 sec.	On	15	120
400 grit	None	30 sec.	On	15	120
600 grit	None	30 sec.	On	15	120
Metadi Supreme Polycrystalline Diamond polishing suspension, 6 micron	Texmet	2 min, spray diamond suspension every 5 sec for 1 min 40 sec and then rinse for 20 sec. The samples were sonified using a Cole-Parmer #8853 sonifier for 2 min in a 20% mixture of ultramet sonic cleaning solution.	Off	15	120
Metadi Supreme Polycrystalline Diamond polishing suspension, 3 micron	Texmet	2 min, spray diamond suspension every 5 sec for 1 min 40 sec and then rinse for 20 sec. Sonify the samples for 2 min.	Off	15	120
Metadi Supreme Polycrystalline Diamond polishing suspension, 1 micron	Mastertex	2 min, spray diamond suspension every 5 sec for 1 min 40 sec and then rinse for 20 sec. Sonify the samples for 2 min.	Off	15	120
Mastermet 2 Colloidal silica, 0.06 micron	Mastertex	2 min, drip colloidal silica suspension every 5 sec for 1 min 40 sec and then rinse for 20 sec. Sonify for 2 min using deionized water only.	Off	15	120

[1] All materials from Buehler Canada, Markham, ON.

4.2.3 Scanning Electron Microscopy Analysis

Before preparation for analysis under the SEM, several small subsamples of coke from each treatment were collected and distributed on weigh paper. This coke was then examined under a light microscope and subsamples that appeared to be representative of the entire sample were chosen for SEM analysis.

The undersides of the aluminum mounts (aluminum specimen mounts, polished, SPI Supplies, West Chester, PA, USA) used for preparation of the coke samples for examination in the SEM were first labeled. A carbon conductive tab (25 mm) (Pelco International, Redding, CA, USA) was then placed onto the top of the mounts. A portion of the coke subsample was stuck to the carbon tab on the mount, and then examined under the light microscope to determine if the sample had adequately adhered to the carbon tab. For larger particles (i.e. Suncor coke), two drops of carbon paint (conducting graphite paint, Soquelec Ltd., Montreal, QC) were placed on the mount before applying the particle(s), and the samples allowed to sit until dry.

The samples were analyzed using a Hitachi S2500 Scanning Electron Microscope (Hitachi High Technologies Canada Inc., Rexdale, ON) with an Oxford Instruments INCAx-sight (Model 6074) energy dispersant system (Oxford Instruments, Ottawa, ON) at the Syncrude Canada Ltd. Research Centre in Edmonton, AB. The resolution of the SEM S2500 was 3.5 nm. A photograph was taken of a representative area of each of the coke samples.

4.3 Results

Figures 4.2 to 4.5 show selected images of Syncrude and Suncor coke as photographed under the polarized light microscope. These examples were chosen based on the clarity of the image, and how well they illustrated the general effects observed in the weathered coke. Table 4.3 summarizes the results of both Syncrude and Suncor coke as analyzed under both polarized light and scanning electron microscopy.

Syncrude coke had a very organized, layered, onion-like structure, which is clearly shown using the polarized light technique (Figure 4.2). There appeared (qualitatively) to be a greater amount of fractured coke particles observed in weathered compared to unweathered Syncrude coke. This fracturing consisted of pieces that seemed to have broken off around the edges of a coke particle, but still remained associated with the original coke particle (as shown in Figure 4.3). Weathered Syncrude coke seemed to exhibit a similar amount of fracturing for all five weathered treatments when compared to unweathered Syncrude coke (Table 4.3).

There appeared to be no visible difference in the microscopic structure of Suncor coke among treatments. Suncor coke exhibited no particle definition using the polarized light microscope technique (Figures 4.4 and 4.5). However, there were a variety of colours (e.g. darker purples and turquoise) obtained for Suncor coke. This assortment of colours was not displayed in Syncrude coke, meaning that the ordering of the two coke types was quite different.

Figures 4.6 to 4.9 show examples of Syncrude and Suncor coke as analyzed using SEM. No differences were visible between weathered and unweathered treatments for either coke type using this method. However, several general observations about each coke type were noted. First, Suncor coke was observed to be more porous, with a sponge-like texture on the coke surface (Figure 4.8). Suncor coke was also “chunky” in shape with sharp edges throughout the particles. In contrast, Syncrude coke did not contain any visible pores and had a more spherical structure with a bumpy surface (Figure 4.6).

Table 4.3. Observations of Syncrude Canada Ltd. and Suncor Energy Inc. coke samples analyzed by polarized light and scanning electron microscopy techniques.

	Polarized Light Microscopy		**Scanning Electron Microscopy**	
Treatment	**Syncrude Coke**	**Suncor Coke**	**Syncrude Coke**	**Suncor Coke**
Unweathered	A very organized, layered, onion-like structure, majority of particles seem to be intact.	No particle definition, but there were a variety of colours not observed when examining Syncrude coke.	No visible pores with a spherical structure with a bumpy surface.	Porous, with a sponge-like texture on the surface, also “chunky” in shape with sharp edges throughout the particles.
Low Dissolved Oxygen (30 d)	Increased fracturing of particles compared to unweathered Syncrude coke.	No visible difference in microscopic structure of Suncor coke between treatments.	No visible difference in microscopic structure of Syncrude coke between treatments.	No visible difference in microscopic structure of Suncor coke between treatments.
High Dissolved Oxygen (30 d)	Increased fracturing of particles compared to unweathered Syncrude coke.	No visible difference in microscopic structure of Suncor coke between treatments.	No visible difference in microscopic structure of Syncrude coke between treatments.	No visible difference in microscopic structure of Suncor coke between treatments.
pH 5 (45 d)	Increased fracturing of particles compared to unweathered Syncrude coke.	No visible difference in microscopic structure of Suncor coke between treatments.	No visible difference in microscopic structure of Syncrude coke between treatments.	No visible difference in microscopic structure of Suncor coke between treatments.
pH 7.5 (45 d)	Increased fracturing of particles compared to unweathered Syncrude coke.	No visible difference in microscopic structure of Suncor coke between treatments.	No visible difference in microscopic structure of Syncrude coke between treatments.	No visible difference in microscopic structure of Suncor coke between treatments.
pH 10 (45 d)	Increased fracturing of particles compared to unweathered Syncrude coke.	No visible difference in microscopic structure of Suncor coke between treatments.	No visible difference in microscopic structure of Syncrude coke between treatments.	No visible difference in microscopic structure of Suncor coke between treatments.

Unweathered Syncrude Coke

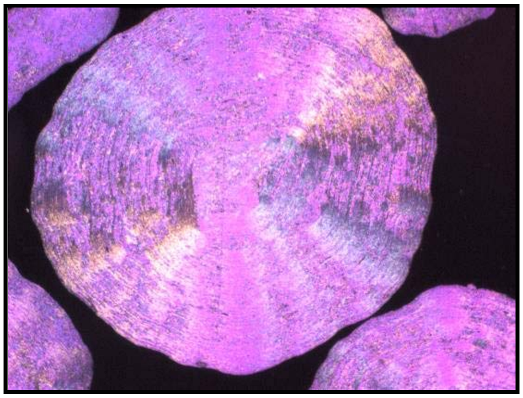

Figure 4.2. A sample of unweathered Syncrude coke as seen under a polarized light microscope, 50X, oil immersion.

Weathered Syncrude Coke

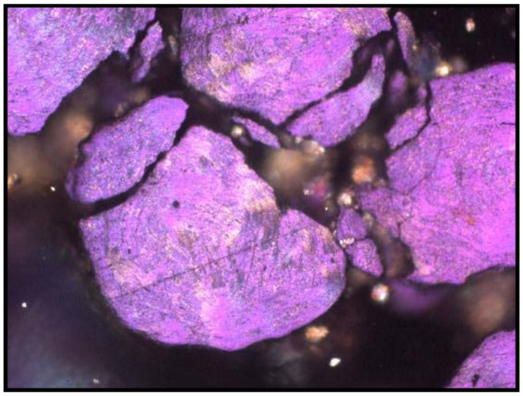

Figure 4.3. A sample of Syncrude coke weathered for 45 days at pH 7.5 as seen under a polarized light microscope, 50X, oil immersion.

Unweathered Suncor Coke

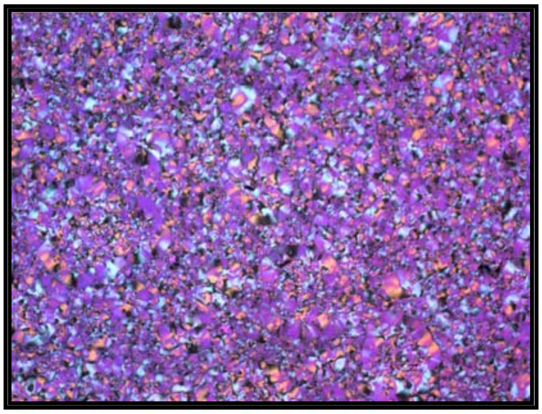

Figure 4.4. A sample of unweathered Suncor coke as seen under a polarized light microscope, 50X, oil immersion.

Weathered Suncor Coke

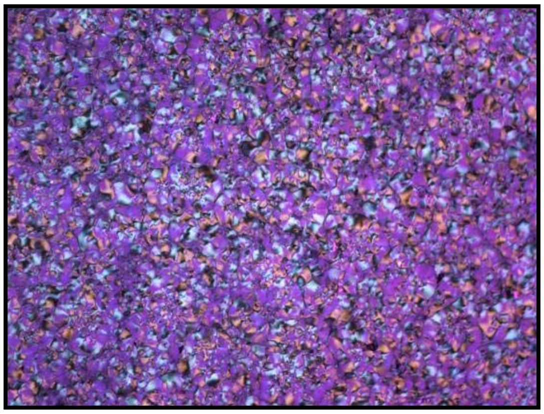

Figure 4.5. A sample of Suncor coke weathered for 45 days at pH 7.5 as seen under a polarized light microscope, 50X, oil immersion.

Unweathered Syncrude Coke

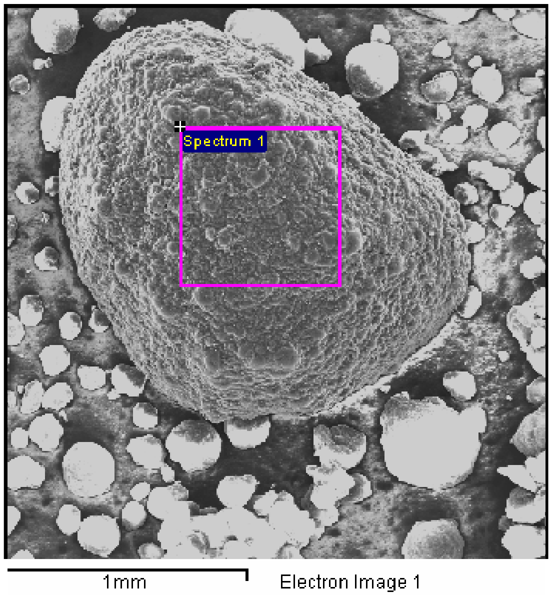

Figure 4.6. An electron photomicrograph of a sample of unweathered Syncrude coke.

Weathered Syncrude Coke

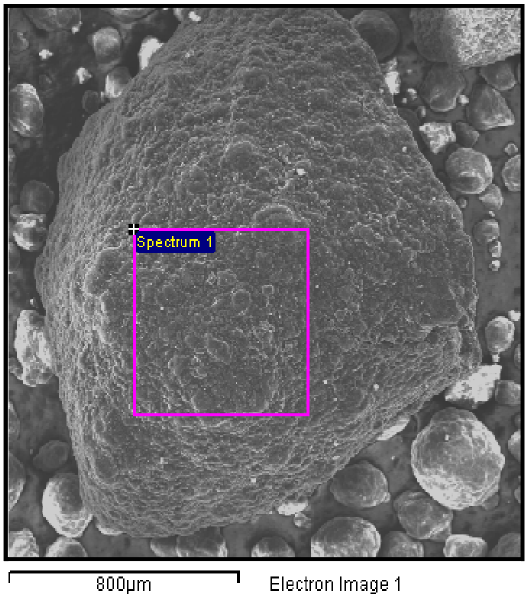

Figure 4.7. An electron photomicrograph of a sample of Syncrude coke weathered for 45 days at pH 10.

Unweathered Suncor Coke

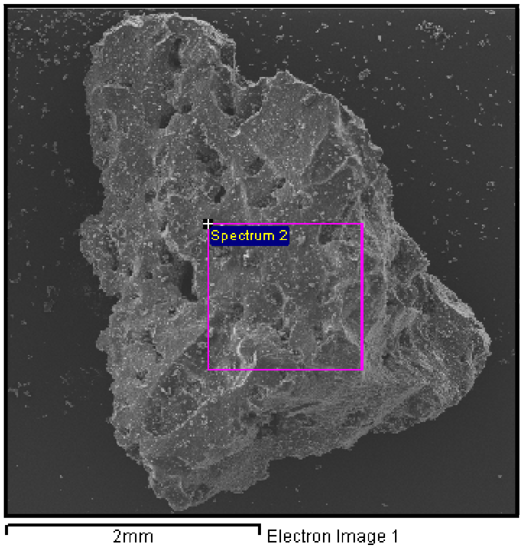

Figure 4.8. An electron photomicrograph of a sample of unweathered Suncor coke.

Weathered Suncor Coke

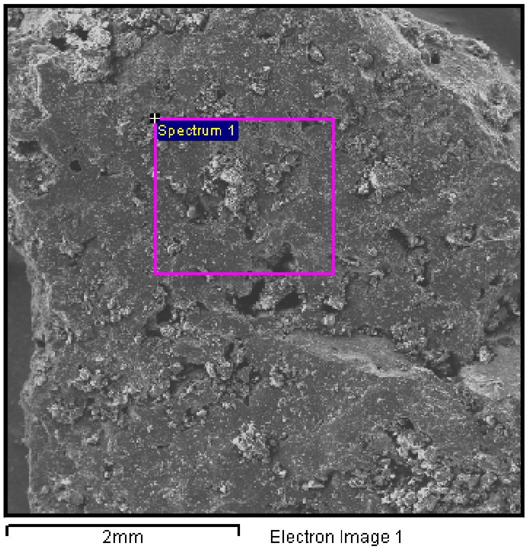

Figure 4.9. An electron photomicrograph of a sample of Syncrude coke weathered for 30 days under low dissolved oxygen conditions.

4.4 Discussion

The physical differences between Syncrude and Suncor coke types were very obvious, and were most likely a result of their method of formation. Suncor coke, which is non-circular, and contains a very porous surface with sharper edges, is very representative of a delayed coking system (Scott and Fedorak, 2004). Delayed coking allows for large chucks of coke to be produced, which are then crushed down to smaller pieces. This process may explain the non-uniform chunky shapes of the coke particles. The spongy texture of Suncor coke surfaces can be explained by the short holding time (approximately 48 hrs) that the coke has in the coker before it is removed (Scott and Fedorak, 2004).

In contrast, Syncrude coke is produced in a fluid coking system, which requires the continual removal of coke during operation (Scott and Fedorak, 2004). This might account for the spherical, uniform structure of Syncrude coke, since it is constantly removed from the coker in the form of a slurry. Syncrude coke's layered structure is also more indicative of a longer holding time in the coker permitting layers to build up on each particle. Har (1981) made similar observations when using SEM to assess the physical properties of Syncrude coke after fractionation, confirming that the growth of a coke particle is by surface deposition of material during the coking process.

No differences between weathered and unweathered samples for either coke type were visible using the SEM. This is most likely because with SEM only single particles could be viewed (Figures 4.6 to 4.9) in comparison to the multi-particle analysis conducted using polarized light microscopy (Figures 4.2 to 4.5) thus making it more difficult to assess any differences in the amount of fracturing among treatments.

There seemed to be a greater amount of fractured Syncrude coke particles present in both types of weathered coke (dissolved oxygen and pH), compared to unweathered coke, when observed using polarized light microscopy. However, it is possible that the same amount of fracturing had occurred in the unweathered coke as in the weathered coke, but went unnoticed due to the random selection of the views of coke chosen in the present study.

The increase in fracturing of Syncrude coke observed within the weathered treatments may also be due to the methods of sample preparation. However, the chances of such a phenomenon are unlikely since all samples (weathered and unweathered) were prepared at the same time using the same methods. Conversely, there is a possibility that the weathering treatments (dissolved oxygen and pH) may have weakened the structure of the coke. This would make it prone to fracture after being placed in epoxy and dried under vacuum.

Suncor coke exhibited no particle definition using the polarized light technique so fracturing could not be assessed. This was either due to the much larger particle size of Suncor coke (which filled the entire field of view on the microscope preventing any particle comparisons), or to the unordered structure of the coke. Because Suncor coke is produced using a delayed coking process, the structure of each particle is not layered. As a result, it is not as easily differentiated as Syncrude coke. This is reflected in the variety of different colours observed when analyzing Suncor coke using the polarized light technique, which were absent when examining Syncrude coke.

Under polarized light, areas of the coke having a different ordered microstructure rotate the light at a different degree. This allows for regions of different order to be differentiated based on apparent brightness. For example, when a sample is rotated perpendicular to the light beam the brightness of an ordered region will change, while a deposit with no order will remain dark (Syncrude Canada Ltd., 2003). The different colours observed in the Suncor coke compared to the Syncrude coke under the polarized light microscopy technique are most likely due to differences in structure within the coke particle, which contributes to the differences in surface texture observed using SEM.

Differences in order could contribute to differences in the leachability and ultimate toxicity of coke if it is used as part of an aquatic reclamation program. Although Syncrude coke has a small particle size thereby increasing the surface area available for leaching, it also has a very smooth, spherical shape. Suncor coke, on the other hand, has a much larger particle size, it is very jagged and chunky, with a rough, porous surface (Scott and Fedorak, 2004). This type of shape and surface can also increase the surface area available for leaching of toxic constituents.

4.5 Conclusions

Syncrude and Suncor coke display very different physical characteristics, such as particle size, shape and texture. These may lead to differences in leaching of chemical constituents and therefore possibly in toxicity when placed in an aquatic environment. Syncrude coke, with its smaller particle size and thus potentially larger surface area to volume ratio, could potentially leach more toxic constituents into the overlying water than the larger Suncor coke. However, the porous surface texture of Suncor coke would also result in an increase in surface area leading to a greater degree of leaching.

Even though we were unable to make a reliable quantitative analysis of the amount of fracturing for each weathering treatment, it appeared that while weathering in general caused increased fractioning of coke, the specific type of weathering (i.e., dissolved oxygen or pH) does not have an appreciable effect on the amount of fracturing, at least not over the time periods studied here. Therefore it can only be concluded that weathering under common environmental conditions may alter the physical properties of coke particles, compared to unweathered coke. This may influence the amount of metals and other constituents leaching out of the coke in a long-term aquatic reclamation strategy.

Weathering can thus theoretically cause a substantial increase in the surface area of coke particles since the particles evaluated here appeared to be broken down into smaller sized fractions. This increases the potential for leaching of toxic constituents from the coke when weathered over a longer period of time, since a larger surface area of coke is exposed to the overlying or pore waters. It is anticipated that eventually particles could become too small to fraction any further, and therefore would reach a steady state of fractionation (MacKinnon, 2004). This implies that the amount of constituents leaching out of the coke would eventually reach a threshold and come into equilibrium with the surrounding aquatic environment. It is uncertain, at this time if or when this would happen, and how much fractioning of coke particles would contribute to this.

It is recommended that samples of coke which have undergone a longer period of weathering be collected and compared to the samples analyzed in the present study.

Such comparisons could lead to a better understanding of how the fractioning of coke may change over a longer time frame. In addition, such analysis could further determine how fractioning affects the potential leaching of constituents from coke in an aquatic reclamation strategy

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5. THE EFFECTS OF ACCELERATED WEATHERING ON THE LEACHING OF METALS FROM COKE AND THE INFLUENCE OF COKE PARTICLE SIZE ON THE SURVIVAL AND GROWTH OF *CHIRONOMUS TENTANS*

5.1 Introduction

One of the major industries in the province of Alberta, Canada, is the oil sands industry. Oil sands are natural sand deposits containing a dense, viscous petroleum called bitumen. The two major oil sands mining companies currently producing synthetic crude oil in Alberta are Syncrude Canada Ltd. and Suncor Energy Inc. In 2003, Syncrude produced about 13% of Canada's petroleum needs, amounting to approximately 77.3 million barrels of oil (Syncrude Canada Ltd., 2004).

A waste product called coke is produced during part of the bitumen upgrading processes at the Alberta oil sands. Coking is an essential part of this upgrading system since it enables oil sands companies to convert less profitable heavy oil fractions into the more valuable light fractions. Syncrude and Suncor produce coke through two different processes, fluid and delayed coking. Due to these different processes, some of the physical properties of Syncrude and Suncor coke, such as particle size, are very different.

At present, Syncrude produces approximately 2 million tonnes of coke per year, with planned expansions in the next few years increasing this number to 3 million tonnes per year. Suncor already produces over 3 million tonnes of coke per year (Komex International Ltd., 1998; Scott and Fedorak, 2004). Most of this coke is stored directly onsite at the oil sands operations, although some of the coke produced via delayed coking is sold and shipped off site (Chung *et al.*, 1996; Scott and Fedorak, 2004).

Current reclamation strategies for mined out leases at the Alberta oil sands include constructing wetlands using layers of waste product, such as tailings and coke. Coke contains a high amount of organic carbon, a fundamental ingredient in the establishment of a viable benthic community in aquatic ecosystems. This makes coke an attractive capping option in an aquatic reclamation strategy at the Alberta oil sands since other waste products, such as tailings, contain very low levels of natural organic carbon making them unsuitable as the sole substrate in an aquatic reclamation strategy.

Coke as it is presently stored on site in coke cells or large piles contains small volumes of soil or sediment matter, such as clay particles. These particles can contain naturally elevated levels of heavy metals due to the presence of oil sands in the region (Scott and Fedorak, 2004). It is therefore possible that the metals previously shown to leach from the coke (see Chapter 3) may actually be originating from these soil/sediment particles, or loosely bound to the surface of the coke. This could be the cause of the initial, rapid release of metals which was previously shown to leach into the overlying water and pore water of coke (Chapter 3).

Toxicity experiments discussed in Chapter 3 of this thesis suggested that the particle size of coke may play a key role in the observed effects on survival and growth of the aquatic macroinvertebrate, *Chironomus tentans*. In those experiments, Syncrude coke, which has a smaller particle size, resulted in a significant increase in *C. tentans* growth compared to Suncor coke, which has a much larger particle size. Particle size, therefore, has the potential to play an important role in the feasibility of using coke as a reclamation substrate by limiting the ability of some aquatic macroinvertebrates, such as *C. tentans*, to utilize it as a building material for habitat (tube) construction (Berg, 1995).

The first objective of the following experiments was to determine whether the leaching of certain metals into the overlying and pore waters of the coke as observed in previous experiments is from: (a) loose debris and/or weakly bound metals associated with the coke during storage, (b) foreign matter adhering to the surface of the coke, or (c) the coke matrix itself. The second objective was to determine whether or not the particle size of Suncor coke has an effect on the survival and/or growth of *C. tentans*.

5.2 Materials and Methods

5.2.1 Accelerated Weathering Experiment

5.2.1.1 Study Design

Cokes from Syncrude and Suncor were exposed to three different pre-treatments (untreated, water rinsed, and peroxide treated) before undergoing a 30-d leaching period. Untreated coke was manipulated as done in previous experiments (Chapter 3). This treatment is considered to be a control treatment and will be compared with the other two treatments (see below).

The rinsed coke treatment was designed to remove the loose debris associated with coke (e.g. clay), as well as any metals that may be weakly adsorbed to the surface of the coke. Each coke type was mixed with reconstituted water (the properties of which are listed in Table 3.1) at a ratio of coke:water of 1:1 (400 mL of coke with 400 mL of water) and shaken for 30 seconds. The mixture was left undisturbed until the coke had settled enough to see a clear definition between the coke and the overlying water layer. At this point, the rinse water was carefully decanted and saved. This procedure was repeated for a total of four times and the rinse water combined to provide a total volume of 1600 mL This is equal to the amount of overlying water generated in previous leaching experiments (Chapter 3). A composite sample of this rinse water was sent for trace metal analysis. The procedures for the sampling and analysis of trace metal samples were the same as those outlined in Chapter 3.

To remove matter that may be more strongly bound to the surface of the coke particles, hydrogen peroxide (H_2O_2) was used. Hydrogen peroxide is generally used to oxidize organic matter in soil and sediment that can become bound to metals (Tessler *et al*., 1979). Under oxidizing conditions in natural waters organic matter can be degraded, leading to a release of soluble metals (Tessler *et al.,* 1979). Water rinsed coke (as outlined above) was submerged in a 10% solution of H_2O_2 at a ratio of coke:peroxide of 1:1 and left for 30 minutes. After this time, the peroxide was decanted and the coke rinsed with 400 mL of reconstituted water an additional four times to ensure that none of the peroxide remained. Composite samples of both the peroxide and reconstituted water rinses were sent for trace metal analysis. The procedures for sampling and analysis of trace metal samples were outlined in Chapter 3.

5.2.1.2 Experimental Methods and Sampling

After pre-treated as described above, coke was leached in 2 L glass jars for a total of 30 days at 23 ± 1°C. The overlying water (1600 mL) was reconstituted water adjusted and maintained at pH 5 throughout the experiment. A previous experiment had showed this pH to have the greatest effect on leaching of most metals (see Chapter 3). There was no aeration of the test vessels during this experiment, since it was conducted in an airtight system to better maintain stable pH levels. Samples of overlying and pore waters were taken on Days 0, 15 and 30, and followed the same procedures as outlined in Chapter 3. These were analyzed for standard water quality variables (ammonia, conductivity, pH, hardness and alkalinity) at the Toxicology Centre, University of Saskatchewan, Saskatoon, SK. Sub-samples of overlying water were further filtered using 0.45-µm Nalgene® membrane filter before being transferred into pre-cleaned 15-mL Nalgene® bottles (Nalge Nunc International, Rochester, NY) for trace metal analysis. Trace metal analysis was performed in the Department of Geological Sciences at the University of Saskatchewan using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Single composite samples of each coke type from the water rinsed and peroxide pre-treated cokes were obtained on Day 30 of the leaching experiment. These samples were dried at 60 ºC for 24 h and sent to Syncrude Research Centre, Edmonton, AB, to undergo scanning electron microscopy (SEM) and polarized light microscopy analysis as described in Chapter 4. In addition, a sub-sample of these coke samples were sent to Acme Analytical Laboratories Ltd. (Vancouver, BC) for elemental analysis using ICP-MS and ICP-ES techniques.

5.2.2 Particle Size Experiment

This experiment was designed to assess the effect of Suncor coke particle size on the survival and growth of *C. tentans*. The treatments for this experiment consisted of control sand, untreated Syncrude coke, untreated Suncor coke and crushed Suncor coke. These allowed for a comparison between each coke type, and the crushed (i.e. smaller sized) Suncor coke.

Suncor coke was crushed manually with a standard glass mortar and pestle. After crushing, the coke was passed through a 425 μm mesh sieve. This size was chosen because it was the smallest mesh size that Syncrude coke could pass easily through. This provided a reasonable comparison between the particle sizes of crushed Suncor coke and untreated Syncrude coke. After the coke was crushed, all four treatments (control sand, Syncrude coke, Suncor coke and crushed Suncor coke) were rinsed briefly to remove any fine particulate matter.

A 10-d toxicity test using *C. tentans* was performed using four replicates of each treatment with 10 animals per replicate. The overlying water was reconstituted water made to mimic the hardness and alkalinity values found in water sampled at the Syncrude mine site in northern Alberta (Table 3.1). The remainder of the general experimental design and procedures are based on the protocol outlined by Environment Canada (1997) and are described in Chapter 3 (Section 3.2.3).

5.2.3 Data Analysis

Mass balance calculations were conducted for metals identified to be of concern during the accelerated weathering leaching experiment. These calculations used the peak concentrations of the identified metals of concern in both overlying water and pore water, and compared them to their respective, total concentration in the untreated coke (i.e. coke that had not undergone any leaching). If the concentration in the corresponding leached coke was greater than the concentration in the untreated coke, the leached coke value was used. Peak values were utilized in these calculations in order to calculate the maximum percentage of metals observed to leach from the coke.

Statistical analyses were performed using the computer program SigmaStat®, version 2.03 (SPSS Inc., Chicago, IL, USA) at a 95% ($\alpha = 0.05$) level of confidence. Two-way ANOVAs were conducted on metals data from the accelerated weathering leaching experiment to determine differences in metal concentrations between overlying water and pore water, and also among treatments (untreated, water rinsed, and peroxide treated). Two-way ANOVAs were conducted on the ranked data when tests and transformations for homogeneity of variance failed. If statistical differences were found, a Holm-Sidak multiple comparison test was run for each ANOVA test.

The endpoints for the toxicity test were survival and growth of *C. tentans*. A one-way ANOVA was conducted to test for any statistical difference between the four substrate treatments (control sand, Syncrude coke, Suncor coke, crushed Suncor coke). The test used for normality was Kolmogorov-Smirnov and the test for homogeneity of variance was the Levene median test. If statistical differences were found, a Holm-Sidak multiple comparison test was run.

5.3 Results

5.3.1 Accelerated Weathering Experiment

5.3.1.1 Water Chemistry

The highest single metal concentration measured over all time points for the metals identified to be of potential concern in the accelerated leaching experiment are listed in Table 5.1. These metal concentrations either exceeded the Canadian Water Quality Guidelines for the protection of aquatic life, or published LC_{50} values for *Chironomus* species. More detailed metal concentration data for this experiment are summarized in Appendix IV.

An immediate release of metals into the pore water and overlying water occurred at the beginning (i.e. within the first few hours) of the experiment. In treatments with Syncrude coke, metal concentrations in both the pore water and overlying water tended to start high and then decrease over the 30-d leaching period (Figure 5.1). In treatments with Suncor coke, most metal concentrations increased in both the pore water and overlying water over the duration of the leaching period, but generally were lower on day 0 than Syncrude coke (Figure 5.2). The concentrations of metals in pore water tended to be similar to or exceed the metal concentrations in the overlying waters on day 30 for both coke types.

Metal leaching was observed in all three treatments for both coke types. However, untreated coke was observed to leach the highest metal concentrations only 19% of the time when pooled over all three time points for Syncrude coke, and 43% of the time when pooled over all three time points for Suncor coke (Figures 5.1 and 5.2). Untreated coke generally showed the greatest leaching on day 0 (except for Mo and V). Metal concentrations then tended to decrease over the remainder of the leaching period. When Suncor coke was used as a substrate, there was a spike in metal concentrations for untreated coke on day 15 (except for Cu, Mo and V). Day 15 metal concentrations either remained relatively constant or decreased slightly by day 30.

The water-rinsed coke leached higher concentrations of metals than the peroxide treated coke 59% of the time for Syncrude coke and 27% of the time for Suncor coke, when pooled over all three time points. Metal concentrations in the water rinsed and peroxide treated Syncrude coke either decreased or remained relatively constant over all three time points, with the exception of copper, which showed a spike in concentration on Day 30. However, water rinsed and peroxide treated Suncor coke tended to follow the trend of the untreated Suncor coke by showing a spike in metal concentration on day 15, before leveling off or decreasing by day 30. There were some exceptions with Syncrude coke (Co, Cu, Mn) and Suncor coke (Cu, Mo, V) where the peroxide treated coke leached the most metals, and untreated the least at different time points during the leaching period (Figures 5.1 and 5.2).

The mean concentrations of metals found in the rinse solutions for the water rinsed coke and the peroxide treated coke are listed in Table 5.2. It is evident that higher concentrations of metals were removed with the peroxide treatment versus the water rinse for both coke types. Higher metal concentrations were found in the rinse solutions of Syncrude coke than Suncor coke with both of these pre-treatments. When metal concentrations in the rinse solutions are compared against the mean overlying water metal concentration on day 30 in the subsequent leaching study (Figures 5.1 and 5.2) the concentrations in the rinse solutions either exceed or were similar to those from the samples collected from the overlying water.

Table 5.1. Peak concentrations (µg/L) measured over three time points for several metals that reached levels of concern in the overlying water (leachate) and coke pore water during the accelerated weathering leaching experiment: (a) Syncrude coke, (b) Suncor coke.

(a)

		Overlying Water			**Pore water**				
Element	**Detection Limit**	**Untreated**	**Rinsed**	**Peroxide**	**Untreated**	**Rinsed**	**Peroxide**	**CWQG[1] (µg/L)**	**C*hironomus* sp. LC$_{50}$ (µg/L)**
Cobalt	0.03	5.1	5.8	5.9	31.5	40.8	29.1	--[2]	n/a
Copper	0.42	4.4	7.3	8.8	3.4	2.5	2.8	3	54[3]
Manganese	0.54	188.9	65.9	143.0	683.5	366.7	354.0	50	55[4]
Molybdenum	0.11	91.4	31.1	31.6	851.5	93.9	48.1	73	360[4]
Nickel	0.97	653.8	114.8	113.0	2590.2	1048.0	1041.1	25-150	10,200[5]
Vanadium	0.88	761.2	630.0	529.0	1427.6	1034.8	305.3	--[2]	240[4]
Zinc	20.07	46.1	11.0	13.0	199.5	89.6	115.5	30	1125[3]

(b)

		Overlying Water			**Pore water**				
Element	**Detection Limit**	**Untreated**	**Rinsed**	**Peroxide**	**Untreated**	**Rinsed**	**Peroxide**	**CWQG[1] (µg/L)**	**C*hironomus* sp. LC$_{50}$ (µg/L)**
Cobalt	0.03	15.0	7.3	6.4	74.1	25.9	31.6	--[2]	n/a
Copper	0.42	8.2	4.6	5.8	8.4	3.7	16.2	3	54[3]
Manganese	0.54	342.4	132.9	208.9	1612.5	518.6	645.9	50	55[4]
Molybdenum	0.11	2.3	13.3	13.0	4.8	4.2	13.2	73	360[4]
Nickel	0.97	68.8	43.0	39.6	334.9	100.9	138.3	25-150	10,200[5]
Vanadium	0.88	3.7	1097.0	983.0	5.4	4.1	69.9	--[2]	240[4]
Zinc	20.07	42.4	25.4	37.8	111.1	53.0	80.9	30	1125[3]

[1] Canadian Water Quality Guidelines (CCME, 2003); [2] No Canadian Guideline available; [3] (Phipps *et al*., 1995); [4] (Fargašová, 1997)

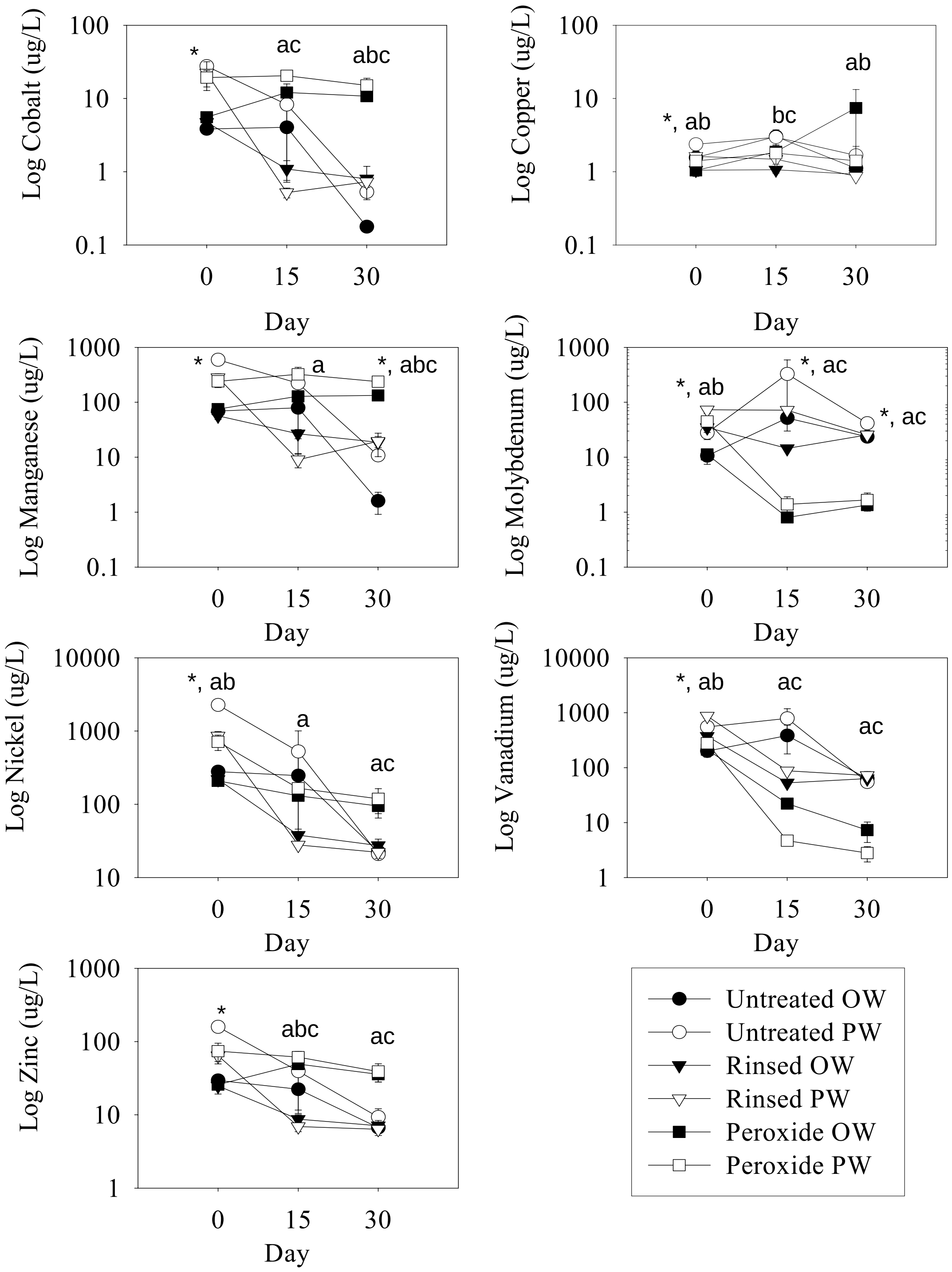

Figure 5.1. Log mean concentrations ± standard errors of selected metals in overlying water and pore water for Syncrude coke during a 30-d accelerated weathering leaching experiment. (* denotes significant differences between overlying water and pore water. [a] denotes significant differences between water rinsed and peroxide treated coke, [b] between water rinsed and untreated coke and [c] between untreated and peroxide treated coke).

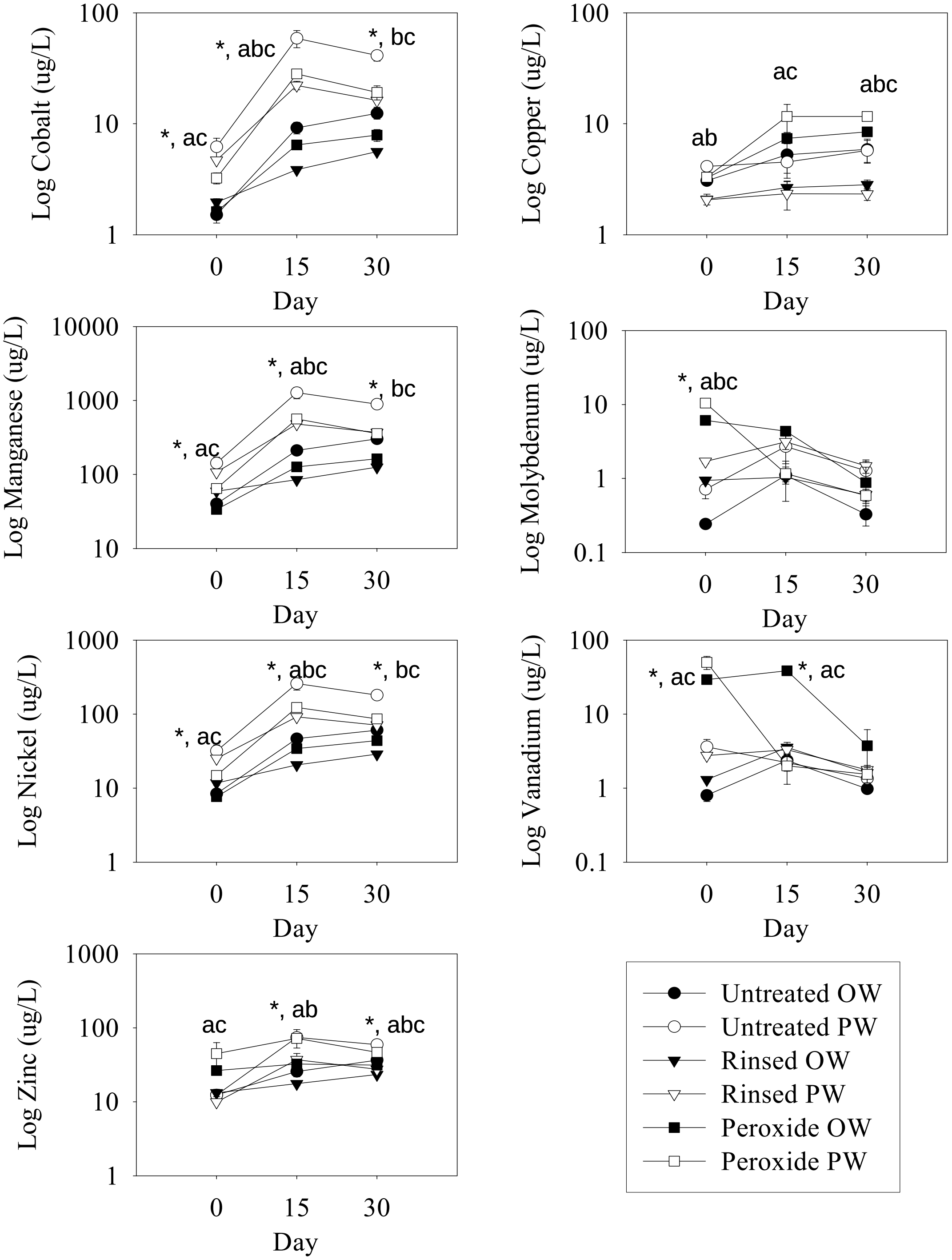

Figure 5.2. Log mean concentrations ± standard errors of selected metals in overlying water and pore water for Suncor coke during a 30-d accelerated weathering leaching experiment. (* denotes significant differences between overlying water and pore water. ^{a} denotes significant differences between water rinsed and peroxide treated coke, ^{b} between water rinsed and untreated coke and ^{c} between untreated and peroxide treated coke).

Table 5.2. Mean concentrations ± standard errors (μg/L) of selected metals in the rinse solutions of the water rinsed and peroxide treated Syncrude and Suncor coke.

	Syncrude Coke		**Suncor Coke**	
Element	**Water Rinse**	**Peroxide Rinse**	**Water Rinse**	**Peroxide Rinse**
Cobalt	1.8 ± 0.8	100.5 ± 28.1	5.2 ± 0.8	39.4 ± 11.2
Copper	0.6 ± 0.0	69.8 ± 33.2	2.2 ± 1.0	48.6 ± 14.6
Manganese	46.6 ± 17.6	944.5 ± 223.9	165.8 ± 18.3	694.4 ± 194.8
Molybdenum	16.7 ± 3.7	116.8 ± 11.6	3.0 ± 0.5	187.8 ± 56.4
Nickel	120.3 ± 54.4	1534.2 ± 260.9	30.0 ± 4.5	298.5 ± 82.6
Vanadium	260.6 ± 103.0	12748.5 ± 4609.4	2.2 ± 0.4	715.2 ± 185.3
Zinc	27.7 ± 1.3	332.3 ± 121.9	< 20.1	83.8 ± 20.3

5.3.1.2 Coke Chemistry

5.3.1.2.1 Elemental Analysis of coke

There did not appear to be many differences in measured elemental concentrations between coke that had been rinsed with water only and coke that had been pre-treated with peroxide for either Syncrude or Suncor coke types (Table 5.3a). None of the metal concentrations leached into the overlying waters exceeded 3% of the total metal available in the coke (Table 5.3b). The greatest percentage (2.2% for zinc) was seen in the peroxide treated Syncrude coke.

Table 5.3. Measured concentrations (µg/g) (a) of metals in weathered Syncrude and Suncor coke after pre-treatment with either a water rinse or a peroxide treatment (*n* = 1), and the associated percentage of each metal (b) using peak concentrations of metals in both overlying water and pore water and their respective measured concentration in coke.

(a)

Element	**Syncrude Rinsed**	**Syncrude Peroxide**	**Suncor Rinsed**	**Suncor Peroxide**
Cobalt	5.8	5.9	7.3	6.4
Copper	7.3	8.8	4.6	5.8
Molybdenum	31.1	31.6	13.3	13.0
Nickel	114.8	113.0	43.0	39.6
Vanadium	630.0	529.0	1097.0	983.0
Zinc	11.0	13.0	8.0	10.0

(b)

Element	**Syncrude Rinsed**	**Syncrude Peroxide**	**Suncor Rinsed**	**Suncor Peroxide**
Cobalt	0.7	1.2	0.4	0.8
Copper	0.1	1.1	0.4	0.9
Molybdenum	0.8	0.2	0.1	0.3
Nickel	1.2	1.1	0.4	0.7
Vanadium	0.4	0.3	0.0	0.0
Zinc	1.8	2.2	1.6	1.9

5.3.1.2.2 Polarized Light and SEM Analysis

Figures 5.3 to 5.6 show representative examples of the polarized light pictures obtained for water rinsed and peroxide treated Syncrude and Suncor coke after leaching for 30-d. In general, Syncrude coke had a very organized, layered, onion-like structure, very similar to the samples discussed in Chapter 4. Water rinsed coke appeared to be more fragmented than coke treated with peroxide for both Syncrude and Suncor coke. However, unlike the fragmentation seen in the samples analyzed in Chapter 4, these fragments did not appear to be associated with larger coke particles. Instead, they seemed to be small chunks of coke that had “floated” away from the parent particle.

Figures 5.7 to 5.10 are representative SEM pictures of water rinsed and peroxide treated Syncrude and Suncor coke after leaching for 30-d. No obvious differences between water rinsed and peroxide pre-treated coke for Syncrude coke were visible using this method. However, the surface of the peroxide treated Suncor coke appeared to be rougher than coke that was rinsed only with reconstituted water prior to weathering.

Syncrude Coke, Water Rinsed

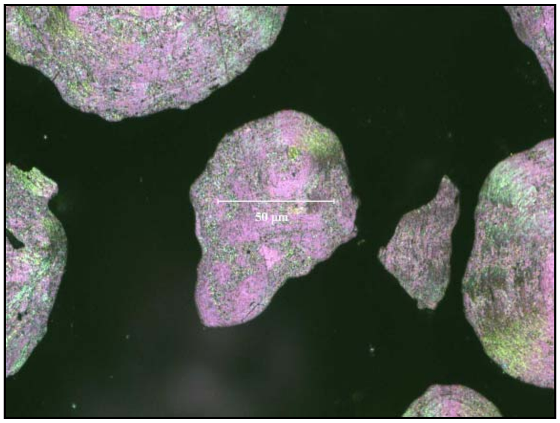

Figure 5.3. A sample of water rinsed Syncrude coke, as seen under a polarized light microscope, 50X, oil immersion.

Syncrude Coke, Peroxide Treated

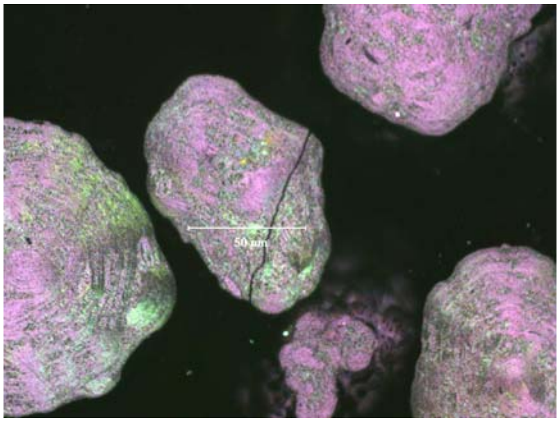

Figure 5.4. A sample of peroxide treated Syncrude coke, as seen under a polarized light microscope, 50X, oil immersion.

Suncor Coke, Water Rinsed

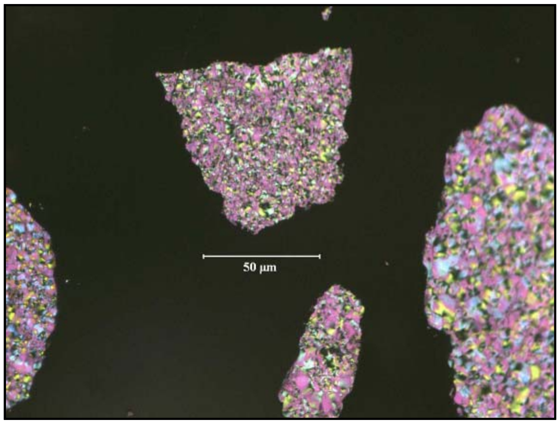

Figure 5.5. A sample of water rinsed Suncor coke, as seen under a polarized light microscope, 50X, oil immersion.

Suncor Coke, Peroxide Treated

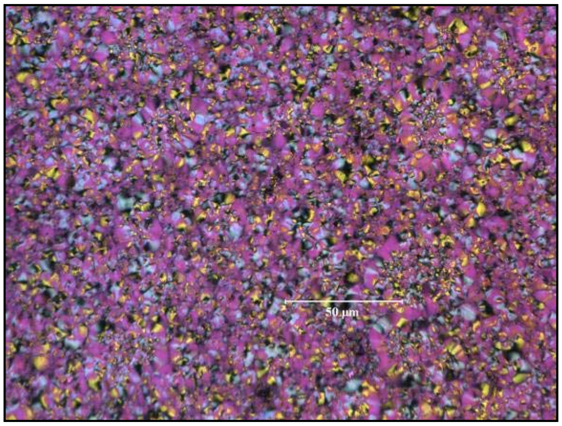

Figure 5.6. A sample of peroxide treated Suncor coke, as seen under a polarized light microscope, 50X, oil immersion.

Syncrude Coke, Water Rinsed

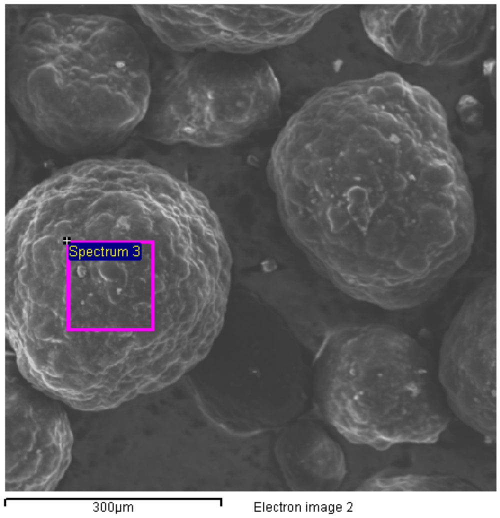

Figure 5.7. An electron photomicrograph of a sample of Syncrude coke after rinsing with water.

Syncrude Coke, Peroxide Treated

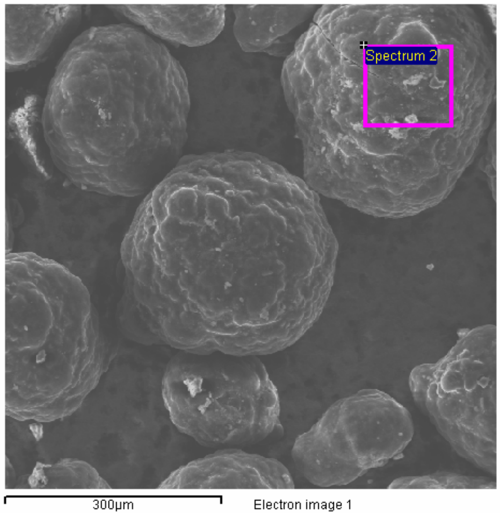

Figure 5.8. An electron photomicrograph of a sample of Syncrude coke after treatment with peroxide.

Suncor Coke, Water Rinsed

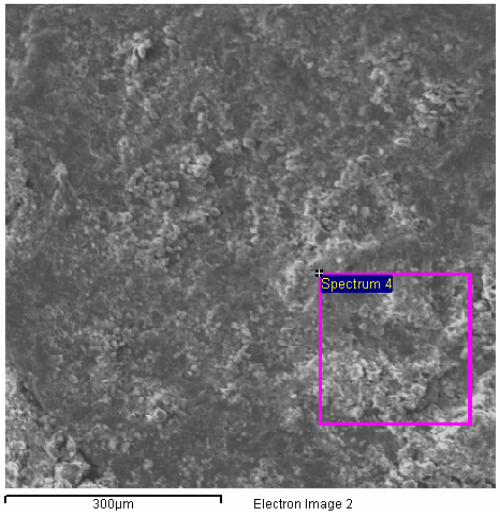

Figure 5.9. An electron photomicrograph of a sample of Suncor coke after rinsing with water.

Suncor Coke, Peroxide Treated

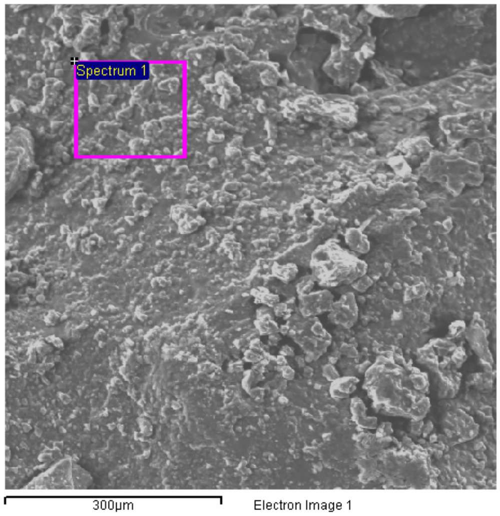

Figure 5.10. An electron photomicrograph of a sample of Suncor coke after treatment with peroxide.

5.3.2 Particle Size Experiment

There was a significant decrease in *C. tentans* survival for the treatment containing unmanipulated Suncor coke as a substrate when compared to the three other treatments: control sand, Syncrude coke ($p < 0.001$) and crushed Suncor coke ($p < 0.05$) (Figure 5.11a). The treatment containing crushed Suncor coke as a substrate showed a significant increase in survival of *C. tentans* when compared with unmanipulated Suncor coke ($p < 0.05$). However, survival was still significantly lower than in the treatment using control sand as a substrate ($p < 0.05$) (Figure 5.11a).

No significant differences were observed in growth of *C. tentans* among any of the four treatments ($p = 0.769$) (Figure 5.11b). However, there was a trend of increased growth with crushed Suncor coke compared to unmanipulated Suncor coke.

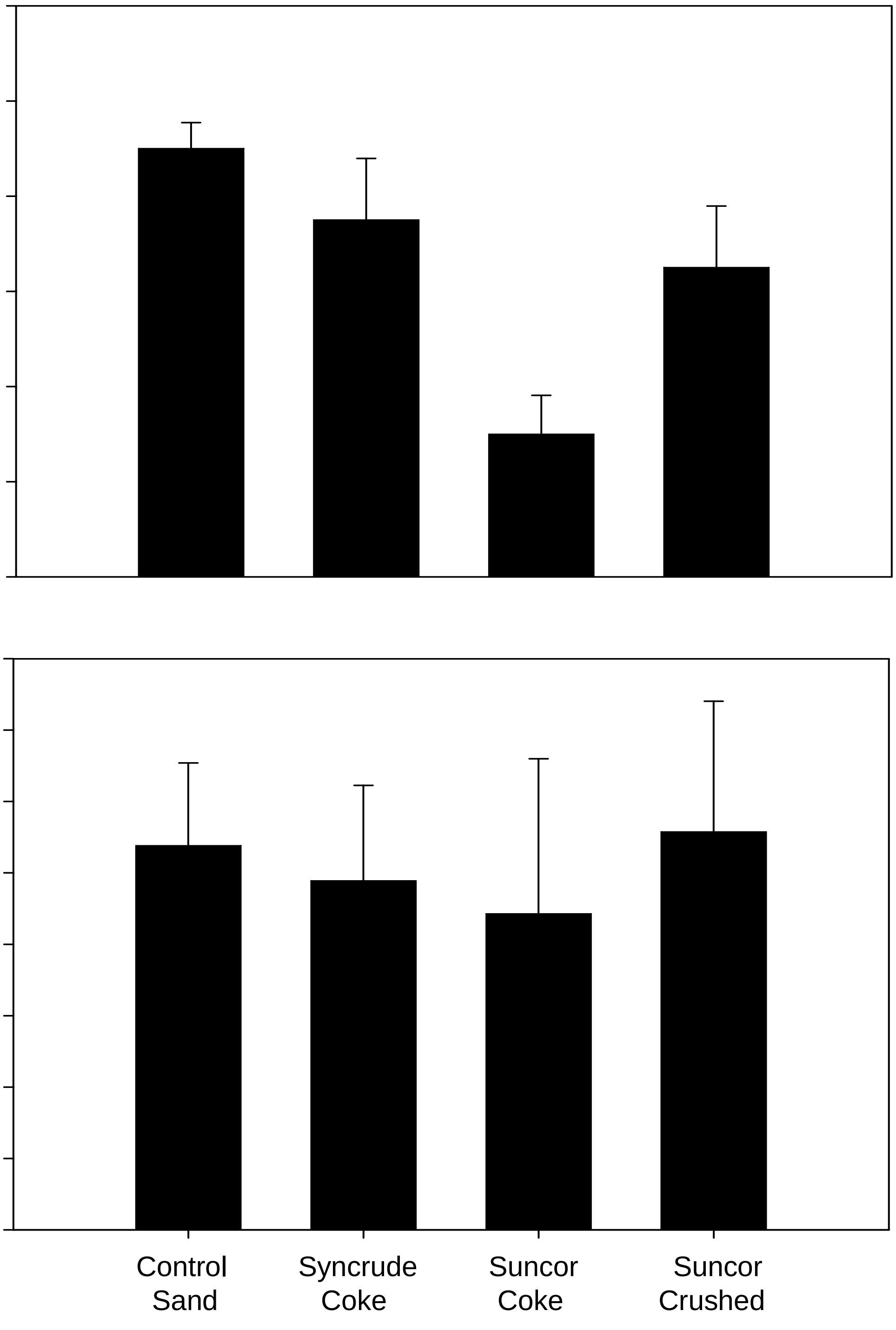

Figure 5.11. Mean (± SE) survival (a) and growth, measured as dry weight, (b) of *Chironomus tentans* larvae after a 10-d bioassay using different particle sized coke samples. *** denotes a significant difference from Syncrude coke, ** denotes a significant difference from Suncor coke, * denotes a significant difference from control sand.

5.4 Discussion

5.4.1 Accelerated Weathering Experiment

There was an immediate release of metals into the pore water and overlying water for all three treatments for both Syncrude and Suncor coke. This trend is similar to what was seen in the leaching experiments described in Chapter 3. In the untreated coke, these metals could be either weakly bound to the surface of the coke particles, or associated with the natural soil and sediment particles found among the coke after storage in the field. As soon as the coke came in contact with water, these loosely bound metals could have been released, causing a spike in dissolved metal concentrations. However, metals released from the water rinsed and peroxide treated coke are less likely from these sources since these pre-treatments should have removed the natural soil and sediment particles, and any metals weakly adsorbed to the surface of the coke. Instead, these metals may be from any leftover rinse water that was not fully removed during pre-treatment. Future experiments could account for this issue by performing additional rinses or filtering the coke before leaching to ensure that none of the rinse water remained behind.

Metal concentrations in both the pore water and overlying water of Syncrude coke tended to start high before decreasing over the 30-d leaching period. In treatments using Suncor coke, most metal concentrations increased in both the pore water and overlying water over the duration of the leaching period. These different leaching trends may be a consequence of the finer particle size of Syncrude coke, which makes it more difficult to rinse during pre-treatment. It is possible that rinse water, which contained a high concentration of metals, was not removed as effectively as with the larger particle size Suncor coke, causing this initial high concentration of metals in both the pore water and overlying water.

Metal concentrations leaching from the untreated Syncrude coke were generally higher than metal concentrations leaching from the water rinsed and peroxide treated Syncrude coke at day 0 (except for Mo and V). This is most likely a result of metals leaching either from the soil and sediment debris, or metals loosely bound to the surface of the coke. Such metals could easily dissociate into the pore water within the first few hours of the leaching experiment.

When Suncor coke was leached, the greatest concentrations of metals were generally observed on day 15 rather than day 0. This could be a result of differences in the soil and sediment debris which are known to contaminate the coke when stored outside. Although it was not measured in this experiment, there may have been less of this debris in the Suncor coke. However, it is also possible that these results are due to the different physical properties of Syncrude and Suncor coke. Since the samples collected on day 0 were taken within hours of the coke coming in contact with water, it is possible that the larger sized Suncor coke, which has less surface area available for leaching than the same volume of Syncrude coke, did not have sufficient time for the loosely bound metals to leach before the initial sampling. Therefore, a greater concentration of metals was observed later on in the leaching period, rather than immediately as was found with the smaller sized Syncrude coke.

Water rinsed and peroxide treated coke showed little change in metal leaching over all three time points for Syncrude coke. This may be because the pre-treatments (i.e. water rinse and peroxide treatment) effectively removed the metals loosely associated with the coke which would have caused metal concentrations to increase over the duration of the leaching period. Instead, a fairly constant concentration of metals over the three sampling times were observed, which was most likely due to an equilibrium establishing between the coke and the pore water (i.e. the release and reabsorbtion of metals from the coke).

When Suncor coke was used as a substrate, water rinsed and peroxide treated coke tended to mimic the untreated coke by showing spikes in metal concentrations at day 15, before decreasing or remaining relatively constant by day 30. Therefore, equilibrium between the dissolved metals in pore water and those bound to the coke was not established with Suncor coke. However, it is also possible that this result was due to the difference in particle sizes between Suncor and Syncrude cokes as described previously. Therefore, greater concentrations of metals would be observed later on in the leaching period, rather than at the beginning of the leaching period, as was observed with the smaller sized Syncrude coke.

The highest concentrations of metals were observed to leach into the pore water and overlying water from either the untreated or water rinsed coke the majority of the time. Since the water rinse would have removed any soil and sediment debris and loosely bound metals on the coke surface, it may be concluded that a proportion of the metals released was actually from the coke matrix itself. This makes metal concentrations leaching from the rinsed coke comparable to those leaching from the untreated coke. Therefore, we can conclude that a portion of the metals released is coming from the coke itself. There was not a substantial difference between the leaching trends of the water rinsed and peroxide treated coke, therefore the greatest portion of the metals were most likely bound to the surface of the coke in such a way that they were not completely removed by pre-rinsing the coke with water or peroxide.

Some of the highest concentrations of metals (especially on days 15 and 30) were released from coke that had been pre-treated with peroxide. Accelerated oxidation of sediment using H_2O_2 is a recognized practice (Jennings *et al.*, 2000). It has been previously shown to successfully assess the response of common sulfide and sulphate minerals, such as those likely found within coke, under oxidizing conditions (Jennings *et al.*, 2000). The pre-treatments used in this experiment (water and peroxide) were at least partially effective at removing metals as evidenced by the high concentrations of metals sampled in the rinse solutions. A portion of the metals released from the coke into the pore water and overlying water during the 30-d leaching period may, in fact, be partially attributed to metals leaching directly from the coke matrix.

There were some instances (Cu, Mo, and V) where the greatest amount of metal leaching into the pore water and overlying water were not from the untreated coke. In these particular cases the peroxide treatment often leached the most, and untreated the least, amount of metals. Molybdenum and vanadium, as discussed in Chapter 3, have a great affinity for oxygen donors, and if H_2O_2 is added to aqueous solutions these metals have been shown to become more soluble (Greenwood and Earnshaw, 1997). Copper has also been shown to dissolve more readily in aqueous solutions containing H_2O_2 (Greenwood and Earnshaw, 1997). These properties may explain the differences in leaching among the metals discussed in this experiment once coke is pre-treated with a strong oxidizing agent such as H_2O_2. These results also demonstrate the importance of understanding the behaviour of individual metals in an aqueous environment before considering coke as part of an aquatic reclamation strategy.

Total metal concentrations measured within the coke did not appear to change substantially with any of the weathering treatments. The minute changes that did occur could be due to natural variation in the coke, reflecting natural variations in the starting oil sands material. Mass balance calculations showed that none of the metals that leached into the overlying water and pore water exceeded 3% of the total metal present in the coke. These metal percentages are too small to show up as significant changes in the coke itself. These observations are similar to those seen in the experiments described in Chapter 3, and indicate the majority of the metals are most likely contained within the coke matrix, or attached to the coke surface in such a way as to be mostly unavailable using the weathering techniques and rinse durations employed in these experiments.

When analyzed using polarized light microscopy, coke that had been water rinsed appeared to be more fragmented than coke that had been treated with peroxide. The absence of fragmentation in the peroxide treatment was most likely due to the increased number of rinses that the peroxide treatment underwent prior to leaching. The peroxide treated coke was rinsed four times with reconstituted water, then once with peroxide, and finally four additional times with reconstituted water, for a total of nine times. The water rinsed coke was only rinsed four times with reconstituted water. Therefore, the peroxide treated coke underwent five additional shakings and rinses. This additional handling could have caused the smaller coke fragments to be removed along with the rinse water prior to leaching.

Analysis with SEM showed that the surface of the peroxide treated Suncor coke tended to be slightly rougher than the surface of the water rinsed coke. This may be due to the chemical effect of peroxide on the coke surface. Nevertheless, the mass balance calculations suggested that the majority of the metals remained contained within the coke itself. Therefore, the surface effect observed using SEM was not significant in terms of the amount of metal leaching into the pore water and overlying water.

5.4.2 Particle Size Experiment

There were no significant differences in the survival or growth of *C. tentans* when exposed to Syncrude coke and crushed Suncor coke. However, there was a significant decrease in *C. tentans* survival in unmanipulated Suncor coke compared to control sand. Therefore, once the particle size of the crushed Suncor coke was comparable to that of Syncrude coke, its effect on *C. tentans* decreased significantly, making the particle size of Suncor coke an important factor in its adverse effect on this organism. This is most likely due to the inability of *C. tentans* to utilize coarse coke for tube building as effectively as they can smaller sized substrates.

Tube building is initiated by first or second instar larvae by applying salivary secretions along the edge of sediment or algae particles and attaching pieces together. Once several large bundles have been constructed and transferred to its anterior prolegs, the larva crawls through the bundle to form a tunnel. This process continues for one to three hours until the tube is complete (Berg, 1995). Therefore, the substrate particle size has the potential to play an important role in the viability of coke as a substrate amendment by limiting the ability of some aquatic macroinvertebrates to utilize it as a building material for habitat construction.

The larger the particle size, the more unlikely it can be used as a substrate for tube building (Ruse, 2002). Tubes are important for the survival and growth of *C. tentans* as the animals move water through the tubes with their bodies, replenishing oxygen and removing carbon dioxide and metabolites (Pinder, 1995). The ability of chironomids to construct tubes also decreases the risk of predation, and may minimize their dislodgement by currents (Berg, 1995). Therefore, as shown in this experiment, Suncor coke may have too large a particle size for the *C. tentans* to properly utilize it in tube building. This factor could contribute to decreased survival and growth of these and other tube-building organisms if Suncor coke is used as a substrate amendment at the Alberta oil sands without crushing, or without the addition of finer-sized reclamation amendment materials (e.g. peat or reclamation soil). However, the habitat requirements of other aquatic organisms must also be considered as finer particle sized substrates are not ideal for all invertebrates. Therefore, a variety of substrate sizes would likely provide the ideal option when constructing these reclamation wetlands.

5.5 Conclusions

Since most metals in the accelerated leaching experiment initially leached to a greater degree from the untreated coke, it can be concluded that these metals were from either the natural soil or sediment particles that become associated with the coke during storage, or were weakly bound to the surface of the coke. Rinsing the coke with water removed the soil/sediment debris and metals loosely bound to the surface of the coke, thereby reducing the amount of metals subsequently leaching out into the overlying water and pore water. Therefore, rinsing the coke with water before adding it as a substrate amendment in an aquatic reclamation strategy may decrease the potential for toxicity to aquatic organisms by reducing the initial amount of metals available to the organisms in the pore and overlying waters. However, since coke has been shown to contain toxicologically significant amounts of metals, rinsing away debris will not eliminate the potential for metal release from coke into the aquatic environment.

Coke particle size was hypothesized to be one of the major causes of the previously observed decrease in survival and growth of *C. tentans* when Suncor coke was used as a substrate (see Chapter 3). The results from the particle size experiment conducted here showed that once the particle size of Suncor coke was reduced, its adverse effects on *C. tentans* decreased significantly. Reducing the particle size of Suncor coke would therefore allow aquatic macroinvertebrates to utilize it as a substrate for habitat construction during initial colonization in an aquatic reclamation strategy. Based on these results, it would be useful for Suncor to consider either reducing their coke to a smaller particle size before using it as a substrate amendment in an aquatic reclamation strategy, or adding a thin capping material with a finer particle size, such as natural soil or sediment.

6. TOXICITY ASSESSMENT OF FIELD-SAMPLED AND LABORATORY-PREPARED SUBSTRATES COMPRISED OF VARIOUS COMBINATIONS OF OIL SANDS RECLAMATION MATERIALS

6.1 Introduction

One of the major industries in the province of Alberta, Canada, is the oil sands industry. Oil sands, also known as tar sands or bituminous sands, are sand deposits impregnated with dense, viscous petroleum called bitumen. Such deposits are found throughout the world, often in the same geographical areas as conventional petroleum.

One of the primary waste products produced during the upgrading of oil sands to crude oil is coke. Petroleum coke is a solid, carbonaceous residue that forms during the cracking of petroleum distillates (Scott and Fedorak, 2004). The amount of coke produced at the two major Alberta oil sands mining companies, Syncrude Canada Ltd. and Suncor Energy Inc., (over 2,000 tonnes per day per operation) is significantly more than what can be combusted and/or sold. Therefore, the excess coke must be stored on site in coke cells which then become a necessary component of the closure/reclamation landscapes.

The goal of reclamation at the oil sands is to achieve maintenance-free, self-sustaining ecosystems with capabilities equivalent to or better than pre-disturbance conditions (Golder Associates Ltd., 2000). In aquatic ecosystems, the invertebrate community is established early in the successional/developmental process and becomes an integral component of the food web. Thus, the benthic macroinvertebrate community structure in wetlands which receive industrial inputs is relevant to the sustainability of such a wetland (Bendell-Young *et al.*, 2000).

There is concern that the development of a benthic community in aquatic reclamation landscapes receiving industrial inputs from the Alberta oil sands operations will be slower than desired. These industrial inputs (i.e. tailings and sand) which would form the primary substrates of these reclamation landscapes contain little or no organic carbon, a substance required for the development of a sustainable benthic community. It has been previously shown that the extent of benthic colonization positively correlates with the organic carbon content of the sediment (Pinder, 1995). Therefore, a healthy and diverse benthic invertebrate community could not successfully develop without the presence of organic carbon. The abundance of coke, with its high percentage of organic carbon, makes it a very attractive option for use as a substrate in reclamation practices at the Alberta oil sands.

One proposed reclamation strategy at the Alberta oil sands operations is a wetland landscape. This would involve the layering of different waste products (such as tailings) in mined-out areas. The two types of tailings produced at the Alberta oil sands are mature fine tailings (MFT) and composite or consolidated tailings (CT). In one proposal, the tailings layer would be capped by a layer of coke, followed by water. Coke would then act as a buffer between the more toxic tailings and the overlying cap of clean water. A further amendment of peat or overburden (terrestrial soil removed prior to surface mining) has been proposed. This amendment would be placed over the coke layer as a way of providing additional buffering for the tailings layer, and to act as a barrier between the potentially toxic coke and the overlying water cap.

The main objective of the experiments described here was to assess the potential toxicity of both fresh and field-aged combinations of peat, native soil, tailing sand, mature fine tails (MFT) (Syncrude), composite tails (CT) (Syncrude) and coke (Syncrude and Suncor). Combinations of fresh materials were aged in Deep Wetland on the Syncrude Canada Ltd. mine site for a period of 2 and 14 months. A secondary objective of these experiments was to determine if the presence of peat as a capping material affected the potential toxicity of any of the other reclamation materials.

6.2 Materials and Methods

Researchers from the University of Windsor, ON, designed and installed two types of experimental test systems to investigate the viability of using the above-mentioned amendment options in an aquatic reclamation strategy (Baker, 2004). These systems were set up during May of 2002 at the Deep Wetland field research site located on Syncrude Canada Ltd. property near Fort McMurray, AB.

The first of these systems was substrate amendment pits. These small pits were constructed by inserting a bottomless 80 L (40 cm diameter) garbage container 10 cm into the sediment of the wetland. The interior or the container was then excavated and this space filled with various combinations of amendment substances (tailing sand, native sediment, coke (from both Suncor and Syncrude) and peat (obtained from the overburden layer)). After this, the perimeter of the container was marked with bamboo poles stuck into the sediment and marked with flagging tape (Figure 6.1a). Finally, the container was removed and the amendment substances allowed to be in free contact with the surrounding native sediment. The substrate amendment pits allowed for the natural movement of benthic organisms and pore water between the test substrates and the surrounding undisturbed sediment.

The second type of experiment system was plastic totes. These consisted of Rubbermaid® totes (53.0 L) that were filled with various three-layered combinations of peat, native soil, tailing sand, coke, mature fine tailings, and composite tailings, all obtained from Syncrude operations. The totes were inserted into holes dug into the bottom of Syncrude Deep Wetland until they were flush with the surface of the surrounding, undisturbed sediment (Figure 6.1b). This allowed for the movement of benthic organisms along the surface of the sediment into the totes; however there was no opportunity for movement of pore water between the surrounding sediment and test substrates. This could result in more concentrated levels of toxic constituents in the substrate pore water. Such conditions may occur in a worst-case scenario if these amendments were used as part of an aquatic reclamation strategy where they covered the entire wetland bottom.

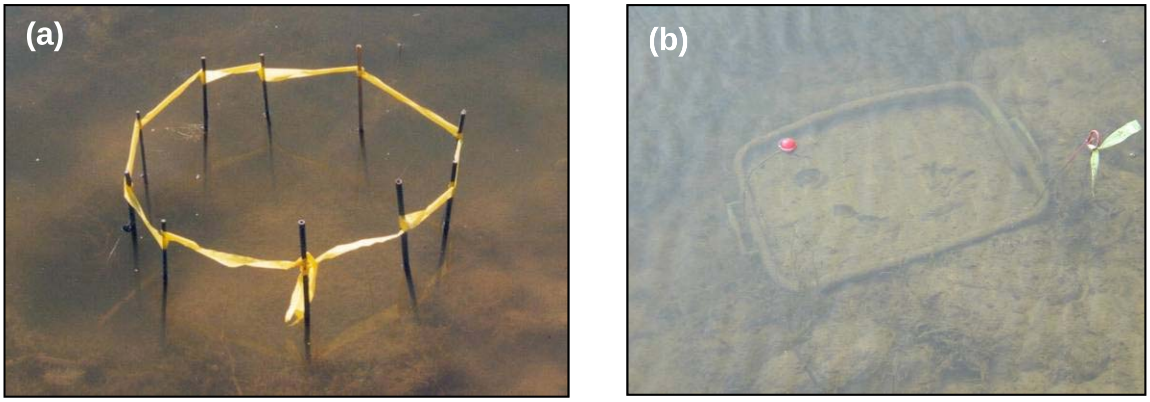

Figure 6.1. Substrate amendment pit (a) and plastic tote (b) units as constructed in Deep Wetland on the Syncrude Canada Ltd. mine site.

6.2.1 Field Samples

During July 2002, two months after construction of the substrate amendment pit units, sediment core samples were collected from various units with different combinations of test substrates. The various combinations of substrates used in the substrate amendment pits that were selected for sampling are shown in Table 6.1. Samples were taken by inserting a clear acrylic tube (length 10.5 cm, diameter 4.8 cm) into the substrates of each unit. When the tube was gently removed, a cap was quickly placed over the bottom as it was brought to the sediment surface, thereby retaining the sample inside the tube. Any headspace at the top of the tube was filled with overlying water from Deep Wetland, before being capped and sealed for transport.

In July 2003, fourteen months after construction of the substrate amendment pit units, core samples were taken from the same units as sampled at 2 months (July 2002), as well as selected tote units (Table 6.2). The tote units had three distinct layers of materials while the substrate amendment pits had only two. However, the core tubes used for sampling were only 10 cm tall, and therefore, were only able to sample the top layer (~2 cm) and part of the middle layer (~8 cm). After collection, core samples were stored at 4ºC and shipped via ground transport to the Toxicology Centre at the University of Saskatchewan, Saskatoon, SK, for testing and analysis. In addition, samples of surface water from Deep Wetland were collected in 10-L plastic containers and shipped to the laboratory along with the sediment cores.

Once samples arrived at the Toxicology Centre, observations were made of the height, texture and layering of each core, and any indigenous fauna were removed. Substrate cores were then carefully transferred into 250-mL glass beakers, taking care to ensure that the different layers remain relatively intact, and beakers were filled with the untreated surface water taken from Deep Wetland at the time of collection. Core samples were allowed to settle, after which time the overlying water was gently aerated overnight, as per Environment Canada (1997) protocol, to ensure that the levels of dissolved oxygen in each beaker were above 40 % saturation before test animals are added.

Table 6.1. Treatment combinations sampled from substrate amendment pits located in Deep Wetland at the Syncrude Canada Ltd. mine site.

Bottom Layer (10 cm)	**Top Layer (2 cm)**
Native Soil	Native Soil
Native Soil	Peat
Tailings Sand	Tailings Sand
Tailings Sand	Peat
Syncrude Coke	Syncrude Coke
Syncrude Coke	Peat
Suncor Coke	Suncor Coke
Suncor Coke	Peat

Table 6.2. Treatment combinations sampled from plastic totes located in Deep Wetland at the Syncrude Canada Ltd. mine site.

Bottom Layer (29 cm)	**Middle Layer (10 cm)**	**Top Layer (2 cm)**
Mature Fine Tailings	Syncrude Coke	Syncrude Coke
Mature Fine Tailings	Syncrude Coke	Peat
Composite Tailings	Syncrude Coke	Syncrude Coke
Composite Tailings	Syncrude Coke	Peat

6.2.2 Laboratory Prepared Samples

In addition to the field-collected core samples described above, complementary samples were prepared in the laboratory, directly in 250-mL beakers, using the same substrate combinations as those sampled from both the field substrate amendment pits and tote units. These samples were prepared immediately prior to testing the field samples collected from the Deep Wetland field site at 14 months. These samples represented fresh (0 months aging in the field) substrate combinations and were run simultaneous with the 14 month field samples to evaluate if the toxicity of these combinations changed over time. The fresh samples were prepared on Day –1 of the experiment, and aerated and allowed to settle exactly as the field samples were in preparation for bioassay testing.

6.2.3 Test Conditions

The animals used in this experiment were the aquatic macroinvertebrate, *Chironomus tentans*. This benthic invertebrate is an ideal choice for these types of tests, since most of its life cycle occurs in the sediment, allowing for increased contact with the test substances.

Chironomus tentans were obtained from a laboratory culture maintained at the Toxicology Centre, University of Saskatchewan. Organisms were cultured in an environmental chamber at a photoperiod of 16:8 h light:dark and a temperature of 23 ± 1°C. The culture was maintained using performance-based techniques according to culturing protocols outlined by Environment Canada (1997). Culture organisms were fed three times per week with Tetramin® fish food slurry. The culture water was carbon-filtered, City of Saskatoon municipal water aerated overnight prior to addition to the culture tanks to ensure that the correct temperature and dissolved oxygen levels were obtained.

Test animals were acquired by aspirating fully emerged adults from the main colony into a 500-mL Erlenmeyer flask. The adults were then transferred to a glass breeding jar containing a piece of Parafilm® floating on a thin layer of culture of water and two strips of plastic netting, thus providing ample surface area for mating. Each morning, the breeding jar was checked for egg masses, which, if present, were then transferred to 10-L glass aquaria (2-3 masses per aquaria) containing a thin layer of rinsed culture sand (particle size 250-425 μm) and aerated culture water. After the first 48 h, animals were fed three times per week with 2.5 ml of a 6 mg/L Tetramin® fish food slurry. After 10 d, larvae (second instar) were transferred from these tanks to glass pans where they were separated from their cases using plastic pipettes before being added to test beakers.

A total of ten 10-d old *C. tentans* larvae were added to each beaker containing a sediment core at the start of the test. For samples collected after field aging for 2 months, tests were run directly in the core tubes used for sampling. Because of low survival in this test, bioassays using the treatment combinations from the substrate amendment pit units aged 0 and 14 months were run in 250-mL beakers as described above.

At the end of all tests, each beaker or tube was assessed for changes in survival and growth (measured as dry weight after 48 h at 60ºC) of *C. tentans* larvae. These were static tests and both dissolved oxygen (mg/L) and temperature (º C) in the overlying water were checked on a daily basis in all test vessels. Overlying water was also sampled (10 mL) on days 5 and 10 for ammonia to ensure that these levels were not so high as to cause toxicity, thereby confounding results. Separate samples of the overlying water (10 mL) were collected and analyzed for alkalinity, hardness, conductivity and pH at the end of the 10 d test to ensure that these variables were within the acceptable range for proper *C. tentans* survival and growth.

6.2.4 Statistics

Statistical analyses were performed using the computer program SigmaStat®, version 3.0 (SPSS Inc., Chicago, IL, USA) at a 95% (α= 0.05) level of confidence. Significant differences among substrate combinations from the substrate amendment pit units for both *C. tentans* survival and growth (dry weight) were assessed for each sampling time (0, 2 and 14 months) using two-way analysis of variance (ANOVA) with substrate type (bottom layer) and presence/absence of peat amendment (top layer) as the two factors. Survival at 14 months failed the test and transformation for normality, so a

Kruskal-Wallis one-way ANOVA on Ranks was used to evaluate differences among treatments. Multiple pairwise comparisons were evaluated with a Holm-Sidak test for both ANOVA tests.

Significant differences among survival and growth (dry weight) of *C. tentans* for different substrate treatments from the tote units for 0 months (fresh) and 14 months (aged) were assessed using one-way ANOVA. The test used for normality was Kolmogorov-Smirnov and the test for homogeneity of variance was the Levene median test. Survival and growth at both 0 and 14 months failed the test and transformation for homogeneity of variances, so a Kruskal-Wallis one-way ANOVA on Ranks was used to evaluate differences among treatments. Multiple pairwise comparisons were evaluated with a Holm-Sidak test.

6.3 Results

6.3.1 Substrate Amendment Pit Units

Survival and growth of *C. tentans* larvae for tests using substrates from the substrate amendment pit units are shown in Figure 6.2. Data for the 2-month sampling time cannot be directly compared to the 0-and 14-month test data due to the differences in test methods (i.e. tested in core tubes vs. beakers). Animals that were removed from the weathered samples consisted mostly of snails. Other fauna may initially have been present, but not observed if they died and decomposed before the cores were analyzed.

No significant differences for either survival or growth of *C. tentans* ($p > 0.05$) were observed between substrate treatments containing peat and those without peat for any sampling time. Furthermore, no significant differences were observed in survival of *C. tentans* for any substrate treatment at each individual sampling time. However, there was poor survival (16.7%) in the 2 month aged treatments compared to the 0 and 14 month substrate treatment combinations. Growth data for this same time point (2 months) show that the growth of *C. tentans* was better than or equal to that observed for the 0 month samples.

Growth of *C. tentans* in the 0 month (fresh) samples was significantly less than in the 14-month aged samples across all substrate types. This trend was also observed in the survival data, excluding the tailings sand treatment, although it was not statistically significant (Figure 6.2a).

Tailings sand and both Syncrude and Suncor coke treatments at 0 months had significantly ($p < 0.05$) lower *C. tentans* growth than the native sediment treatment at this same time point. However, these differences were not observed for any of the treatments at 2 and 14 months. Growth of *C. tentans* was also significantly decreased ($p < 0.001$) in treatments with Suncor coke compared to both Syncrude coke and tailings sand (Figure 6.2b).

Observations on the heights and layering of the core samples from the substrate amendment pits taken after aging for 2 and 14 months in Deep Wetland are listed in Table 6.3. These data show that the thickness of the peat layer in most of the treatments had decreased substantially after aging in Deep Wetland for 2 and 14 months. However, there also appeared to be a trend of organic matter depositing on the surface of some of the treatments without peat previously added, especially after 14 months of aging.

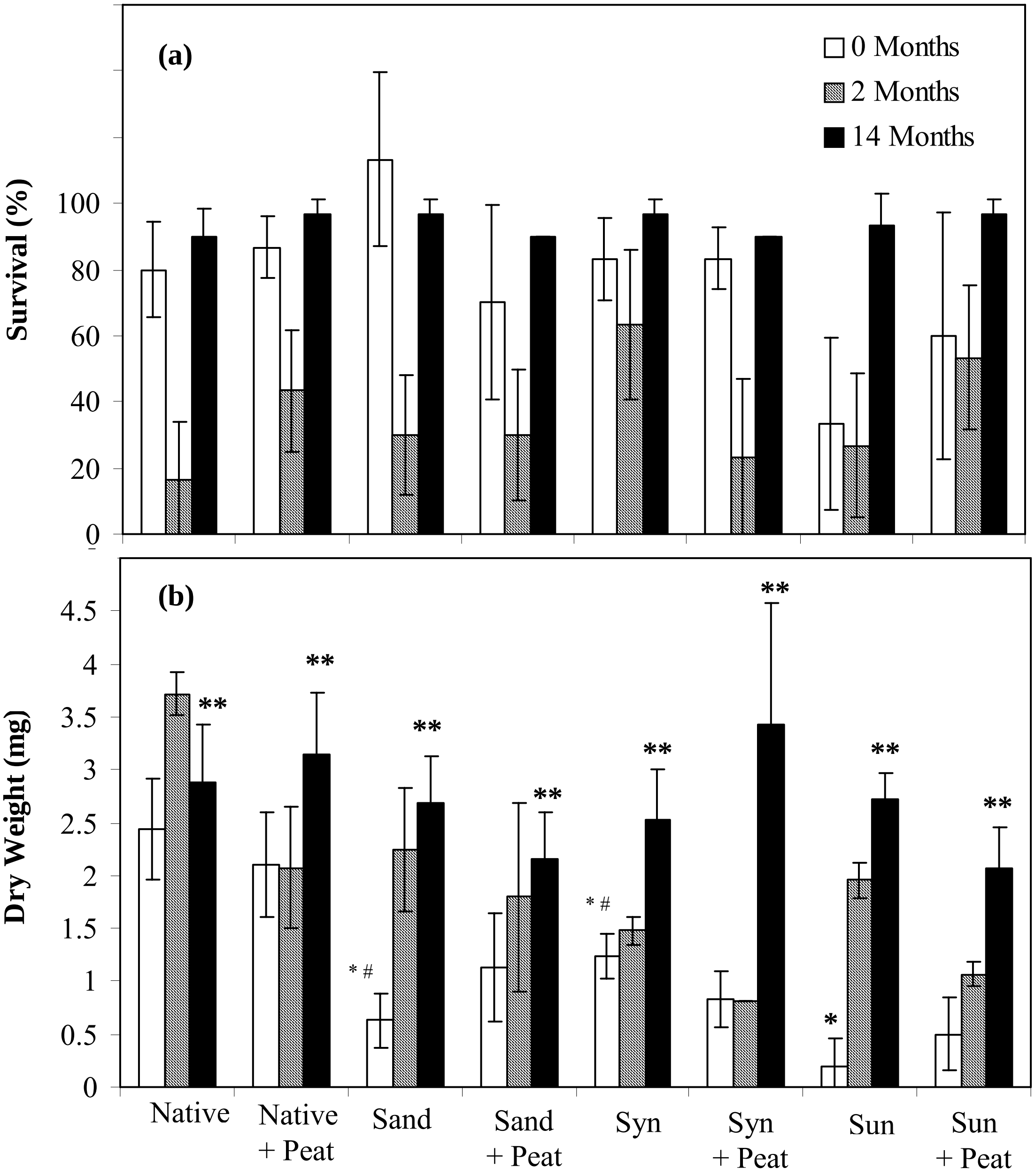

Figure 6.2. Mean (± SE) survival (a) and growth, measured as dry weight, (b) of *Chironomus tentans* larvae after a 10-d bioassay using sediment cores taken from substrate amendment pit units constructed at the Deep Wetland field site at Syncrude Canada Ltd. * Denotes a statistical difference from the native sediment treatment, # denotes a statistical difference from the Suncor coke treatment, and ** denotes a significant difference from the corresponding 0 months aged treatment. Open bars indicate cores constructed using fresh substrates in the laboratory (0 months), and hatched and solid bars indicate cores taken after aging for 2 and 14 months, respectively, at the Deep Wetland field site. (Native denotes the sediment pre-existing at the Deep Wetland field site, sand denotes the tailings sand produced during the bitumen extraction process, Syn denotes Syncrude coke, and Sun denotes Suncor coke).

Table 6.3. Visual observations made on substrate combinations sampled from the substrate amendment pits after aging for 2 and 14 months in Deep Wetland, Syncrude Canada Ltd.

Original Substrate Combination	**Observations after aging for 2 months**	**Observations after aging for 14 months**
Native Soil	-Organic matter (i.e. leaves, grass, small sticks) on top of core samples -Soil layer is 1.5 to 5.7 cm high	-Thin (0.1 cm) layer of organic matter (i.e. leaves, grass, small sticks) on top of core samples -Soil layer is 2.1 to 5.1 cm high
Native Soil + Peat	-Thin brown organic layer on top of core with some grass and leaves present -Soil layer is 1.2 to 4.7 cm high	-Thin brown organic layer on top of cores with some grass and leaves present -Soil layer is 6.0 to 8.2 cm high
Tailings Sand	-No organic matter visible on top of core -Sand is granular, brown with black speaks -Sand layer is 2.5 to 5.7 cm high	-Layer of organic matter (0.1 to 1.0 cm) visible on top of cores -Sand layer is 5.5 to 8.1 cm high
Tailings Sand + Peat	-Thin visible dark brown peat layer -Small sticks and grass on surface of core -Sand layer is 3.9 to 5.5 cm high	-Thin (0.3 to 0.4 cm) visible dark brown peat layer -Lots of small sticks and grass on surface of cores -Sand layer is 3.9 to 5.5 cm high
Syncrude Coke	-Thin light brown/tan layer on top of coke layer -Coke layer is 4.5 to 5.7 cm high	-Thin (0.1 to 1.0 cm) light grey organic layer on top of coke layer -Coke layer is 6.0 to 7.3 cm high
Syncrude Coke + Peat	-Thin layer (0.1 cm) of brown organic matter on top with some grass and leaves -Coke layer is 5.0 to 5.7 cm high	-Thin layer (0.1to 1.0 cm) of brown organic matter on top with some grass and leaves -Coke layer is 6.3 to 8.1 cm high
Suncor Coke	-Some organic matter observed on top of cores (i.e. grass and roots) -Coke is black with large chunks, very porous -Coke layer is 1.5 to 4.5 cm high	-Thin (0.1 cm) light grey organic layer observed on top of cores (i.e. grass and roots) -Coke is black with large chunks, very porous -Coke layer is 4.5 to 7.3 cm high
Suncor Coke + Peat	-Some organic matter on top of cores -Thin uneven dark brown layer on surface -Coke layer is 1.0 to 3.5 cm high	-Some organic matter on top of cores -Thin (0.3 to 0.8 cm) dark brown layer on surface -Coke layer is 4.1 to 6.8 cm high

6.3.2 Tote Units

Survival and growth data for tests with substrate cores from the tote units are shown in Figure 6.3. No significant differences in either survival or growth of *C. tentans* larvae were observed between substrate treatments containing a top layer of peat and substrate treatments without peat. There were also no significant differences in survival or growth between fresh substrate treatments (0 months) and tote substrate treatments aged for 14 months in Deep Wetland. Despite the absence of statistical significance, there was a trend of lower survival and growth of *C. tentans* in the 0 months samples. In addition, the lowest *C. tentans* survival occurred in both of the MFT treatments, with the lowest being in the treatment without the peat layer added.

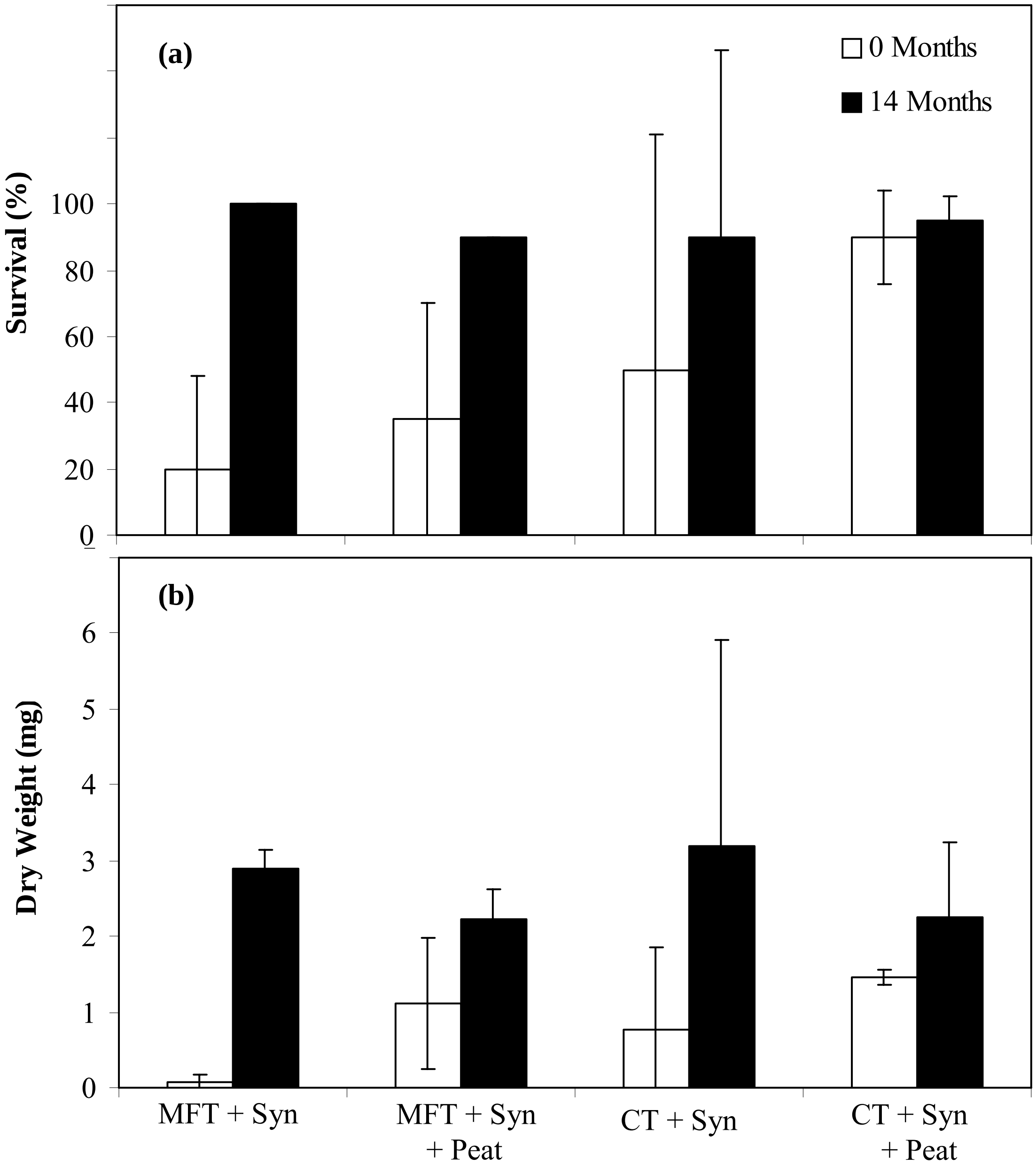

Figure 6.3. Mean (± SE) survival (a) and growth, measured as dry weight, (b) of *Chironomus tentans* larvae after a 10-d bioassay using sediment cores taken from tote units constructed at the Deep Wetland field site at Syncrude Canada Ltd. (solid bars) and sediment cores constructed using fresh substrates in the laboratory (open bars). (Syn denotes Syncrude coke, Sun denotes Suncor coke, MFT denotes mature fine tailings, and CT denotes composite/consolidated tailings).

6.4 Discussion

6.4.1 Substrate Amendment Pit Units

Bioassays with the substrate amendment pit treatment combinations aged for 2 months yielded poor survival of *C. tentans* in the majority of the treatments, but growth of *C. tentans* did not show the same trend. The increased growth of surviving organisms in the native sediment may have been due to decreased competition among test organisms for food and space rather than any direct, positive influence of the test treatment. The lower density of organisms would allow for a greater availability of resources per organism, theoretically translating into an increase in growth per individual.

The influence of density on organism growth has previously been observed in an experiment where the abundance of *Chironomus plumosus* larvae was artificially increased. In this experiment, growth and development of larvae was negatively impacted by increasing population density. It was concluded that the exploitation of food resources was the main cause of this result (Tokeshi, 1995). A separate field study conducted with *Chironomus riparius* also showed that growth rate was retarded by density and that this, in turn, could affect the number of generations produced during a season (Rasmussen, 1985).

There were no statistical differences in observed survival of *C. tentans* between the 0 and 14 month aged treatments for any substrate type in the substrate amendment pit units. This was, at least in the majority of cases, most likely due to the high standard error for this endpoint (Figure 6.2a). High standard error is common in tests with field-collected substrates (Conquest, 2000), so these results were not completely unexpected.

There was a statistically significant increase in growth of *C. tentans* in 14 month aged treatments when compared to fresh, 0-month treatments (i.e. unweathered), for every substrate type in the substrate amendment pit units. This observation is promising since it implies that any adverse effects of using these substrate combinations may decrease overtime when they are placed in an aquatic environment. Previous research with field soils confirms the hypothesis that toxicant bioavailability decreases with the amount of aging it undergoes (Lock and Janssen, 2003). Environmental variables such as pH, soil moisture content, drying and rewetting cycles, and temperature seem to have the greatest affect on the rate of aging and detoxification (Lock and Janssen, 2003).

A significant difference in *C. tentans* growth between aged and fresh native sediment was unexpected. However, water saturation to near 100% at the sediment surface for a substantial part of the year (as occurs in wetland areas) limits oxygen diffusion deep into the soil. As a result, available dissolved oxygen is consumed by microbial respiration, creating an environment with a high biochemical oxygen demand (BOD) (Gambrell, 1994). The BOD is defined as a measure of the amount of oxygen (in mg O_2 per litre of water) used up during oxidation by aerobic bacteria (Schwedt, 2001). The fresh native sediment used in these experiments was sampled directly as wet sediment from Deep Wetland and stored in sealed pails for approximately a year before being utilized as a substrate in this experiment. This could have maintained a high BOD and consequently, may have contributed to the differences in toxicity between the non-weathered and weathered treatments. Although the overlying water for both fresh and aged samples was aerated and allowed to sit for 24 h before adding the test organisms, the level of dissolved oxygen in the pore water (unmeasured) of the native sediment may have been lower than that required for the "normal" growth of *C. tentans*. This would not have been the case for the remaining substrates (sand, Syncrude coke and Suncor coke) since these were sampled and stored in sealed pails as dry materials.

There was a significant difference in the growth of *C. tentans* between Suncor coke and Syncrude coke for the 0 months (fresh) treatments. These differences were not seen for the 14 months aged treatments. Weathering (aging) may cause the lighter, coarser parts of Suncor coke to be washed away, decreasing the overall particle size of this treatment. This was illustrated by the large amounts of Suncor coke observed to be floating and congregating on the water surface at the ends of Deep Wetland immediately after construction of the substrate amendment pits. A smaller particle size may make Suncor coke a more hospitable environment for the growth of *C. tentans* larvae. However, this phenomenon does create the potential for toxicants to be spread through connected wetland areas if the overlying water containing the floating Suncor coke is able to flow between them.

There were no statistical differences in the survival or growth of *C. tentans* between substrates with or without a peat amendment for any of the substrate combinations tested. This may be because the lighter density of the peat caused some of it to be washed "downstream" (much like some of the Suncor coke layer) in the wetland and away from the substrate amendment pits after their construction. This resulted in less of the peat actually staying on the surface of the substrate amendments as observed in the core samples taken after aging for 2 and 14 months (Table 6.3). In some cases, although peat was still present on the surface of the cores, the thickness of some of the peat layers had decreased substantially after aging for 14 months.

6.4.2 Tote Units

No significant differences in either survival or growth of *C. tentans* were observed between treatments aged for 0 and 14 months. However, there was a general trend of lower survival and growth in the fresh substrates (0 months) versus those aged for 14 months for all substrate treatment types. This observation parallels trends observed with the substrate combinations tested in the substrate amendment pit units.

The 14 months aged substrates from in Deep Wetland had the opportunity for toxicants contained within these substrates to leach out and be "washed" away or diluted with the overlying water. Conversely, the fresh substrates were only capped with the clean water added to each test beaker (200 mL) prior to the bioassay. Therefore, any potentially toxic constituents that could readily leach out of these substrates would be concentrated in a much smaller volume of water compared to the aged treatments in Deep Wetland.

The research of Nix and Martin (1992) found that in test tanks containing oil sands tailings, detoxification occurred though the migration of toxic compounds from the tailings layer into the overlying water. It is probable that the trends of lower survival and growth of *C. tentans* as observed in the tote unit samples was due to the leaching of toxicants from the substrate layer into the overlying water. The fresh treatments did not have the opportunity for detoxification by leaching into the wetland, like the 14 months aged treatments, before their exposure to *C. tentans*.

In the fresh, 0 month aged treatments there was lower *C. tentans* survival in both of the MFT treatments compared to the CT treatments, with the lowest being in the MFT treatment without the peat layer added. This lower *C. tentans* survival in the MFT treatments could be a result of the greater water content of MFT (65% water in MFT versus 42% water in CT) (MacKinnon, 1989; Matthews *et al.*, 2000). As the solids in the MFT slowly consolidate in the tote units, the interstitial water, which contains potentially toxic constituents, forms a layer on top of the solids. This water layer can then migrate through the coke and peat layers and potentially reach the clean overlying water cap (van den Heuvel *et al.*, 1999; Matthews *et al.*, 2000). However, the trend of lower toxicity in the peat-capped treatments implies that peat has the potential to either provide an adequate buffer by binding the toxic constituents found in the coke and/or tailings layers before they reach the clean water cap, or it can provide an adequate base (i.e. organic matter and particle size) for improved survival of *C. tentans*.

6.5 Conclusions

Overall, there were few statistically significant differences in the survival and growth of *C. tentans* when these animals were exposed to different substrate combinations from the substrate amendment pit units. However, there was a significant decrease *C. tentans* growth in the fresh treatment (0 months) compared to the aged treatment (14 months). This observation implies that the toxicity, or stress caused by different oil sands waste products, once used as part of an aquatic reclamation strategy, can decrease with the amount of aging or weathering it undergoes.

There is the potential for greater initial stress or toxicity to aquatic organisms when the substrates are freshly added to the reclaimed wetlands. Colonization of reclaimed wetlands by benthic invertebrates may therefore initially be slow. As a result, a detoxification (aging) period may have to occur prior to colonization to allow for the potential toxicity of the substrates to decrease to a more viable level.

There was a trend of increased survival and growth in substrates from the tote units capped with peat versus those without peat. This peat layer may have provided a buffer between the coke/tailings layer and the overlying water cap. Having an additional layer over the more toxic substrates (such as tailings and coke) could reduce the leaching of toxic constituents from the waste material into the overlying water, thus reducing exposure and potential toxicity to aquatic organisms. However, this hypothesis should be further evaluated in order to ensure that using a capping option, such as peat, in future aquatic reclamation practices at the Alberta oil sands is both worthwhile and ecologically viable.

Previous research has identified the nature of the substrate as an important factor influencing patterns of Chironomid distribution and community structure. Although some organisms display habitat preferences for certain sediment characteristics, such as particle size, many species of *Chironomus* are capable of adapting to and utilizing a variety of substrate types (Pinder, 1995). Nevertheless, it is possible that the differences in *C. tentans* growth seen in this study were a result of the physical characteristics of the substrates, rather than the presence of toxic constituents. Dissolved oxygen levels in some substrates (unmeasured) may also have been low and thus caused some level of stress. However, most tube-building Chironomidae can counteract this phenomenon by raising the openings of their tubes above the level of the sediment. This allows them to maintain an adequate concentration of dissolved oxygen by using their bodies to drive fresh water through the tubes. This mechanism replenishes oxygen while flushing out metabolites and carbon dioxide (Pinder, 1995).

Based on the results obtained in these experiments, there is little reason to suspect that exposure to aged oil sands materials would substantially impede the colonization of reclamation wetlands by benthic macroinvertebrates, such as *Chironomus tentans*. However, the amounts of waste materials used in the construction of the substrate amendment pits and tote units may have been too small to accurately assess the impacts from a full-scale aquatic reclamation program. The greater amount of waste material that would be used in the construction of these wetlands could possibly produce a significant effect once placed in an aquatic environment. It is recommended that a larger scale reclamation study using more realistic amounts of waste materials (relative to the volume of overlying water) be conducted to better determine the potential impacts of these waste inputs on the associated aquatic ecosystem.

7. GENERAL DISSCUSSION

7.1 Project Rationale

The goal of reclamation at the Athabasca oil sands is to achieve maintenance-free, self-sustaining ecosystems with capabilities equivalent to or better than pre-disturbance conditions (Golder Associates Ltd., 2000). The main sources of toxicity from the oil sand mining process to the surrounding ecosystem have been identified as the tailings (fine and coarse), process water, sulfur, and coke. Both Suncor and Syncrude maintain a no discharge policy in regards to these contaminants. Therefore, these waste products are stored on site until reclamation occurs.

The waste product coke is produced during the heavy oil upgrading processes. Syncrude Canada Ltd. uses an unconventional continuous fluid coking system, involving the use of both a reactor and a burner. Suncor Inc. uses a delayed coking process, which is a 'batch by batch' procedure with each coker unit containing a heater and a pair of drums.

The amount of coke produced currently at the Syncrude and Suncor operations (over 2,000 tonnes per operation per day) is significantly more than can be combusted and/or sold. Therefore, it must be stored on site in "coke cells" and these then become a necessary component of the reclamation landscapes. Coke contains a high amount of organic carbon. The additional input of organic carbon is useful for the timely development of sustainable wetlands on old oil sands leases where organic matter is not very abundant. As a result, the abundance of coke, with its high percentage of organic matter, makes it a very attractive option for use in the aquatic reclamation process.

It is as yet unclear whether or not coke poses a significant toxicological risk (i.e. through leaching of constituent chemicals and elements) to the aquatic or terrestrial environments if used in a long-term reclamation capacity. The primary objective of this research was to evaluate whether stockpiled Syncrude Canada Ltd. and Suncor Energy Inc. coke can safely and effectively be used as a substrate amendment in an aquatic reclamation option.

7.2 Leaching Experiments

7.2.1 Leachability of Coke

Several aging/weathering experiments were conducted as part of this thesis to determine under what conditions coke would most likely release potentially toxic constituents into the surrounding reclamation landscape. This was done by exposing the coke to different overlying water quality conditions (i.e. DO, pH and freeze-thaw) for periods of 30 or 90 days. These treatments were designed to better assess the extent to which toxicants are released from the coke in an aquatic environment and to identify what conditions are most important when considering coke as a substrate amendment in a reclamation landscape.

Upon the exposure of coke to water, an immediate release (i.e. within a few hours) of metals was measured in both the pore water and overlying water. After this initial release, metal concentrations tended to increase in overlying waters and at the same time, decrease in the coke pore waters over the remainder of the leaching period. This resulted in the establishment of near equilibrium conditions between the pore and overlying water phases presumably since metals released into pore waters can diffuse into the less concentrated overlying waters (Barna *et al.*, 2005). This shows the potential of coke to leach toxic constituents into the environment if incorporated as a substrate amendment in an aquatic reclamation program.

Coke from the Syncrude operations tended to release higher concentrations of metals into the pore water and overlying water than coke from the Suncor operations. This could be due to differences in particle size between the two coke types. Syncrude coke has a much smaller particle size than Suncor coke. Therefore, there is more surface area available for leaching to take place with Syncrude coke compared to the same volume of Suncor coke.

Some metals which were identified to be of particular concern in these leaching experiments were cobalt, copper, manganese, molybdenum, nickel, vanadium and zinc. These elements reached concentrations in the pore water and overlying water that are considered to be toxicologically relevant (i.e. higher than the CWQG and published LC_{50} values for *Chironomus* sp.). However, elemental analyses of weathered versus unweathered coke showed that the greatest mass ($\geq$ 69%) of metals still remained within the coke itself. The concentrations of trace metals found within the coke did not appear to change substantially as a result of any of the weathering treatments. The small changes that did occur can likely be attributed to the natural variation in coke that occurs due to the variations in the starting oil sand material (i.e. bitumen). Since there were no substantial changes in the elemental composition of coke between weathered and unweathered samples, it can be assumed that the majority of the metals are either bound tightly or trapped within the coke matrix, or they are attached to the coke surface in such a way as to be unavailable using the weathering techniques and test durations employed in these experiments.

There were few differences between the leaching patterns of metals from coke among the different water quality conditions (dissolved oxygen, pH and freeze-thaw cycles) evaluated as part of this thesis. The treatment which showed the greatest influence on metal leaching from coke was pH. In the pH leaching experiment, the majority of metals leached to a greater extent at low pH. This suggests that trace metals may leach from coke once placed in an acidic, aqueous environment. This is a real a possibility in a reclamation situation, where the overlying waters will have pH levels as low as 6 due to layering with other waste products such as tailings (Golder Associates Ltd., 2000). It is recommended that this variable be monitored in future studies to better assess its potential impact on the leaching of metals from coke in an aquatic reclamation wetland.

7.2.2 Accelerated Weathering Experiment

The immediate release of metals when coke was exposed to water in the dissolved oxygen, pH and freeze-thaw leaching experiments was hypothesized to be from one or all of three sources. These are: (i) metals associated with the natural soil or sediment contaminating the coke during storage: (ii) metals that were weakly bound to the surface of the coke, and/or (iii) metals bound or trapped within the coke matrix itself. To determine from which of these sources this immediate release of metals was originating, cokes from both Syncrude and Suncor were pre-treated before being leached for 30 days. Coke was either rinsed with water to remove natural soil/sediment debris, or rinsed with water and then treated with peroxide which removed both the natural soil/sediment debris and any metals weakly bound to the coke surface.

Even though leaching occurred from all treatments (untreated, water rinsed and peroxide treated) for most metals, the highest concentrations were observed to leach from the untreated and water rinsed coke. Rinsing the coke with water before leaching should have removed any soil and sediment debris, as well as any weakly surface bound metals. Therefore, metals which leached from water rinsed coke must have been either bound to the coke surface in such a way as to not be released through rinsing alone, or these metals leached directly from the coke matrix.

There was a greater concentration of metals at the begining of the leaching period in the untreated coke, but not in the water rinsed coke. Rinsing the coke could have removed soil and sediment debris, thereby reducing the amount of metals leaching into the pore water and overlying water. This decreased the potential toxicity of coke to aquatic organisms by reducing the amount of metals leaching into the pore water and overlying water. Therefore, the potential toxicity of coke if used as a substrate in an aquatic reclamation strategy may be reduced by pre-rinsing with water.

7.3 Toxicity of Coke in an Aquatic Environment

7.3.1 Toxicity of Coke and its Leachate to *C. tentans*

On the last day of each leaching experiment, a 10-d toxicity test using the aquatic macroinvertebrate, *Chironomus tentans*, was conducted. For each treatment, the combination of coke and leachate, as well as the leachate independently were tested. This allowed for the effects (both lethal and sublethal) of coke and its leachate to be assessed separately.

In these experiments, Suncor coke had a significant negative effect on *C. tentans* survival and growth when used as a substrate. However, these reductions were not seen in treatments containing leachate without the presence of Suncor coke as a substrate. Therefore, it was concluded that these effects were due to the physical properties of the coke itself (i.e. particle size), rather than any potentially toxic constituents which leached from the coke into the overlying water.

Macroinvertebrates such as *C. tentans* need to build tubes or burrows in or on the sediment/substrate in order to successfully feed, breathe and protect themselves from predation (Hare *et al*., 2001). In treatments containing Suncor coke as the substrate, *C. tentans* had difficultly building tubes due to the larger particle size of Suncor coke. Therefore, the stress created from the inability of these invertebrates to construct proper tubes may have produced the significant decrease in both survival and growth of *C. tentans* observed in the treatments using Suncor coke as the substrate.

Results from the leaching experiments showed that Syncrude coke had a higher concentration of trace metals leaching into the pore water and overlying water than Suncor coke. However, despite this greater potential for toxicity, no significant toxic effects were seen in any of the *C. tentans* tests. Instead, a significant positive effect on the growth of *C. tentans* was observed in the treatments containing Syncrude coke as a substrate. Therefore, the compounds released into the leachate waters from Syncrude coke were either not in a biologically active or available form, or the test animals used in these experiments were able to tolerate the respective metal exposure concentrations.

7.3.2 Influence of Particle Size on the Toxicity of Coke to *C. tentans*

Particle size was thought to be one of the major reasons for the decreased survival and growth of *C. tentans* observed when Suncor coke was used as a substrate. To address this hypothesis, Suncor coke was crushed to a size comparable to that of Syncrude coke. These coke types, along with control sand and uncrushed Suncor coke, were used as substrates in a 10-d toxicity test with *C. tentans*.

This experiment showed that once the particle size of Suncor was reduced, its effect on *C. tentans* decreased significantly. Based on these results, it may be useful for Suncor to crush their coke to a smaller particle size before using it as a substrate amendment in an aquatic reclamation strategy. Reducing the particle size of Suncor coke, or covering it with a finer particle layer, would allow aquatic macroinvertebrates living in this substrate to better utilize it for habitat construction, thus increasing the success of initial substrate colonization in an aquatic reclamation strategy.

7.4 Field Experiments

Two types of experimental field systems were implemented at the Deep Wetland field research site located on Syncrude Canada Ltd. property. These systems were used to investigate the viability of using waste products from the Alberta oil sands as amendment options in an aquatic reclamation strategy. The first of these systems were substrate amendment pits which consisted of a hole dug into the natural sediment of the wetland and filled with various combinations of oil sands waste materials. The second type of experiment units were plastic totes that were filled with various three-layered combinations of substrates and inserted into holes dug into the sediment of Deep Wetland.

Core samples from the different substrate combinations from the substrate amendment pits and tote units were collected at different points over two field seasons (2002 and 2003). Toxicity tests using *C. tentans* were run with these samples, along with samples that were prepared with fresh materials in the laboratory. This was done in order to compare the toxicity of fresh substrates with those that had aged in the field for 14 months.

Overall, there were few statistically significant differences in the survival and growth of *C. tentans* when these animals were exposed to different substrate combinations from the substrate amendment pit units. However, there was a significant decrease *C. tentans* growth in the fresh treatment (0 months) compared to the aged treatment (14 months). This observation implies that the toxicity, or stress caused by different oil sands waste products, once used as part of an aquatic reclamation strategy, can decrease with the amount of aging or weathering it undergoes.

Results from these experiments showed the potential for acute toxicity to aquatic organisms when reclamation substrates are initially added to a reclamation wetland. Colonization of a reclaimed wetland by benthic invertebrates may therefore be slow due to this toxicity. A period of detoxification may have to occur prior to adding waste materials to a reclamation wetland. Allowing the substrates to age may reduce their initial toxicity to aquatic organisms to a level viable for the sustainability of aquatic reclamation landscapes.

7.5 Toxicology of Metals of Concern

Cobalt: The reported 96-hr LC_{50} for cobalt to fathead minnow (*Pimephales promelas*) is 91.9 mg/L (Marr *et al*., 1998). Few studies appear to exist that assess the toxicological impacts and mode of action of cobalt in aquatic organisms. Due to this lack of data, Canadian Water Quality Guidelines for the protection of aquatic life have not been developed.

Copper: Copper is considered an essential metal. Therefore, many aquatic organisms have developed strategies to regulate their body Cu concentrations (Rainbow and Dallinger, 1993). Copper may bind to nitrogen and sulfur atoms in the proteins of aquatic macroinvertebrates (Borgmann and Norwood, 2002). Accumulation of copper in *Chironomus riparius* larvae has been shown to cause significant growth impairment at exposure concentrations of 0.09 mg (Timmermans *et al*., 1992). Accumulation of copper in the gills of freshwater fish has been shown to inhibit Na ion influx and reduce Na-K ATPase activity (Santore *et al*., 2001).

Manganese: A study conducted by Fargašová (1997) found that the 96-hr LC_{50} of manganese for *Chironomus plumosus* larvae was 0.055 mg/L. Manganese activates an essential part of enzyme systems that metabolize proteins and energy in all animals (Reimer, 1998). It concentrates in the mitochondria and is therefore present in higher concentrations in tissues rich in mitochondria. Manganese concentrations in fish tissue were found to be higher in liver and gill tissue than in muscle tissue (Reimer, 1998).

Molybdenum: At sufficiently low concentrations, molybdenum is a required micronutrient (Naddy *et al*., 1995). In a study conducted by Khangarot (1991) the 96-hr LC_{50} for the worm *Tubifex tubifex* was 28.91 mg/L. Although the mode of toxicity in aquatic invertebrates is not currently understood, molybdenum has been shown to inhibit copper uptake in mammals (Whiting *et al*., 1994).

Nickel: *Chironomus riparis* larvae have been shown to be relatively tolerant of nickel concentrations when compared to other species (Powlesland and George, 1986). Nickel has been shown to bind to oxygen atoms in protein ligands of aquatic organisms (Borgmann and Norwood, 2002). Nickel is considered a respiratory toxicant in fish by causing significant damage to gills, thereby impairing gas exchange, leading to suffocation (Pane *et al*., 2003).

Vanadium: Little data are available on the impact of vanadium on aquatic organisms (Ringelband, 2001). However, a study conducted by Fargašová (1997) found that the 96-hr LC_{50} for *Chironomus plumosus* larvae was 0.24 mg/L. Vanadium has been shown to have inhibitory effects on the activity of the membrane-bound enzyme Na, K-ATPase of the brackish water hydroid *Cordylophora caspia* (Ringelband, 2001).

Zinc: The genus *Chironomus* can regulate the bioaccumulation of zinc, as it is an essential metal (Rainbow and Dallinger, 1993). However, Zn concentrations in *C. riparius* larvae of 2500 ug/g dry weight has been shown to significantly decrease their normal development and growth (Timmermans *et al*., 1992). The mode of action for acute Zn toxicity in fish has been identified as hypocalcaemia, which is a decreased blood concentration of Ca due to competition with Zn at Ca channels (de Schamphelaere and Janssen, 2004a).

7.6 Integration of Results

As part of the proposed aquatic reclamation strategy at the Alberta oil sands, coke would be used as one substrate layer in a wetland landscape. The possible long-term effects that the waste product coke could produce on an aquatic environment have not been investigated previously. Laboratory leaching studies conducted as part of this thesis provide the first insight into the possible chemical and biological impacts of coke on an aquatic environment. Results demonstrated that Syncrude and Suncor cokes contain metals that can leach into the surrounding environment if used as a substrate in an aquatic reclamation program. Some of these metals exceeded published LC_{50} values for *Chironomus* species and Canadian Water Quality Guidelines for the protection of aquatic life, showing that coke has the potential to pose a significant risk to biota if used as part of an aquatic reclamation strategy at the Alberta oil sands.

Further experimentation with coke showed that a portion of the metals could be leaching from the soil or sediment debris associated with the coke, or from metals bound to the surface of the coke, which are then immediately dissolved after coming into contact with water. Field experimentation showed the potential for the toxicity of oil sand waste materials to decrease with weathering in a natural aquatic environment. Therefore, the potential impact of incorporating coke as a substrate in an aquatic reclamation strategy appears to be greatest shortly after incorporation. It is therefore recommended that either active rinsing or a period of leaching be applied before coke is used as a substrate in an aquatic environment. However, the potential for metals leaching directly from the coke matrix after coke is allowed to weather for an extended period of time must be considered. This may be a possible source of risk when applying coke as a substrate in a permanent reclamation wetland.

Despite the potential for toxic effects on aquatic biota living in wetlands constructed using coke as a substrate, experiments conducted as part of this thesis did not observe any direct effects on the aquatic macroinvertebrate *C. tentans* as a result of the release of metals from coke into pore water and overlying water. This could be a result of the test species chosen for these experiments. Due to their ability to regulate some metals, *C. tentans* is not considered to be the most sensitive species for evaluating the effects of metal toxicity in an aquatic environment (Besser and Rabeni, 1987). Furthermore, the endpoints (survival and growth) used to evaluate the toxicity of coke to *C. tentans* are not as sensitive as those that can be evaluated in a longer duration toxicity experiment. Therefore, a life-cycle experiment evaluating the effects of coke leachate on the reproduction and behaviour of these insects may have shown some toxic effect from the metals measured in the coke leachate.

Even though no toxic effects could be attributed to the coke leachate, some decreases in the growth and survival of *C. tentans* were observed when Suncor coke was used as a substrate in toxicity tests. These decreases may lead to effects on the populations of future generations, thereby decreasing the long-term effectiveness of using coke as a substrate in reclamation wetlands at the Alberta oil sands. In addition, the particle size of Suncor coke was shown to contribute to its effects on *C. tentans*. Therefore, either reducing the particle size of Suncor coke, or supplementing this substrate with a smaller sized substrate layer, should reduce these negative effects.

7.7 Recommendations for Future Work

Leaching experiments conducted as part of this thesis looked at the effect of different overlying water conditions (DO, pH and freeze-thaw) on the leaching of potentially toxic constituents from coke. There are, however, other general water quality conditions, such as water hardness and dissolved organic carbon, (DOC) that should also be evaluated before coke should be considered for use as part of an aquatic reclamation strategy. Water hardness and DOC have been shown to be important in influencing the bioavailability of metals and other toxic constituents in aquatic systems (Chirenje and Ma, 1999). Therefore, further leaching studies, such as those conducted in this thesis, should be considered as a way to assess the effects of these variables on the leaching potential of coke.

Based on the bioavailability and consequent toxicity of constituents within coke to aquatic organisms, toxicity threshold levels should be established to determine if the constituents leaching from coke during an aquatic reclamation strategy at the Alberta oil sands have the potential to impair aquatic biota. These thresholds could be based on either pre-existing or newly developed long-term aquatic toxicity data. It is important to consider the most sensitive test species and endpoint (such as reproduction) when conducting toxicity testing to establish thresholds. The data used to develop these thresholds should be specific to the northern Alberta environment, which may already contains background levels of these constituents as part of the natural oil sand deposits. Thresholds can provide an accurate way of quantatively determining the risk of using coke in an aquatic reclamation strategy.

As part of the field studies conducted in this thesis, a trend of decreasing toxicity was seen for substrates capped with a layer of peat versus those without this capping layer. The peat layer may have provided a buffer between the waste amendments layer and the overlying water. This would theoretically reduce the leaching of toxic constituents from the waste material (coke) into the overlying water, thus reducing contaminant exposure and potential toxicity to aquatic organisms. Since the findings discussed in this thesis could not verify statistically that an overlying layer of peat can reduce the toxicity of oil sands waste to aquatic organisms, it is important that further research be conducted to confirm this hypothesis. Both field and controlled laboratory studies comparing the addition of peat as an additional substrate layer over coke would be useful in determining if peat does indeed provide a significant positive effect when coke and other waste materials are used as substrates in future aquatic reclamation practices at the Alberta oil sands.

Using indigenous *C. tentans* populations from the oil sands region in toxicity testing should also be explored. Indigenous organisms may have built a tolerance to existing background levels of oil sands toxic constituents in order to adapt and survive in this area. Using these organisms in future toxicity experiments with oil sands waste materials may help to differentiate between the impact of increased loading of toxic constituents from using coke as part of an aquatic reclamation strategy, and those present due to the oil sand deposits found naturally in the Athabasca region (Groenendijk *et al*., 2002).

The discrepancies between conclusions drawn from the chemical data (i.e. metal leaching) and biological data (i.e. growth and survival of *C. tentans*) limit our ability to draw definite conclusions about the viability of using oil sands coke as a substrate amendment in an aquatic reclamation strategy. Often, laboratory studies have limitations because their design can not account for many of the chemical and biological complexities of the natural systems being considered. In these systems, the metal concentrations and animals vary over time, therefore predicting toxicity in nature on the basis of laboratory toxicity tests can be difficult (Hare, 1992). Long-term weathering/leaching studies using coke as a substrate should therefore be conducted to address these discrepancies. With these studies, the effects of the release of toxic constituents from coke on different trophic levels within an aquatic ecosystem could be more accurately assessed. The results obtained from these experiments could aid in predicting the behaviour of coke and the metals leaching from the coke if used as part of a long-term aquatic reclamation strategy at the Alberta oil sands.

Based on the results obtained from toxicity experiments conducted as part of this thesis, there is little reason to suspect that exposure to aged oil sands materials would impede the colonization of reclamation wetlands by benthic macroinvertebrates, such as *Chironomus tentans*. However, a greater amount of waste material would be used during the construction of full-scale reclamation wetlands. This additional loading may alter the effects of coke on the surrounding aquatic system. It is therefore recommended that a reclamation study using larger, more realistic amounts of waste materials be conducted to better determine the impacts these waste inputs would have on the surrounding aquatic ecosystem.

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APPENDIX A: Mean ± SE metal concentrations (µg/L) from the dissolved oxygen leaching experiment using Syncrude (a) and Suncor (b) cokes. (*n* = 3) (BDL = below detection limit)

(a)	**Treatment**	**Al**	**As**	**Au**	**Ba**	**Ca**	**Ce**
Pore Water	High Dissolved Oxygen Day 0	BDL	BDL	BDL	1.1 ± 0.5	5416.9 ± 1465.6	BDL
	High Dissolved Oxygen Day 10	BDL	BDL	BDL	0.7 ± 0.3	4212.2 ± 226.4	BDL
	High Dissolved Oxygen Day 30	BDL	BDL	BDL	1.0 ± 0.1	6676.2 ± 264.9	BDL
	Low Dissolved Oxygen Day 0	BDL	0.6 ± 0.0	BDL	1.5 ± 0.3	6469.9 ± 597.3	0.0 ± 0.0
	Low Dissolved Oxygen Day 10	BDL	BDL	BDL	1.0 ± 0.1	5347.0 ± 591.3	BDL
	Low Dissolved Oxygen Day 30	4.5 ± 0.0	BDL	BDL	1.5 ± 0.2	6632.2 ± 297.8	0.0 ± 0.0
Overlying Water	High Dissolved Oxygen Day 0	BDL	BDL	BDL	0.3 ± 0.0	2911.2 ± 58.7	BDL
	High Dissolved Oxygen Day 10	BDL	BDL	BDL	1.1 ± 0.7	3708.4 ± 567.1	BDL
	High Dissolved Oxygen Day 30	13.8 ± 0.0	BDL	BDL	0.6 ± 0.0	4365.3 ± 320.0	BDL
	Low Dissolved Oxygen Day 0	BDL	BDL	BDL	0.3 ± 0.1	3436.5 ± 21.9	BDL
	Low Dissolved Oxygen Day 10	17.6 ± 0.0	BDL	BDL	0.8 ± 0.2	3554.1 ± 180.1	BDL
	Low Dissolved Oxygen Day 30	8.6 ± 0.0	BDL	BDL	0.5 ± 0.0	4983.2 ± 148.8	0.0 ± 0.0

(b)	**Treatment**	**Al**	**As**	**Au**	**Ba**	**Ca**	**Ce**
Pore Water	High Dissolved Oxygen Day 0	BDL	BDL	BDL	0.4 ± 0.0	3246.4 ± 25.1	BDL
	High Dissolved Oxygen Day 10	27.9 ± 0.0	BDL	BDL	0.7 ± 0.0	5418.9 ± 1793.1	BDL
	High Dissolved Oxygen Day 30	BDL	BDL	BDL	0.5 ± 0.0	6483.0 ± 57.2	BDL
	Low Dissolved Oxygen Day 0	BDL	BDL	BDL	BDL	3074.6 ± 28.8	BDL
	Low Dissolved Oxygen Day 10	BDL	BDL	BDL	0.2 ± 0.0	3926.0 ± 187.1	BDL
	Low Dissolved Oxygen Day 30	9.3 ± 0.0	BDL	BDL	0.2 ± 0.0	7395.0 ± 308.2	BDL
Overlying Water	High Dissolved Oxygen Day 0	BDL	BDL	BDL	0.2 ± 0.1	3350.1 ± 233.9	BDL
	High Dissolved Oxygen Day 10	13.4 ± 0.2	BDL	BDL	0.3 ± 0.0	3342.1 ± 587.2	BDL
	High Dissolved Oxygen Day 30	BDL	BDL	BDL	0.3 ± 0.0	4676.2 ± 289.8	0.0 ± 0.0
	Low Dissolved Oxygen Day 0	BDL	BDL	BDL	0.2 ± 0.0	3038.2 ± 335.7	BDL
	Low Dissolved Oxygen Day 10	12.8 ± 0.0	BDL	BDL	0.3 ± 0.0	3831.0 ± 331.4	BDL
	Low Dissolved Oxygen Day 30	41.0 ± 0.0	BDL	BDL	0.2 ± 0.0	5850.0 ± 111.3	BDL

Appendix A continued

(a)	Treatment	Co	Cr	Cu	Dy	Er	Eu
Pore Water	High Dissolved Oxygen Day 0	0.3 ± 0.1	BDL	4.7 ± 0.2	BDL	BDL	BDL
	High Dissolved Oxygen Day 10	0.2 ± 0.0	BDL	1.0 ± 0.0	BDL	BDL	BDL
	High Dissolved Oxygen Day 30	BDL	81.9 ± 72.9	BDL	BDL	BDL	BDL
	Low Dissolved Oxygen Day 0	0.4 ± 0.0	BDL	3.5 ± 0.6	BDL	BDL	BDL
	Low Dissolved Oxygen Day 10	BDL	29.4 ± 4.7	1.1 ± 0.7	BDL	BDL	BDL
	Low Dissolved Oxygen Day 30	BDL	26.9 ± 7.0	BDL	BDL	BDL	BDL
Overlying Water	High Dissolved Oxygen Day 0	0.2 ± 0.0	BDL	BDL	0.0 ± 0.0	BDL	BDL
	High Dissolved Oxygen Day 10	0.1 ± 0.0	BDL	BDL	0.1 ± 0.0	BDL	BDL
	High Dissolved Oxygen Day 30	0.2 ± 0.0	BDL	BDL	0.1 ± 0.0	BDL	BDL
	Low Dissolved Oxygen Day 0	0.2 ± 0.0	BDL	1.1 ± 0.0	0.1 ± 0.0	BDL	BDL
	Low Dissolved Oxygen Day 10	0.1 ± 0.0	BDL	BDL	0.1 ± 0.0	BDL	BDL
	Low Dissolved Oxygen Day 30	BDL	BDL	BDL	0.1 ±0.0	BDL	BDL

(b)	Treatment	Co	Cr	Cu	Dy	Er	Eu
Pore Water	High Dissolved Oxygen Day 0	10.7 ± 3.4	BDL	1.3 ± 0.1	BDL	BDL	BDL
	High Dissolved Oxygen Day 10	2.6 ± 0.4	BDL	1.7 ± 0.1	BDL	BDL	BDL
	High Dissolved Oxygen Day 30	1.1 ± 0.0	BDL	0.7 ±0.0	BDL	BDL	0.1 ± 0.0
	Low Dissolved Oxygen Day 0	20.5 ± 13.4	BDL	1.6 ± 0.1	BDL	BDL	BDL
	Low Dissolved Oxygen Day 10	2.5 ± 0.0	BDL	0.6 ± 0.1	BDL	BDL	BDL
	Low Dissolved Oxygen Day 30	0.8 ± 0.5	BDL	0.6 ± 0.0	0.2 ± 0.0	BDL	BDL
Overlying Water	High Dissolved Oxygen Day 0	3.5 ± 0.0	BDL	BDL	0.1 ± 0.0	BDL	BDL
	High Dissolved Oxygen Day 10	0.5 ± 0.0	BDL	BDL	BDL	BDL	BDL
	High Dissolved Oxygen Day 30	0.9 ± 0.1	BDL	0.6 ± 0.0	0.1 ± 0.0	BDL	BDL
	Low Dissolved Oxygen Day 0	3.4 ± 0.5	BDL	22.2 ± 0.0	BDL	BDL	BDL
	Low Dissolved Oxygen Day 10	0.3 ± 0.1	BDL	BDL	0.2 ± 0.0	BDL	BDL
	Low Dissolved Oxygen Day 30	0.1 ± 0.0	BDL	0.7 ± 0.0	BDL	BDL	BDL

Appendix A continued

(a)	**Treatment**	**Fe**	**Gd**	**Hf**	**Hg**	**Ho**	**La**
Pore Water	High Dissolved Oxygen Day 0	BDL	BDL	0.7 ± 0.0	BDL	BDL	BDL
	High Dissolved Oxygen Day 10	18.2 ± 0.0	BDL	BDL	BDL	BDL	BDL
	High Dissolved Oxygen Day 30	88.2 ± 0.0	BDL	0.1 ± 0.0	BDL	BDL	0.0 ± 0.0
	Low Dissolved Oxygen Day 0	BDL	BDL	0.1 ± 0.0	BDL	BDL	BDL
	Low Dissolved Oxygen Day 10	BDL	BDL	0.5 ± 0.0	BDL	BDL	BDL
	Low Dissolved Oxygen Day 30	BDL	BDL	0.4 ± 0.0	BDL	BDL	BDL
Overlying Water	High Dissolved Oxygen Day 0	BDL	0.0 ± 0.0	0.4 ± 0.2	BDL	BDL	BDL
	High Dissolved Oxygen Day 10	BDL	0.1 ± 0.0	0.0 ± 0.0	BDL	BDL	BDL
	High Dissolved Oxygen Day 30	BDL	BDL	BDL	BDL	BDL	BDL
	Low Dissolved Oxygen Day 0	BDL	BDL	0.1 ± 0.0	BDL	BDL	BDL
	Low Dissolved Oxygen Day 10	BDL	0.1 ± 0.0	0.1 ± 0.0	BDL	BDL	BDL
	Low Dissolved Oxygen Day 30	BDL	0.1 ± 0.0	0.0 ± 0.0	BDL	BDL	BDL

(b)	**Treatment**	**Fe**	**Gd**	**Hf**	**Hg**	**Ho**	**La**
Pore Water	High Dissolved Oxygen Day 0	BDL	BDL	0.3 ± 0.2	BDL	BDL	BDL
	High Dissolved Oxygen Day 10	BDL	BDL	0.2 ± 0.0	BDL	BDL	0.0 ± 0.0
	High Dissolved Oxygen Day 30	BDL	BDL	BDL	BDL	BDL	BDL
	Low Dissolved Oxygen Day 0	BDL	BDL	0.1 ±0.0	BDL	BDL	BDL
	Low Dissolved Oxygen Day 10	BDL	BDL	0.1 ± 0.0	BDL	BDL	BDL
	Low Dissolved Oxygen Day 30	BDL	BDL	BDL	BDL	BDL	BDL
Overlying Water	High Dissolved Oxygen Day 0	BDL	0.1 ± 0.0	0.1 ± 0.0	BDL	BDL	BDL
	High Dissolved Oxygen Day 10	BDL	BDL	0.0 ± 0.0	BDL	BDL	BDL
	High Dissolved Oxygen Day 30	BDL	BDL	0.2 ± 0.2	BDL	BDL	BDL
	Low Dissolved Oxygen Day 0	28.5 ± 0.0	0.1 ± 0.0	0.2 ± 0.2	BDL	BDL	BDL
	Low Dissolved Oxygen Day 10	BDL	BDL	0.5 ± 0.0	BDL	BDL	BDL
	Low Dissolved Oxygen Day 30	BDL	BDL	BDL	BDL	BDL	BDL

Appendix A continued

(a)	Treatment	Lu	Mg	Mn	Mo	Nb	Nd
Pore Water	High Dissolved Oxygen Day 0	0.0 ± 0.0	27474.4 ± 5048.6	1.5 ± 0.8	489.2 ± 70.8	BDL	BDL
	High Dissolved Oxygen Day 10	0.0 ± 0.0	19772.1 ± 71.0	0.6 ± 0.2	150.7 ± 52.2	BDL	BDL
	High Dissolved Oxygen Day 30	0.0 ± 0.0	20024.8 ± 713.0	3.2 ± 1.0	89.3 ± 21.0	BDL	BDL
	Low Dissolved Oxygen Day 0	0.1 ± 0.0	28894.5 ± 3132.4	1.3 ± 0.5	59.6 ± 97.7	BDL	BDL
	Low Dissolved Oxygen Day 10	0.1 ± 0.0	23140.0 ± 580.2	0.5 ± 0.0	196.5 ± 15.8	BDL	BDL
	Low Dissolved Oxygen Day 30	0.1 ± 0.0	20373.8 ± 298.6	6.7 ± 2.0	175.9 ± 36.6	BDL	BDL
Overlying Water	High Dissolved Oxygen Day 0	0.2 ± 0.0	21013.3 ± 540.6	7.0 ± 1.4	10.1 ± 2.3	BDL	BDL
	High Dissolved Oxygen Day 10	0.1 ± 0.1	20868.2 ± 447.0	0.3 ± 0.0	43.1 ± 18.6	BDL	BDL
	High Dissolved Oxygen Day 30	0.1 ± 0.0	21944.1 ± 769.9	BDL	65.0 ± 11.6	BDL	0.1 ± 0.0
	Low Dissolved Oxygen Day 0	0.1 ± 0.0	22120.3 ± 649.0	5.6 ± 0.9	17.3 ± 2.0	BDL	BDL
	Low Dissolved Oxygen Day 10	0.2 ± 0.0	22000.2 ± 1194.3	0.3 ± 0.0	38.0 ± 7.7	BDL	BDL
	Low Dissolved Oxygen Day 30	0.2 ± 0.0	21756.0 ± 152.0	0.4 ± 0.0	81.4 ± 4.5	BDL	BDL

(b)	Treatment	Lu	Mo	Mg	Mn	Nb	Nd
Pore Water	High Dissolved Oxygen Day 0	0.1 ± 0.0	72.1 ± 16.4	17698.1 ± 924.4	957.1 ± 0.9	BDL	BDL
	High Dissolved Oxygen Day 10	0.1 ± 0.0	71.7 ± 6.7	23095.9 ± 682.3	368.5 ± 0.1	BDL	BDL
	High Dissolved Oxygen Day 30	0.1 ± 0.0	47.5 ± 1.6	26842.1 ± 348.2	141.2 ± 38.2	BDL	BDL
	Low Dissolved Oxygen Day 0	0.1 ± 0.0	43.5 ± 0.2	19558.7 ± 1945.1	1082.1 ± 473.5	BDL	BDL
	Low Dissolved Oxygen Day 10	0.1 ± 0.0	90.8 ± 6.4	19206.1 ± 2235.4	413.7 ± 7.5	BDL	BDL
	Low Dissolved Oxygen Day 30	0.1 ± 0.0	38.0 ± 1.8	26361.2 ± 773.3	102.6 ± 51.2	BDL	BDL
Overlying Water	High Dissolved Oxygen Day 0	0.2 ± 0.0	4.6 ± 0.4	22167.3 ± 429.2	138.4 ± 6.2	BDL	BDL
	High Dissolved Oxygen Day 10	0.2 ± 0.0	15.0 ± 0.9	22537.9 ± 2825.5	18.6 ± 3.4	BDL	BDL
	High Dissolved Oxygen Day 30	0.1 ± 0.1	29.5 ± 6.7	23366.9 ± 2975.0	62.0 ± 7.8	BDL	0.2 ± 0.0
	Low Dissolved Oxygen Day 0	0.2 ± 0.0	5.0 ± 0.2	19740.2 ± 937.1	146.7 ± 14.7	BDL	BDL
	Low Dissolved Oxygen Day 10	0.2 ± 0.0	18.8 ± 2.5	21206.4 ± 32.9	11.9 ± 1.7	BDL	0.2 ± 0.0
	Low Dissolved Oxygen Day 30	0.1 ± 0.0	26.1 ± 1.0	23139.1 ± 1978.8	10.2 ± 2.1	BDL	BDL

Appendix A continued

(a)	Treatment	Ni	Pb	Pr	Rb	Sb	Sc
Pore Water	High Dissolved Oxygen Day 0	BDL	0.1 ± 0.0	0.0 ± 0.0	4.0 ± 0.0	1.3 ± 0.0	3.6 ± 0.5
	High Dissolved Oxygen Day 10	BDL	BDL	BDL	2.8 ± 0.1	0.6 ± 0.1	4.4 ± 1.7
	High Dissolved Oxygen Day 30	BDL	BDL	0.0 ± 0.0	2.5 ± 0.2	0.5 ± 0.0	3.7 ± 0.7
	Low Dissolved Oxygen Day 0	BDL	0.1 ± 0.0	BDL	5.7 ± 0.6	1.2 ± 0.3	5.9 ± 1.2
	Low Dissolved Oxygen Day 10	BDL	BDL	0.0 ± 0.0	3.4 ± 0.3	0.84 ± 0.1	5.6 ± 0.4
	Low Dissolved Oxygen Day 30	BDL	BDL	0.0 ± 0.0	4.8 ± 0.3	0.7 ± 0.1	5.9 ± 0.4
Overlying Water	High Dissolved Oxygen Day 0	BDL	BDL	BDL	1.3 ± 0.3	0.1 ± 0.0	6.5 ± 0.9
	High Dissolved Oxygen Day 10	BDL	BDL	BDL	2.2 ± 0.1	0.2 ± 0.0	3.9 ± 0.4
	High Dissolved Oxygen Day 30	BDL	0.1 ± 0.0	BDL	3.2 ± 0.1	0.41 ± 0.1	4.5 ± 0.9
	Low Dissolved Oxygen Day 0	BDL	BDL	BDL	1.1 ± 0.0	0.1 ± 0.0	5.9 ± 0.9
	Low Dissolved Oxygen Day 10	BDL	BDL	BDL	2.1 ± 0.3	0.2 ± 0.0	3.3 ± 0.1
	Low Dissolved Oxygen Day 30	BDL	BDL	BDL	3.0 ± 0.0	0.4 ± 0.0	2.6 ± 0.3

(b)	Treatment	Ni	Pb	Pr	Rb	Sb	Sc
Pore Water	High Dissolved Oxygen Day 0	BDL	BDL	0.0 ± 0.0	2.1 ± 0.1	0.1 ± 0.0	2.3 ± 1.9
	High Dissolved Oxygen Day 10	BDL	BDL	0.0 ± 0.0	1.9 ± 0.0	0.3 ± 0.1	3.5 ± 0.3
	High Dissolved Oxygen Day 30	BDL	BDL	0.0 ± 0.0	1.3 ± 0.1	0.2 ± 0.0	4.4 ± 0.3
	Low Dissolved Oxygen Day 0	BDL	BDL	BDL	2.1 ± 0.4	BDL	2.0 ± 0.2
	Low Dissolved Oxygen Day 10	BDL	BDL	0.0 ± 0.0	1.8 ± 0.2	0.2 ± 0.1	1.6 ± 0.1
	Low Dissolved Oxygen Day 30	BDL	BDL	0.0 ± 0.0	1.2 ± 0.0	0.2 ± 0.0	3.4 ± 0.4
Overlying Water	High Dissolved Oxygen Day 0	BDL	BDL	BDL	0.6 ± 0.1	BDL	4.4 ± 0.1
	High Dissolved Oxygen Day 10	BDL	BDL	BDL	0.8 ± 0.0	0.1 ± 0.0	3.5 ± 0.5
	High Dissolved Oxygen Day 30	BDL	BDL	0.0 ± 0.0	1.3 ± 0.2	0.1 ± 0.0	2.6 ± 0.9
	Low Dissolved Oxygen Day 0	BDL	3.2 ± 0.0	BDL	0.6 ± 0.1	0.1 ± 0.0	4.2 ± 0.8
	Low Dissolved Oxygen Day 10	BDL	BDL	BDL	1.1 ± 0.0	0.1 ± 0.0	3.1 ± 0.7
	Low Dissolved Oxygen Day 30	BDL	BDL	0.0 ± 0.0	1.1 ± 0.0	BDL	3.3 ± 0.6

Appendix A continued

(a)	**Treatment**	**Sm**	**Sr**	**Ta**	**Th**	**Ti**	**Tl**	**Tm**
Pore Water	High Dissolved Oxygen Day 0	BDL	108.3 ± 13.5	BDL	0.0 ± 0.0	3.3 ± 1.0	0.0 ± 0.0	0.0 ± 0.0
	High Dissolved Oxygen Day 10	BDL	95.6 ± 5.0	BDL	0.0 ± 0.0	2.6 ± 1.7	0.0 ± 0.0	0.0 ± 0.0
	High Dissolved Oxygen Day 30	BDL	118.0 ± 0.2	BDL	BDL	1.6 ± 0.1	BDL	0.0 ± 0.0
	Low Dissolved Oxygen Day 0	BDL	133.4 ± 0.9	BDL	0.1 ± 0.0	2.2 ± 1.0	BDL	0.0 ± 0.0
	Low Dissolved Oxygen Day 10	BDL	113.4 ± 0.1	BDL	0.1 ± 0.1	2.7 ± 0.7	0.0 ± 0.0	BDL
	Low Dissolved Oxygen Day 30	BDL	141.8 ± 3.2	BDL	0.1 ± 0.1	2.0 ± 0.0	0.1 ± 0.0	BDL
Overlying Water	High Dissolved Oxygen Day 0	BDL	87.0± 5.9	BDL	0.1 ± 0.0	1.6 ± 0.3	0.2 ± 0.0	BDL
	High Dissolved Oxygen Day 10	BDL	109.4 ± 9.3	BDL	BDL	1.5 ± 0.0	BDL	BDL
	High Dissolved Oxygen Day 30	BDL	91.6 ± 0.4	BDL	0.0 ± 0.0	1.8 ± 0.0	0.1 ± 0.0	BDL
	Low Dissolved Oxygen Day 0	BDL	94.9 ± 0.9	BDL	BDL	1.7 ± 0.1	0.1 ± 0.0	BDL
	Low Dissolved Oxygen Day 10	BDL	114.2 ± 2.3	BDL	BDL	1.8 ± 0.2	BDL	BDL
	Low Dissolved Oxygen Day 30	BDL	123.8 ± 3.6	BDL	BDL	2.5 ± 0.0	BDL	BDL

(b)	**Treatment**	**Sm**	**Sr**	**Ta**	**Th**	**Ti**	**Tl**	**Tm**
Pore Water	High Dissolved Oxygen Day 0	BDL	29.6 ± 6.7	BDL	0.1 ± 0.0	2.2 ± 0.4	0.1 ± 0.0	0.0 ± 0.0
	High Dissolved Oxygen Day 10	BDL	66.4 ± 3.5	BDL	0.1 ± 0.0	2.7 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	High Dissolved Oxygen Day 30	BDL	100.3 ± 3.5	BDL	0.1 ± 0.0	2.1 ± 0.0	BDL	BDL
	Low Dissolved Oxygen Day 0	BDL	69.9 ± 17.5	BDL	0.0 ± 0.0	2.4 ± 0.3	0.0 ± 0.0	0.0 ± 0.0
	Low Dissolved Oxygen Day 10	BDL	71.6 ± 5.8	BDL	BDL	2.5 ± 0.5	0.0 ± 0.0	0.0 ± 0.0
	Low Dissolved Oxygen Day 30	BDL	157.0 ± 9.9	BDL	BDL	BDL	BDL	0.0 ± 0.0
Overlying Water	High Dissolved Oxygen Day 0	BDL	80.4 ± 9.3	BDL	BDL	BDL	0.1 ± 0.0	BDL
	High Dissolved Oxygen Day 10	BDL	85.3 ± 15.3	BDL	BDL	BDL	BDL	0.0 ± 0.0
	High Dissolved Oxygen Day 30	BDL	86.8 ± 9.3	BDL	0.2 ± 0.1	BDL	0.0 ± 0.0	0.0 ± 0.0
	Low Dissolved Oxygen Day 0	BDL	82.9 ± 4.0	BDL	0.2 ± 0.0	BDL	0.1 ± 0.0	BDL
	Low Dissolved Oxygen Day 10	BDL	97.1 ± 7.0	BDL	0.2 ± 0.0	BDL	0.1 ± 0.0	BDL
	Low Dissolved Oxygen Day 30	BDL	114.0 ± 0.4	BDL	BDL	1.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

Appendix A continued

(a)	**Treatment**	**U**	**V**	**W**	**Y**	**Yb**	**Zn**	**Zr**
Pore Water	High Dissolved Oxygen Day 0	0.7 ± 0.5	1149.4 ± 126.6	BDL	0.15 ± 0.0	BDL	150.8 ± 60.0	7.2 ± 7.2
	High Dissolved Oxygen Day 10	1.3 ± 0.1	467.0 ± 463.3	BDL	0.2 ± 0.0	0.1 ± 0.0	6.7 ± 2.5	0.0 ± 0.0
	High Dissolved Oxygen Day 30	0.5 ± 0.1	261.6 ± 249.5	BDL	0.2 ± 0.1	0.1 ± 0.0	4.7 ± 0.2	BDL
	Low Dissolved Oxygen Day 0	BDL	1923.1 ± 437.4	BDL	0.3 ± 0.0	BDL	43.5 ± 14.2	0.0 ± 0.0
	Low Dissolved Oxygen Day 10	0.4 ± 0.1	994.8 ± 179.9	BDL	0.2 ± 0.0	BDL	5.1 ± 2.0	0.2 ± 0.0
	Low Dissolved Oxygen Day 30	0.1 ± 0.0	678.2 ± 247.3	BDL	0.3 ± 0.0	BDL	5.8 ± 1.4	0.1 ± 0.1
Overlying Water	High Dissolved Oxygen Day 0	0.0 ± 0.0	112.2 ± 29.5	BDL	0.11 ± 0.0	BDL	5.9 ± 1.4	0.4 ± 0.3
	High Dissolved Oxygen Day 10	0.2 ± 0.0	377.9 ± 173.3	BDL	0.2 ± 0.1	0.1 ± 0.0	2.5 ± 0.1	0.0 ± 0.0
	High Dissolved Oxygen Day 30	0.2 ± 0.0	546.7 ± 60.7	BDL	0.2 ± 0.1	BDL	3.6 ± 0.6	0.0 ± 0.0
	Low Dissolved Oxygen Day 0	0.0 ± 0.0	196.0 ± 18.8	BDL	0.2 ± 0.0	BDL	4.1 ± 0.2	0.1 ± 0.0
	Low Dissolved Oxygen Day 10	0.1 ± 0.0	368.8 v 107.4	BDL	0.2 ± 0.0	BDL	3.8 ± 1.1	BDL
	Low Dissolved Oxygen Day 30	0.1 ± 0.0	695.1 ± 61.9	BDL	0.2 ± 0.0	BDL	3.2 ± 0.2	0.0 ± 0.0

(b)	**Treatment**	**U**	**V**	**W**	**Y**	**Yb**	**Zn**	**Zr**
Pore Water	High Dissolved Oxygen Day 0	0.3 ± 0.0	5.4 ± 0.5	BDL	0.0	0.1 ± 0.0	7.7 ± 1.9	0.1 ± 0.1
	High Dissolved Oxygen Day 10	0.4 ± 0.2	10.8 ± 0.1	BDL	0.1 ± 0.0	0.7 ± 0.0	11.7 ± 1.8	0.0 ± 0.0
	High Dissolved Oxygen Day 30	0.2 ± 0.0	18.7 ± 0.0	BDL	0.2 ± 0.0	BDL	2.7 ± 0.2	0.1 ± 0.0
	Low Dissolved Oxygen Day 0	0.1 ± 0.0	6.1 ± 0.6	BDL	0.2 ± 0.0	0.1 ± 0.0	22.4 ± 1.3	0.9 ± 0.9
	Low Dissolved Oxygen Day 10	0.2 ± 0.0	10.3 ± 2.1	BDL	0.2 ± 0.0	0.1 ± 0.0	3.6 ± 0.1	0.0 ± 0.0
	Low Dissolved Oxygen Day 30	0.1 ± 0.0	20.2 ± 1.3	BDL	0.3 ± 0.0	0.2 ± 0.0	2.5 ± 0.1	BDL
Overlying Water	High Dissolved Oxygen Day 0	0.0 ± 0.0	5.7 ± 0.3	BDL	0.2 ± 0.0	BDL	4.4 ± 0.2	0.1 ± 0.0
	High Dissolved Oxygen Day 10	0.2 ± 0.1	26.9 ± 0.5	BDL	0.1 ± 0.0	BDL	2.9 ± 0.7	0.0 ± 0.0
	High Dissolved Oxygen Day 30	0.1 ± 0.0	34.3 ± 5.8	BDL	0.2 ± 0.0	BDL	4.3 ± 0.5	0.1 ± 0.1
	Low Dissolved Oxygen Day 0	0.1 ± 0.0	8.4 ± 0.2	BDL	0.1 ± 0.0	0.2 ± 0.0	12.2 ± 7.8	0.1 ± 0.0
	Low Dissolved Oxygen Day 10	0.1 ± 0.0	29.4 ± 2.9	BDL	0.2 ± 0.0	0.1 ± 0.0	2.8 ± 1.2	0.2 ± 0.0
	Low Dissolved Oxygen Day 30	0.1 ± 0.0	63.7 ± 4.8	BDL	0.2 ± 0.0	0.1 ± 0.0	1.9 ± 0.3	0.0 ± 0.0

APPENDIX B: Mean ± SE metal concentrations (µg/L) from the pH leaching experiment using Syncrude (a) and Suncor (b) cokes. (*n* = 3) (BDL = below detection limit)

(a)	**Treatment**	**Ag**	**Al**	**As**	**Ba**	**Ca**	**Ce**
Pore Water	pH 5 Day 0	BDL	0.0 ± 0.0	0.8 ± 0.0	24.6 ± 1.9	137496.3 ± 17250.9	0.0 ± 0.0
	pH 5 Day 45	BDL	0.0 ± 0.0	0.5 ± 0.5	22.6 ± 4.9	80579.4 ± 13758.5	0.1 ± 0.0
	pH 5 Day 90	BDL	1209.4 ± 499.6	BDL	28.5 ± 0.7	73020.0 ± 2291.9	1.0 ± 0.3
	pH 7.5 Day 0	BDL	8.4 ± 0.0	0.8 ± 0.0	24.3 ± 1.2	104349.7 ± 11425.3	BDL
	pH 7.5 Day 45	BDL	0.0 ± 0.0	0.5 ± 0.1	19.3± 1.2	41814.1 ± 76.0	0.0 ± 0.0
	pH 7.5 Day 90	BDL	9.7 ± 0.0	0.3 ± 0.0	18.0 ± 0.9	55844.0 ± 897.1	BDL
	pH10 Day 0	BDL	13.9 ± 0.0	BDL	22.3 ± 1.3	140215.5 ± 3130.0	0.1 ± 0.0
	pH 10 Day 45	BDL	48.1 ± 8.0	1.2 ± 0.1	12.9 ± 1.1	19657.5 ± 1262.9	0.2 ± 0.0
	pH 10 Day 90	BDL	44.9 ± 10.6	0.8 ± 0.2	7.7 ± 0.6	18493.8 ± 347.8	BDL
Overlying Water	pH 5 Day 0	BDL	26.0 ± 0.0	BDL	5.1 ± 4.8	22943.7 ± 17390.2	BDL
	pH 5 Day 45	0.0 ± 0.0	137.4 ± 75.4	0.1 ± 0.1	26.4 ± 2.8	63490.7 ± 5346.9	0.5 ± 0.2
	pH 5 Day 90	0.0 ± 0.0	25.7 ± 3.4	0.0 ± 0.0	1.9 ± 0.2	11723.0 ± 1126.8	0.0 ± 0.0
	pH 7.5 Day 0	BDL	0.0 ± 0.0	BDL	5.2 ± 4.8	22245.6 ± 16603.9	BDL
	pH 7.5 Day 45	0.0 ± 0.0	29.6 ± 5.4	0.1 ± 0.0	19.9 ± 0.1	49462.0 ± 2082.4	0.0 ± 0.0
	pH 7.5 Day 90	0.0 ± 0.0	57.1 ± 3.0	0.1 ± 0.0	0.6 ± 0.4	6400.7 ± 28.1	0.0 ± 0.0
	pH10 Day 0	BDL	153.3 ± 36.6	BDL	4.5 ± 4.0	18359.5 ± 10311.4	0.1 ± 0.0
	pH 10 Day 45	0.0 ± 0.0	64.1 ± 7.3	0.2 ± 0.0	11.8 ± 0.6	14973.8 ± 575.2	0.0 ± 0.0
	pH 10 Day 90	0.0 ± 0.0	75.9 ± 15.7	0.2 ± 0.0	9.3 ± 0.4	9218.0 ± 139.9	0.0 ± 0.0

Appendix B continued

(b)	Treatment	Ag	Al	As	Ba	Ca	Ce
Pore Water	pH 5 Day 0	BDL	3489.1 ± 3273.7	BDL	15.7 ± 3.9	168482.4 ± 20562.6	23.4 ± 19.6
	pH 5 Day 45	BDL	3528.2 ± 553.2	0.5 ± 0.1	16.2 ± 1.0	86200.4 ± 3784.0	19.3 ± 2.2
	pH 5 Day 90	0.1 ± 0.0	2098.3 ± 468.6	BDL	12.5 ± 0.3	93067.3 ± 5946.3	10.4 ± 0.8
	pH 7.5 Day 0	BDL	467.4 ± 401.1	BDL	10.2 ± 0.8	184013.8 ± 28805.3	6.3 ± 4.8
	pH 7.5 Day 45	BDL	0.0 ± 0.0	BDL	3.5 ± 0.2	68850.8 ± 4589.0	0.1 ± 0.0
	pH 7.5 Day 90	BDL	46.7 ± 8.5	BDL	2.9 ± 0.4	64334.7 ± 6422.3	BDL
	pH10 Day 0	BDL	512.1 ± 357.9	1.6 ± 0.0	0.4 ± 37.5	705974.8 ± 509327.0	BDL
	pH 10 Day 45	BDL	46.1 ± 7.2	0.5 ± 0.0	37.5 ± 26.8	45119.9 ± 11475.4	11.9 ± 8.3
	pH 10 Day 90	0.1 ± 0.0	69.7 ± 5.6	0.6 ± 0.0	2.1 ± 0.5	9390.0 ± 964.4	0.0 ± 0.0
Overlying Water	pH 5 Day 0	0.2 ± 0.0	153.5 ± 15.9	BDL	0.8 ± 0.2	28726.4 ± 11001.9	BDL
	pH 5 Day 45	0.0 ± 0.0	967.3 ± 95.3	0.0 ± 0.0	7.5 ± 0.7	62571.2 ± 1425.7	1.1 ± 0.1
	pH 5 Day 90	0.0 ± 0.0	68.5 ± 10.6	0.1 ± 0.0	14.9 ± 0.2	8660.8 ± 597.7	7.4 ± 0.2
	pH 7.5 Day 0	BDL	70.7 ± 6.5	BDL	1.1 ± 0.1	27925.8 ± 11565.4	0.1 ± 0.0
	pH 7.5 Day 45	0.0 ± 0.0	31.6 ± 8.8	0.0 ± 0.0	5.0 ± 2.4	65102.1 ± 6469.8	0.2 ± 0.0
	pH 7.5 Day 90	0.0 ± 0.0	72.0 ± 18.0	0.0 ± 0.0	6.8 ± 0.1	6747.3 ± 393.9	0.1 ± 0.0
	pH10 Day 0	BDL	228.6 ± 2.2	BDL	0.0 ± 0.0	39334.3 ± 2679.4	0.0 ± 0.0
	pH 10 Day 45	0.0 ± 0.0	72.9 ± 9.4	0.0 ± 0.0	5.9 ± 0.3	47142.8 ± 8379.9	0.1 ± 0.0
	pH 10 Day 90	0.0 ± 0.0	81.0 ± 16.3	0.2 ± 0.0	6.4 ± 0.3	8530.5 ± 888.3	0.0 ± 0.0

Appendix B continued

(a)	Treatment	Co	Cr	Cs	Cu	Dy	Er	Eu
Pore Water	pH 5 Day 0	2.9 ± 0.3	BDL	0.0 ± 0.0	1.8 ± 0.0	0.0 ± 0.0	BDL	BDL
	pH 5 Day 45	1.8 ± 0.7	BDL	0.0 ± 0.0	1.2 ± 0.1	0.0 ± 0.0	BDL	BDL
	pH 5 Day 90	28.6 ± 3.6	BDL	0.0 ± 0.0	1.4 ± 0.2	0.1 ± 0.0	0.1 ± 0.0	BDL
	pH 7.5 Day 0	0.9 ± 0.1	0.2 ± 0.0	0.0 ± 0.0	1.5 ± 0.1	BDL	0.0 ± 0.0	BDL
	pH 7.5 Day 45	0.1 ± 0.0	0.2 ± 0.0	0.0 ± 0.0	0.7 ± 0.0	BDL	0.0 ± 0.0	BDL
	pH 7.5 Day 90	0.1 ± 0.0	0.3 ± 0.0	BDL	0.6 ± 0.1	BDL	BDL	BDL
	pH10 Day 0	1.7 ± 0.6	0.2 ± 0.0	0.0 ± 0.0	2.2 ± 0.2	BDL	BDL	BDL
	pH 10 Day 45	0.2 ± 0.0	0.2 ± 0.0	0.0 ± 0.0	0.7 ± 0.2	BDL	0.0 ± 0.0	BDL
	pH 10 Day 90	0.1 ± 0.0	0.3 ± 0.1	BDL	0.7 ± 0.1	BDL	BDL	BDL
Overlying Water	pH 5 Day 0	0.6 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	2.2 ± 0.2	BDL	0.0 ± 0.0	BDL
	pH 5 Day 45	3.1 ± 0.7	0.0 ± 0.0	0.0 ± 0.0	1.2 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 5 Day 90	12.1 ± 0.7	0.0 ± 0.0	0.0 ± 0.0	1.3 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 7.5 Day 0	0.5 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	1.8 ± 0.3	BDL	BDL	BDL
	pH 7.5 Day 45	0.1 ± 0.0	1.2 ± 0.1	0.0 ± 0.0	1.0 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 7.5 Day 90	0.2 ± 0.0	1.4 ± 0.1	0.0 ± 0.0	0.7 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH10 Day 0	0.2 ± 0.0	0.1 ± 0.0	BDL	1.1 ± 0.3	0.0 ± 0.0	0.0 ± 0.0	BDL
	pH 10 Day 45	0.1 ± 0.0	1.4 ± 0.1	0.0 ± 0.0	0.7 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 10 Day 90	0.1 ± 0.0	2.1 ± 0.4	0.0 ± 0.0	0.5 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

Appendix B continued

(b)	**Treatment**	**Co**	**Cr**	**Cs**	**Cu**	**Dy**	**Er**	**Eu**
Pore Water	pH 5 Day 0	78.1 ± 27.1	3.7 ± 2.7	0.1 ± 0.0	12.7 ± 9.8	1.6 ± 1.4	1.2 ± 0.8	0.7 ± 0.5
	pH 5 Day 45	43.4 ± 3.9	1.1 ± 0.2	0.1 ± 0.0	15.0 ± 5.4	1.7 ± 0.2	0.9 ± 0.1	0.5 ± 0.1
	pH 5 Day 90	24.7 ± 1.5	1.2 ± 0.3	0.0 ± 0.0	12.9 ± 0.2	1.0 ± 0.1	0.5 ± 0.0	0.2 ± 0.0
	pH 7.5 Day 0	79.3 ± 17.0	0.3 ± 0.1	0.1 ± 0.0	3.9 ± 0.5	0.3 ± 0.2	0.2 ± 0.2	0.3 ± 0.0
	pH 7.5 Day 45	4.1 ± 0.2	BDL	BDL	1.0 ± 0.1	0.0 ± 0.0	BDL	BDL
	pH 7.5 Day 90	1.7 ± 0.4	0.1 ± 0.0	0.0 ± 0.0	0.8 ± 0.0	BDL	BDL	BDL
	pH10 Day 0	262.7 ± 186.1	0.7 ± 0.3	BDL	12.6 ± 8.6	BDL	0.3 ± 0.2	BDL
	pH 10 Day 45	1.4 ± 0.4	BDL	0.3 ± 0.2	0.8 ± 0.2	0.4 ± 0.2	BDL	0.2 ± 0.1
	pH 10 Day 90	0.3 ± 0.0	0.2 ± 0.0	BDL	0.6 ± 0.1	0.0 ± 0.0	BDL	BDL
Overlying Water	pH 5 Day 0	3.2 ± 0.5	0.2 ± 0.0	BDL	2.1 ± 0.3	BDL	0.0 ± 0.0	BDL
	pH 5 Day 45	19.0 ± 0.6	1.2 ± 0.2	BDL	3.7 ± 0.3	0.1 ± 0.0	0.3 ± 0.0	BDL
	pH 5 Day 90	19.3 ± 1.7	3.6 ± 0.4	0.0 ± 0.0	6.9 ± 0.1	0.5 ± 0.0	0.0 ± 0.0	0.2 ± 0.0
	pH 7.5 Day 0	2.5 ± 0.2	0.2 ± 0.0	0.0 ± 0.0	0.9 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 7.5 Day 45	3.3 ± 0.2	0.0 ± 0.0	BDL	1.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	BDL
	pH 7.5 Day 90	2.1 ± 0.4	0.2 ± 0.2	0.0 ± 0.0	0.6 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH10 Day 0	1.6 ± 0.2	0.1 ± 0.0	0.0 ± 0.0	1.0 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 10 Day 45	0.9 ± 0.1	0.2 ± 0.2	BDL	0.8 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	BDL
	pH 10 Day 90	0.3 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.7 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

Appendix B continued

(a)	**Treatment**	**Fe**	**Ga**	**Gd**	**Hf**	**Hg**	**Ho**
Pore Water	pH 5 Day 0	371.2 ± 19.7	BDL	BDL	BDL	BDL	BDL
	pH 5 Day 45	233.5 ± 56.1	BDL	BDL	BDL	BDL	BDL
	pH 5 Day 90	188.6 ± 17.9	BDL	0.2 ± 0.1	BDL	BDL	0.0 ± 0.0
	pH 7.5 Day 0	303.0 ± 23.5	BDL	0.0 ± 0.0	BDL	0.3 ± 0.0	BDL
	pH 7.5 Day 45	105.7 ± 2.1	0.1 ± 0.0	0.0 ± 0.0	BDL	BDL	BDL
	pH 7.5 Day 90	152.7 ± 3.5	0.1 ± 0.0	BDL	BDL	0.4 ± 0.0	BDL
	pH10 Day 0	363.9 ± 33.1	0.0 ± 0.0	0.0 ± 0.0	BDL	0.4 ± 0.0	BDL
	pH 10 Day 45	91.9 ± 8.1	0.2 ± 0.0	BDL	BDL	BDL	BDL
	pH 10 Day 90	57.6 ± 3.6	0.2 ± 0.0	BDL	BDL	BDL	BDL
Overlying Water	pH 5 Day 0	158.9 ± 0.0	BDL	BDL	0.1 ± 0.1	BDL	BDL
	pH 5 Day 45	183.4 ± 18.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 5 Day 90	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.1	2.4 ± 1.7	0.0 ± 0.0	0.0 ± 0.0
	pH 7.5 Day 0	124.9 ± 0.0	BDL	BDL	0.0 ± 0.0	BDL	BDL
	pH 7.5 Day 45	131.8 ± 13.9	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 7.5 Day 90	29.7 ± 15.7	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.2	0.0 ± 0.0	0.0 ± 0.0
	pH10 Day 0	124.6 ± 0.0	BDL	BDL	0.0 ± 0.0	BDL	BDL
	pH 10 Day 45	19.6 ± 19.6	0.2 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 10 Day 90	11.8 ± 11.8	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

Appendix B continued

(b)	Treatment	Fe	Ga	Gd	Hf	Hg	Ho
Pore Water	pH 5 Day 0	3584.2 ± 3078.0	1.8 ± 0.0	2.0 ± 1.7	0.1 ± 0.0	0.9 ± 0.0	0.4 ± 0.3
	pH 5 Day 45	1197.9 ± 283.6	BDL	1.9 ± 0.3	BDL	BDL	0.3 ± 0.0
	pH 5 Day 90	1985.5 ± 532.7	0.2 ± 0.0	1.0 ± 0.1	BDL	0.6 ± 0.0	0.2 ± 0.0
	pH 7.5 Day 0	629.6 ± 81.5	0.0 ± 0.0	0.4 ± 0.4	BDL	BDL	0.1 ± 0.0
	pH 7.5 Day 45	183.4 ± 5.5	BDL	BDL	BDL	BDL	BDL
	pH 7.5 Day 90	206.4 ± 21.2	0.1 ± 0.0	BDL	BDL	BDL	BDL
	pH10 Day 0	2618.4 ± 1976.7	0.4 ± 0.2	BDL	0.2 ± 0.0	BDL	0.1 ± 0.0
	pH 10 Day 45	120.5 ± 27.2	0.1 ± 0.0	0.8 ± 0.6	BDL	BDL	BDL
	pH 10 Day 90	46.5 ± 4.2	0.2 ± 0.0	BDL	BDL	BDL	BDL
Overlying Water	pH 5 Day 0	143.7 ± 2.7	BDL	BDL	0.1 ± 0.0	BDL	0.0 ± 0.0
	pH 5 Day 45	483.0 ± 48.8	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	pH 5 Day 90	1405.1 ± 423.8	0.0 ± 0.0	0.9 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
	pH 7.5 Day 0	147.3 ± 12.2	BDL	0.0 ± 0.0	0.1 ± 0.0	BDL	BDL
	pH 7.5 Day 45	149.3 ± 15.0	0.0 ± 0.0	BDL	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 7.5 Day 90	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH10 Day 0	114.2 ± 9.4	BDL	0.0 ± 0.0	BDL	BDL	BDL
	pH 10 Day 45	107.9 ± 5.4	0.1 ± 0.0	BDL	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 10 Day 90	19.6 ± 19.6	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

Appendix B continued

(a)	**Treatment**	**La**	**Li**	**Lu**	**Mg**	**Mn**	**Mo**
Pore Water	pH 5 Day 0	0.0 ± 0.0	58.8 ± 2.7	BDL	97836.3 ± 6171.4	74.6 ± 1.0	52.2 ± 10.2
	pH 5 Day 45	0.0 ± 0.0	17.2 ± 1.4	BDL	58756.4 ± 6464.4	87.3 ± 41.9	28.6 ± 12.7
	pH 5 Day 90	0.8 ± 0.2	24.0 ± 0.3	BDL	48241.1 ± 1902.6	523.4 ± 20.8	1.4 ± 0.2
	pH 7.5 Day 0	0.0 ± 0.0	44.7 ± 7.0	BDL	82903.0 ± 10549.9	12.0 ± 1.1	99.3 ± 26.2
	pH 7.5 Day 45	0.0 ± 0.0	9.1 ± 0.5	BDL	41861.7 ± 1017.1	0.7 ± 0.0	45.8 ± 3.2
	pH 7.5 Day 90	0.0 ± 0.0	3.1 ± 0.0	BDL	38620.1 ± 239.0	0.5 ± 0.2	29.7 ± 0.5
	pH10 Day 0	0.0 ± 0.0	55.8 ± 6.3	BDL	118137.8 ± 4744.2	29.6 ± 17.1	114.7 ± 13.3
	pH 10 Day 45	0.1 ± 0.0	7.5 ± 1.2	BDL	37134.1 ± 2566.4	1.1 ± 0.1	96.7 ± 36.4
	pH 10 Day 90	BDL	5.4 ± 0.3	BDL	40851.7 ± 724.0	0.2 ± 0.0	37.8 ± 7.8
Overlying Water	pH 5 Day 0	BDL	4.8 ± 0.7	BDL	38068.5 ± 3295.9	7.9 ± 1.2	1.1 ± 0.2
	pH 5 Day 45	0.3 ± 0.1	17.2 ± 1.8	0.0 ± 0.0	57195.0 ± 4432.8	67.3 ± 12.3	18.1 ± 7.8
	pH 5 Day 90	0.0 ± 0.0	21.3 ± 1.2	0.0 ± 0.0	50803.1 ± 3738.5	231.0 ± 26.0	4.7 ± 0.5
	pH 7.5 Day 0	0.0 ± 0.0	5.2 ± 0.8	BDL	36643.2 ± 3352.0	8.6 ± 0.5	2.0 ± 0.4
	pH 7.5 Day 45	0.0 ± 0.0	7.9 ± 0.6	0.0 ± 0.0	48626.6 ± 2140.1	0.0 ± 0.0	30.8 ± 2.5
	pH 7.5 Day 90	0.0 ± 0.0	9.0 ± 1.3	0.0 ± 0.0	37119.5 ± 899.1	0.3 ± 0.1	27.4 ± 0.5
	pH10 Day 0	0.1 ± 0.0	5.1 ± 0.5	BDL	41403.8 ± 2814.2	0.9 ± 0.0	3.3 ± 1.2
	pH 10 Day 45	0.0 ± 0.0	8.7 ± 0.2	0.0 ± 0.0	45346.7 ± 602.3	0.2 ± 0.2	51.0 ± 14.1
	pH 10 Day 90	0.0 ± 0.0	9.6 ± 0.2	0.0 ± 0.0	46938.1 ± 1335.3	0.0 ± 0.0	38.0 ± 8.5

Appendix B continued

(b)	**Treatment**	**La**	**Li**	**Lu**	**Mg**	**Mn**	**Mo**
Pore Water	pH 5 Day 0	9.1 ± 7.2	34.6 ± 12.1	BDL	59870.9 ± 3826.2	1683.7 ± 488.1	12.6 ± 2.7
	pH 5 Day 45	7.5 ± 0.9	15.3 ± 2.0	BDL	44411.9 ± 810.0	759.0 ± 71.8	1.2 ± 0.1
	pH 5 Day 90	4.1 ± 0.3	6.6 ± 1.0	BDL	44723.3 ± 2275.7	488.7 ± 18.4	1.4 ± 0.2
	pH 7.5 Day 0	3.0 ± 2.0	48.2 ± 6.7	BDL	62360.2 ± 4562.0	2204.3 ± 506.1	26.1 ± 6.0
	pH 7.5 Day 45	0.0 ± 0.0	3.4 ± 0.2	BDL	41959.4 ± 2842.4	347.7 ± 18.0	31.7 ± 1.1
	pH 7.5 Day 90	BDL	5.0 ± 0.4	BDL	46278.1 ± 1737.5	164.1 ± 63.1	39.0 ± 4.3
	pH10 Day 0	BDL	159.9 ± 109.1	BDL	260766.0 ± 195593.0	8307.0 ± 5932.6	141.2 ± 101.7
	pH 10 Day 45	6.0 ± 4.1	5.3 ± 1.6	BDL	42114.2 ± 2341.3	154.3 ± 53.1	43.5 ± 4.7
	pH 10 Day 90	0.0 ± 0.0	2.3 ± 0.0	BDL	36969.6 ± 1577.7	15.4 ± 8.8	49.0 ± 9.5
Overlying Water	pH 5 Day 0	BDL	3.1 ± 0.0	BDL	40012.9 ± 1725.7	62.3 ± 8.5	0.4 ± 0.1
	pH 5 Day 45	0.4 ± 0.1	7.9 ± 0.4	0.0 ± 0.0	48750.2 ± 2006.8	361.1 ± 3.5	1.3 ± 0.1
	pH 5 Day 90	3.0 ± 0.1	7.7 ± 0.9	0.0 ± 0.0	40107.7 ± 3600.2	377.9 ± 24.8	2.1 ± 0.2
	pH 7.5 Day 0	0.1 ± 0.0	0.8 ± 0.0	BDL	39398.3 ± 5183.6	48.8 ± 4.7	0.5 ± 0.0
	pH 7.5 Day 45	0.1 ± 0.0	7.3 ± 0.7	0.0 ± 0.0	59398.9 ± 2218.9	259.6 ± 22.1	23.9 ± 2.0
	pH 7.5 Day 90	0.0 ± 0.0	8.0 ± 1.3	0.0 ± 0.0	40087.8 ± 5022.8	195.1 ± 51.5	35.9 ± 5.4
	pH10 Day 0	0.0 ± 0.0	2.2 ± 0.7	BDL	54194.5 ± 1355.0	41.7 ± 3.4	0.9 ± 0.1
	pH 10 Day 45	0.1 ± 0.0	7.2 ± 0.7	0.0 ± 0.0	74331.9 ± 9163.4	61.7 ± 30.8	34.6 ± 1.4
	pH 10 Day 90	0.0 ± 0.0	6.8 ± 1.9	0.0 ± 0.0	39672.8 ± 1692.7	12.9 ± 6.6	41.1 ± 8.3

Appendix B continued

(a)	**Treatment**	**Nb**	**Nd**	**Ni**	**P**	**Pb**	**Pr**	**Rb**
Pore Water	pH 5 Day 0	BDL	BDL	64.6 ± 6.8	858.7 ± 19.2	BDL	BDL	8.5 ± 0.1
	pH 5 Day 45	BDL	BDL	58.2 ± 27.8	529.9 ± 33.1	0.7 ± 0.1	0.0 ± 0.0	5.6 ± 0.8
	pH 5 Day 90	BDL	0.5 ± 0.2	375.4 ± 62.9	518.7 ± 37.2	0.3 ± 0.1	0.1 ± 0.0	6.1 ± 0.3
	pH 7.5 Day 0	BDL	BDL	35.5 ± 1.8	755.9 ± 87.6	0.1± 0.0	BDL	7.2 ± 0.3
	pH 7.5 Day 45	BDL	BDL	7.2 ± 0.4	304.2 ± 17.2	0.4 ± 0.0	BDL	3.9 ± 0.0
	pH 7.5 Day 90	BDL	BDL	4.9 ± 0.2	304.4 ± 4.6	0.1 ± 0.0	BDL	4.3 ± 0.2
	pH10 Day 0	BDL	BDL	43.2 ± 6.5	978.4 ± 49.9	0.1 ± 0.0	BDL	8.2 ± 0.5
	pH 10 Day 45	BDL	0.1 ± 0.0	6.8 ± 0.9	277.6 ± 4.2	0.4 ± 0.1	BDL	3.9 ± 0.3
	pH 10 Day 90	BDL	BDL	2.9 ± 0.3	341.6 ± 3.5	0.1 ± 0.0	BDL	4.0 ± 0.2
Overlying Water	pH 5 Day 0	BDL	BDL	19.2 ± 2.3	267.7 ± 31.0	BDL	BDL	1.8 ± 0.1
	pH 5 Day 45	0.0 ± 0.0	0.2 ± 0.1	75.6 ± 13.8	315.1 ± 10.8	1.7 ± 0.1	0.1 ± 0.0	5.5 ± 0.7
	pH 5 Day 90	0.0 ± 0.0	0.0 ± 0.0	235.9 ± 21.7	340.1 ± 20.3	0.0 ± 0.0	0.0 ± 0.0	5.1 ± 0.3
	pH 7.5 Day 0	BDL	0.1 ± 0.0	15.9 ± 1.7	190.4 ± 18.2	3.6 ± 0.0	BDL	1.8 ± 0.2
	pH 7.5 Day 45	0.0 ± 0.0	0.0 ± 0.0	6.5 ± 0.5	167.3 ± 8.4	2.2 ± 0.3	0.0 ± 0.0	3.8 ± 0.1
	pH 7.5 Day 90	0.0 ± 0.0	0.0 ± 0.0	3.7 ± 0.2	207.9 ± 5.3	0.2 ± 0.1	0.0 ± 0.0	3.1 ± 0.1
	pH10 Day 0	BDL	0.2 ± 0.0	6.8 ± 0.4	214.7 ± 37.0	1.3 ± 0.0	BDL	1.7 ± 0.2
	pH 10 Day 45	0.0 ± 0.0	0.0 ± 0.0	2.0 ± 0.3	164.8 ± 8.4	1.0 ± 0.0	0.0 ± 0.0	4.0 ± 0.2
	pH 10 Day 90	0.0 ± 0.0	0.0 ± 0.0	0.9 ± 0.1	245.2 ± 11.0	0.0 ± 0.0	0.0 ± 0.0	3.5 ± 0.1

Appendix B continued

(b)	Treatment	Nb	Nd	Ni	P	Pb	Pr	Rb
Pore Water	pH 5 Day 0	BDL	9.4 ± 8.1	684.1 ± 220.6	756.6 ± 90.7	1.6 ± 1.5	2.4 ± 2.1	3.6 ± 1.1
	pH 5 Day 45	BDL	8.6 ± 1.1	296.0 ± 23.4	534.4 ± 26.7	1.2 ± 0.2	2.1 ± 0.3	2.0 ± 0.1
	pH 5 Day 90	BDL	4.7 ± 0.2	180.3 ± 23.9	620.2 ± 8.6	0.9 ± 0.0	1.2 ± 0.1	2.1 ± 0.2
	pH 7.5 Day 0	BDL	2.4 ± 1.8	714.7 ± 161.9	732.6 ± 64.1	0.1 ± 0.0	0.6 ± 0.5	2.9 ± 0.6
	pH 7.5 Day 45	BDL	BDL	24.0 ± 1.5	374.3 ± 32.2	0.3 ± 0.0	BDL	1.1 ± 0.0
	pH 7.5 Day 90	BDL	BDL	11.6 ± 1.6	451.0 ± 53.9	0.1 ± 0.0	BDL	1.7 ± 0.1
	pH10 Day 0	BDL	BDL	2396.6 ± 1738.5	2991.7 ± 2189.3	0.3 ± 0.2	BDL	10.7 ± 7.2
	pH 10 Day 45	BDL	4.1 ± 2.9	8.0 ± 1.8	371.3 11.9	0.3 ± 0.0	1.0 ± 0.7	1.2 ± 0.0
	pH 10 Day 90	BDL	BDL	2.4 ± 0.1	396.7 ± 34.1	0.1 ± 0.0	BDL	1.7 ± 0.1
Overlying Water	pH 5 Day 0	BDL	0.1 ± 0.0	32.5 ± 5.2	344.0 ± 18.0	0.7 ± 0.0	BDL	0.7 ± 0.0
	pH 5 Day 45	0.0 ± 0.0	0.5 ± 0.0	151.3 ± 6.2	289.2 ± 5.9	1.0 ± 0.2	0.1 ± 0.0	1.6 ± 0.1
	pH 5 Day 90	0.0 ± 0.0	3.2 ± 0.1	139.0 ± 19.2	425.3 ± 10.1	0.2 ± 0.0	0.8 ± 0.0	1.8 ± 0.1
	pH 7.5 Day 0	BDL	0.0 ± 0.0	23.2 ± 1.6	244.8 ± 23.0	BDL	0.0 ± 0.0	0.6 ± 0.1
	pH 7.5 Day 45	0.0 ± 0.0	0.1 ± 0.0	18.0 ± 1.5	210.8 ± 9.6	0.6 ± 0.1	BDL	1.4 ± 0.0
	pH 7.5 Day 90	0.0 ± 0.0	0.0 ± 0.0	11.0 ± 1.4	314.3 ± 48.7	0.0 ± 0.0	0.0 ± 0.0	1.5 ± 0.1
	pH10 Day 0	BDL	0.0 ± 0.0	21.1 ± 1.8	276.1 ± 12.5	BDL	0.0 ± 0.0	0.7 ± 0.0
	pH 10 Day 45	0.0 ± 0.0	0.1 ± 0.0	4.3 ± 0.4	231.8 ± 27.0	1.4 ± 0.0	BDL	1.6 ± 0.1
	pH 10 Day 90	0.0 ± 0.0	0.0 ± 0.0	1.5 ± 0.1	247.8 ± 16.7	0.0 ± 0.0	0.0 ± 0.0	1.3 ± 0.1

Appendix B continued

(a)	**Treatment**	**Sb**	**Sc**	**Sm**	**Sn**	**Sr**	**Ta**
Pore Water	pH 5 Day 0	0.2 ± 0.0	1.7 ± 0.2	BDL	0.2 ± 0.0	1340.9 ± 128.1	BDL
	pH 5 Day 45	0.2 ± 0.0	0.9 ± 0.2	BDL	0.2 ± 0.0	622.6 ± 45.0	BDL
	pH 5 Day 90	BDL	1.5 ± 0.1	BDL	BDL	556.8 ± 11.6	BDL
	pH 7.5 Day 0	0.1 ± 0.0	1.5 ± 0.2	BDL	BDL	1090.0 ± 123.4	BDL
	pH 7.5 Day 45	0.3 ± 0.1	0.6 ± 0.0	BDL	BDL	343.4 ± 7.5	BDL
	pH 7.5 Day 90	0.1 ± 0.0	0.5 ± 0.1	BDL	0.1 ± 0.0	458.9 ± 3.4	BDL
	pH10 Day 0	0.2 ± 0.0	0.6 ± 0.1	BDL	BDL	1436.8 ± 49.7	BDL
	pH 10 Day 45	0.4 ± 0.1	0.5 ± 0.0	BDL	BDL	211.3 ± 12.4	BDL
	pH 10 Day 90	0.2 ± 0.1	0.6 ± 0.0	BDL	BDL	138.0 ± 5.0	BDL
Overlying Water	pH 5 Day 0	0.0 ± 0.0	1.9 ± 0.0	BDL	0.3 ± 0.0	188.4 ± 111.1	BDL
	pH 5 Day 45	0.1 ± 0.0	0.4 ± 0.0	0.0 ± 0.0	0.2 ± 0.2	546.2 ± 35.4	0.0 ± 0.0
	pH 5 Day 90	0.1 ± 0.0	1.4 ± 0.1	0.0 ± 0.0	0.5 ± 0.4	124.5 ± 17.4	0.0 ± 0.0
	pH 7.5 Day 0	0.1 ± 0.0	1.7 ± 0.1	BDL	BDL	179.2 ± 103.1	BDL
	pH 7.5 Day 45	0.1 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	366.6 ± 1.71	0.0 ± 0.0
	pH 7.5 Day 90	0.2 ± 0.0	0.4 ± 0.0	0.0 ± 0.0	0.2 ± 0.0	112.8 ± 0.7	0.0 ± 0.0
	pH10 Day 0	0.0 ± 0.0	0.6 ± 0.4	BDL	0.1 ± 0.0	154.2 ± 95.7	BDL
	pH 10 Day 45	0.2 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	168.3 ± 5.8	0.0 ± 0.0
	pH 10 Day 90	0.2 ± 0.1	0.8 ± 0.1	0.0 ± 0.0	0.1 ± 0.0	83.5 ± 2.8	0.0 ± 0.0

Appendix B continued

(b)	**Treatment**	**Sb**	**Sc**	**Sm**	**Sn**	**Sr**	**Ta**
Pore Water	pH 5 Day 0	BDL	3.2 ± 0.0	3.1 ± 2.2	0.9 ± 0.0	675.1 ± 44.5	BDL
	pH 5 Day 45	BDL	0.5 ± 0.0	1.9 ± 0.3	0.2 ± 0.0	473.1 ± 14.4	BDL
	pH 5 Day 90	BDL	0.6 ± 0.1	1.1 ± 0.1	0.1 ± 0.0	418.2 ± 12.8	BDL
	pH 7.5 Day 0	BDL	BDL	0.5 ± 0.3	0.3 ± 0.0	1017.5 ± 97.1	BDL
	pH 7.5 Day 45	BDL	0.2 ± 0.0	BDL	BDL	278.6 ± 3.0	BDL
	pH 7.5 Day 90	0.0 ± 0.0	0.3 ± 0.1	BDL	BDL	370.9 ± 17.5	BDL
	pH10 Day 0	0.0 ± 0.0	1.2 ± 0.0	BDL	BDL	3943.6 ± 2879.8	BDL
	pH 10 Day 45	BDL	0.2 ± 0.0	0.8 ± 0.3	BDL	205.0 ± 45.6	BDL
	pH 10 Day 90	0.1 ± 0.0	0.3 ± 0.0	BDL	BDL	56.9 ± 4.4	BDL
Overlying Water	pH 5 Day 0	0.1 ± 0.0	0.2 ± 0.0	BDL	0.2 ± 0.0	292.6 ± 98.0	BDL
	pH 5 Day 45	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	403.4 ± 6.5	0.0 ± 0.0
	pH 5 Day 90	0.0 ± 0.0	0.3 ± 0.3	0.7 ± 0.0	0.0 ± 0.0	92.0 ± 6.0	0.0 ± 0.0
	pH 7.5 Day 0	0.0 ± 0.0	BDL	0.0 ± 0.0	0.2 ± 0.2	506.3 ± 177.8	BDL
	pH 7.5 Day 45	BDL	0.0 ± 0.0	BDL	0.1 ± 0.0	308.9 ± 4.3	0.0 ± 0.0
	pH 7.5 Day 90	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	88.7 ± 3.3	0.0 ± 0.0
	pH10 Day 0	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.1	604.0 ± 18.4	BDL
	pH 10 Day 45	BDL	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	179.0 ± 33.5	0.0 ± 0.0
	pH 10 Day 90	0.0 ± 0.0	0.4 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	47.5 ± 1.7	0.0 ± 0.0

Appendix B continued

(a)	Treatment	Th	Ti	Tl	Tm	U
Pore Water	pH 5 Day 0	0.0 ± 0.0	8.8 ± 0.9	BDL	BDL	BDL
	pH 5 Day 45	BDL	8.1 ± 3.4	BDL	BDL	0.0 ± 0.0
	pH 5 Day 90	BDL	4.5 ± 0.8	0.1 ± 0.0	BDL	BDL
	pH 7.5 Day 0	BDL	7.2 ± 0.6	BDL	BDL	0.2 ± 0.0
	pH 7.5 Day 45	BDL	2.2 ± 0.0	BDL	BDL	0.8 ± 0.1
	pH 7.5 Day 90	BDL	4.8 ± 1.5	BDL	BDL	0.8 ± 0.0
	pH10 Day 0	BDL	7.1 ± 0.3	BDL	BDL	0.4 ± 0.3
	pH 10 Day 45	BDL	8.7 ± 0.0	BDL	BDL	1.1 ± 0.4
	pH 10 Day 90	BDL	0.6 ± 0.2	BDL	BDL	0.7 ± 0.0
Overlying Water	pH 5 Day 0	0.0 ± 0.0	4.9 ± 0.7	BDL	BDL	BDL
	pH 5 Day 45	0.0 ± 0.0	2.3 ± 0.3	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 5 Day 90	0.2 ± 0.1	1.9 ± 0.1	0.1± 0.0	0.0 ± 0.0	0.0 ± 0.0
	pH 7.5 Day 0	0.0 ± 0.0	3.9 ± 0.6	BDL	BDL	0.0 ± 0.0
	pH 7.5 Day 45	0.0 ± 0.0	1.8 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.4 ± 0.0
	pH 7.5 Day 90	0.1 ± 0.0	4.1 ± 1.4	0.0 ± 0.0	0.0 ± 0.0	0.4 ± 0.0
	pH10 Day 0	BDL	3.3 ± 1.2	0.0 ± 0.0	BDL	0.0 ± 0.0
	pH 10 Day 45	0.0 ± 0.0	1.1 ± 1.1	0.0 ± 0.0	0.0 ± 0.0	0.5 ± 0.1
	pH 10 Day 90	0.0 ± 0.0	3.2 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.0

(b)	Treatment	Th	Ti	Tl	Tm	U
Pore Water	pH 5 Day 0	1.2 ± 0.9	20.2 ± 9.4	0.1 ± 0.0	0.1 ± 0.1	0.5 ± 0.4
	pH 5 Day 45	0.1 ± 0.0	6.3 ± 0.9	0.1 ± 0.0	0.1 ± 0.0	0.5 ± 0.0
	pH 5 Day 90	0.1 ± 0.0	8.5 ± 1.4	0.0 ± 0.0	0.1 ± 0.0	0.2 ± 0.0
	pH 7.5 Day 0	0.0 ± 0.0	11.7 ± 1.0	BDL	0.1 ± 0.0	0.1 ± 0.0
	pH 7.5 Day 45	BDL	5.8 ± 1.6	BDL	BDL	0.1 ± 0.0
	pH 7.5 Day 90	BDL	4.6 ± 0.8	BDL	BDL	0.2 ± 0.0
	pH10 Day 0	0.0 ± 0.0	50.4 ± 38.2	0.2 ± 0.0	0.1 ± 0.0	0.8 ± 0.6
	pH 10 Day 45	BDL	3.8 ± 0.0	BDL	BDL	0.3 ± 0.0
	pH 10 Day 90	BDL	2.1 ± 1.3	BDL	BDL	0.1 ± 0.0
Overlying Water	pH 5 Day 0	0.1 ± 0.0	2.6 ± 0.2	BDL	BDL	0.1 ± 0.0
	pH 5 Day 45	0.0 ± 0.0	2.3 ± 0.3	0.1 ± 0.0	0.0 ± 0.0	0.2 ± 0.0
	pH 5 Day 90	0.0 ± 0.0	5.3 ± 1.4	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	pH 7.5 Day 0	0.0 ± 0.0	2.4 ± 0.1	BDL	BDL	0.0 ± 0.0
	pH 7.5 Day 45	0.0 ± 0.0	3.0 ± 1.4	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.0
	pH 7.5 Day 90	0.0 ± 0.0	2.1 ± 0.5	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	pH10 Day 0	BDL	2.5 ± 0.3	BDL	BDL	0.0 ± 0.0
	pH 10 Day 45	0.0 ± 0.0	0.5 ± 0.5	0.0 ± 0.0	0.0 ± 0.0	0.3 ± 0.0
	pH 10 Day 90	0.0 ± 0.0	3.6 ± 0.7	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0

Appendix B continued

(a)	Treatment	V	W	Y	Yb	Zn	Zr
Pore Water	pH 5 Day 0	76.2 ± 20.1	BDL	3.6 ± 0.4	BDL	11.6 ± 1.1	0.1 ± 0.0
	pH 5 Day 45	47.3 ± 21.4	BDL	1.5 ± 0.1	BDL	7.5 ± 1.2	0.1 ± 0.0
	pH 5 Day 90	23.5 ± 1.2	BDL	1.9 ± 0.4	0.1 ± 0.0	52.3 ± 9.7	0.1 ± 0.0
	pH 7.5 Day 0	117.8 ± 30.3	BDL	2.7 ± 0.1	BDL	4.4 ± 0.2	0.1 ± 0.0
	pH 7.5 Day 45	274.3 ± 9.1	0.1 ± 0.0	0.8 ± 0.0	BDL	2.7 ± 0.7	0.1 ± 0.0
	pH 7.5 Day 90	228.7 ± 8.7	BDL	1.1 ± 0.0	BDL	2.0 ± 0.1	0.1 ± 0.0
	pH10 Day 0	99.9 ± 24.6	BDL	3.1 ± 0.2	BDL	7.0 ± 0.8	0.2 ± 0.1
	pH 10 Day 45	491.3 ± 119.8	0.2 ± 0.0	0.6 ± 0.0	BDL	3.6 ± 0.6	0.2 ± 0.0
	pH 10 Day 90	328.0 ± 55.5	0.2 ± 0.0	0.4 ± 0.0	BDL	2.3 ± 0.6	0.2 ± 0.0
Overlying Water	pH 5 Day 0	8.9 ± 1.8	0.7 ± 0.2	0.6 ± 0.5	BDL	34.0 ± 1.1	0.1 ± 0.1
	pH 5 Day 45	65.4 ± 19.7	0.0 ± 0.0	1.4 ± 0.2	0.0 ± 0.0	23.1 ± 4.5	0.0 ± 0.0
	pH 5 Day 90	44.0 ± 3.2	1.0 ± 0.4	0.2 ± 0.1	0.0 ± 0.0	52.4 ± 7.3	0.7 ± 0.4
	pH 7.5 Day 0	11.5 ± 0.6	0.3 ± 0.0	0.4 ± 0.2	BDL	16.1 ± 16.1	0.0 ± 0.0
	pH 7.5 Day 45	241.7 ± 15.1	0.0 ± 0.0	0.7 ± 0.0	0.0 ± 0.0	6.4 ± 1.4	0.0 ± 0.0
	pH 7.5 Day 90	204.3 ± 5.5	0.5 ± 0.2	0.2 ± 0.0	0.0 ± 0.0	4.0 ± 0.1	0.2 ± 0.1
	pH10 Day 0	18.4 ± 2.8	BDL	0.6 ± 0.5	BDL	2.6 ± 1.1	0.0 ± 0.0
	pH 10 Day 45	400.0 ± 74.5	0.1 ± 0.0	0.3 ± 0.0	0.0 ± 0.0	4.0 ± 0.8	0.0 ± 0.0
	pH 10 Day 90	352.7 ± 56.3	0.3 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	3.6 ± 0.6	0.2 ± 0.0

Appendix B continued

(b)	**Treatment**	**V**	**W**	**Y**	**Yb**	**Zn**	**Zr**
Pore Water	pH 5 Day 0	102.0 ± 95.3	BDL	10.0 ± 7.0	0.9 ± 0.6	72.8 ± 41.9	1.6 ± 1.5
	pH 5 Day 45	7.9 ± 1.8	BDL	9.7 ± 1.1	0.8 ± 0.1	71.1 ± 7.8	0.2 ± 0.1
	pH 5 Day 90	8.3 ± 2.0	BDL	5.8 ± 0.6	0.3 ± 0.1	43.4 ± 2.9	0.4 ± 0.3
	pH 7.5 Day 0	7.5 ± 0.4	BDL	5.0 ± 1.6	0.3 ± 0.0	44.3 ± 13.8	0.2 ± 0.0
	pH 7.5 Day 45	11.3 ± 0.7	0.1 ± 0.1	0.8 ± 0.0	BDL	2.7 ± 0.6	0.1 ± 0.0
	pH 7.5 Day 90	38.6 ± 1.9	0.3 ± 0.1	0.8 ± 0.1	BDL	2.2 ± 0.4	0.1 ± 0.0
	pH10 Day 0	34.6 ± 23.2	0.1 ± 0.1	12.5 ± 8.8	0.2 ± 0.0	110.9 ± 76.5	1.6 ± 1.5
	pH 10 Day 45	33.4 ± 5.0	0.8 ± 0.7	0.5 ± 0.1	BDL	1.9 ± 0.4	2.1 ± 2.0
	pH 10 Day 90	83.6 ± 23.3	0.4 ± 0.4	0.2 ± 0.0	BDL	2.9 ± 1.2	0.1 ± 0.0
Overlying Water	pH 5 Day 0	3.7 ± 0.2	0.6 ± 0.0	1.1 ± 0.4	BDL	13.5 ± 1.7	0.1 ± 0.0
	pH 5 Day 45	14.9 ± 1.5	0.0 ± 0.0	3.6 ± 0.0	0.2 ± 0.0	46.8 ± 2.3	0.1 ± 0.0
	pH 5 Day 90	33.7 ± 7.5	0.5 ± 0.3	0.2 ± 0.0	0.0 ± 0.0	47.6 ± 2.9	0.1 ± 0.0
	pH 7.5 Day 0	2.6 ± 0.0	0.3 ± 0.0	1.3 ± 0.5	BDL	4.7 ± 0.6	0.1 ± 0.0
	pH 7.5 Day 45	25.8 ± 1.3	0.1 ± 0.1	0.6 ± 0.0	0.0 ± 0.0	5.9 ± 0.2	0.0 ± 0.0
	pH 7.5 Day 90	32.9 4.0	0.5 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	5.9 ± 0.6	0.1 ± 0.0
	pH10 Day 0	5.2 ± 0.4	BDL	1.6 ± 0.1	BDL	2.4 ± 0.2	0.0 ± 0.0
	pH 10 Day 45	62.2 ± 4.7	0.4 ± 0.0	0.5 ± 0.2	0.0 ± 0.0	5.5 ± 0.1	0.0 ± 0.0
	pH 10 Day 90	103.0 ± 30.0	0.7 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	3.9 ± 0.3	0.8 ± 0.5

APPENDIX C: Mean ± SE metal concentrations (µg/L) from the freeze-thaw leaching experiment using Syncrude (a) and Suncor (b) cokes. (*n* = 3) (BDL = below detection limit)

(a)	**Treatment**	**Ag**	**Al**	**As**	**Au**	**Ba**	**Ca**
Pore Water	Unfrozen Cycle 1	BDL	11.6 ± 0.9	0.6 ± 0.1	0.0 ± 0.0	18.2 ± 0.8	94428.5 ± 8264.8
	Unfrozen Cycle 3	BDL	29.1 ± 3.0	0.5 ± 0.1	BDL	23.5 ± 0.5	72903.1 ± 7923.9
	Unfrozen Cycle 6	BDL	25.7 ± 0.9	0.6 ± 0.1	0.0 ± 0.0	20.1 ± 1.4	61079.4 ± 3769.1
	Frozen Cycle 1	BDL	19.9 ± 3.4	0.4 ± 0.0	0.0 ± 0.0	18.8 ± 1.3	96693.7 ± 8866.3
	Frozen Cycle 3	BDL	16.4 ± 3.6	1.1 ± 0.2	0.0 ± 0.0	22.6 ± 1.5	128746.1 ± 8350.2
	Frozen Cycle 6	BDL	58.0 ± 37.3	0.7 ± 0.0	0.0 ± 0.0	18.6 ± 0.7	69870.2 ± 7139.9
Overlying Water	Unfrozen Cycle 1	0.0 ± 0.0	51.8 ± 0.0	BDL	0.0 ± 0.0	18.1 ± 0.3	54056.0 ± 949.0
	Unfrozen Cycle 3	BDL	47.5 ± 5.6	0.5 ± 0.0	0.0 ± 0.0	20.9 ± 0.9	54572.8 ± 1424.7
	Unfrozen Cycle 6	BDL	34.5 ± 12.2	0.4 ± 0.1	BDL	23.1 ± 1.1	56309.4 ± 3812.0
	Frozen Cycle 1	BDL	24.3 ± 2.9	BDL	0.0 ± 0.0	17.0 ± 1.5	47259.4 ± 199.4
	Frozen Cycle 3	BDL	27.3 ± 6.0	BDL	0.0 ± 0.0	15.2 ± 1.0	45536.6 ± 2179.1
	Frozen Cycle 6	BDL	17.3 ± 1.8	0.2 ± 0.0	BDL	15.0 ± 1.1	38931.9 ± 3966.7

(b)	**Treatment**	**Ag**	**Al**	**As**	**Au**	**Ba**	**Ca**
Pore Water	Unfrozen Cycle 1	0.0 ± 0.0	86.5 ± 8.5	BDL	0.0 ± 0.0	8.0 ± 0.5	126482.2 ± 22519.0
	Unfrozen Cycle 3	BDL	116.6 ± 23.0	0.3 ± 0.0	BDL	3.8 ± 0.5	71311.9 ± 4471.8
	Unfrozen Cycle 6	BDL	59.9 ± 5.1	BDL	BDL	5.5 ± 1.2	64224.1 ± 3872.7
	Frozen Cycle 1	BDL	85.2 ± 21.6	0.4 ± 0.0	BDL	5.5 ± 1.2	97748.8 ± 18067.7
	Frozen Cycle 3	0.0 ± 0.0	47.9 ± 5.7	0.4 ± 0.1	BDL	4.7 ± 0.9	97805.7 ± 13154.0
	Frozen Cycle 6	BDL	36.4 ± 2.0	0.3 ± 0.0	BDL	3.6 ± 0.3	84187.2 ± 11301.5
Overlying Water	Unfrozen Cycle 1	BDL	94.7 ± 10.1	BDL	BDL	8.1 ± 0.2	54685.4 ± 1620.3
	Unfrozen Cycle 3	BDL	48.8 ± 12.0	0.2 ± 0.0	BDL	10.5 ± 0.6	61461.4 ± 1137.1
	Unfrozen Cycle 6	BDL	49.0 ± 5.6	0.4 ± 0.0	BDL	7.6 ± 2.1	60812.1 ± 7747.1
	Frozen Cycle 1	BDL	69.6 ± 9.6	BDL	BDL	8.2 ± 0.0	42836.6 ± 2834.2
	Frozen Cycle 3	BDL	38.0 ± 5.2	0.4 ± 0.0	0.0 ± 0.0	7.9 ± 0.1	29952.8 ± 1918.6
	Frozen Cycle 6	BDL	27.8 ± 6.3	BDL	0.0 ± 0.0	9.6 ± 0.3	38574.2 ± 4194.0

Appendix C continued

(a)	**Treatment**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**	**Cu**	**Dy**
Pore Water	Unfrozen Cycle 1	BDL	BDL	0.7 ± 0.0	1.1 ± 0.0	BDL	1.9 ± 0.1	0.0 ± 0.0
	Unfrozen Cycle 3	BDL	0.0 ± 0.0	0.3 ± 0.1	1.0 ± 0.1	0.0 ± 0.0	3.9 ± 1.5	0.0 ± 0.0
	Unfrozen Cycle 6	BDL	0.1 ± 0.0	0.4 ± 0.1	BDL	BDL	0.9 ± 0.1	0.0 ± 0.0
	Frozen Cycle 1	BDL	0.1 ± 0.0	0.7 ± 0.2	1.2 ± 0.0	0.0 ± 0.0	1.8 ± 0.3	0.0 ± 0.0
	Frozen Cycle 3	BDL	0.0 ± 0.0	0.7 ± 0.1	1.4 ± 0.2	0.1 ± 0.0	2.4 ± 0.3	BDL
	Frozen Cycle 6	BDL	0.7 ± 0.0	0.4 ± 0.1	0.9 ± 0.0	0.0 ± 0.0	1.2 ± 0.1	0.0 ± 0.0
Overlying Water	Unfrozen Cycle 1	BDL	BDL	0.2 ± 0.0	1.8 ± 0.0	0.0 ± 0.0	0.7 ± 0.1	BDL
	Unfrozen Cycle 3	BDL	BDL	0.1 ± 0.0	1.4 ± 0.1	0.0 ± 0.0	0.7 ± 0.2	BDL
	Unfrozen Cycle 6	BDL	BDL	0.2 ± 0.0	0.5 ± 0.1	0.0 ± 0.0	0.8 ± 0.1	BDL
	Frozen Cycle 1	BDL	BDL	0.4 ± 0.1	1.3 ± 0.0	0.0 ± 0.0	0.6 ± 0.0	BDL
	Frozen Cycle 3	BDL	BDL	0.1 ± 0.0	1.7 ± 0.0	0.0 ± 0.0	0.5 ± 0.0	BDL
	Frozen Cycle 6	BDL	0.0 ± 0.0	0.1 ± 0.0	0.4 ± 0.0	0.0 ± 0.0	0.8 ± 0.0	0.0 ± 0.0

(b)	**Treatment**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**	**Cu**	**Dy**
Pore Water	Unfrozen Cycle 1	BDL	0.2 ± 0.2	33.9 ± 14.2	1.5 ± 0.0	0.1 ± 0.0	3.2 ± 0.7	BDL
	Unfrozen Cycle 3	BDL	0.2 ± 0.1	11.3± 4.6	1.4 ± 0.0	0.0 ± 0.0	2.1 ± 0.6	BDL
	Unfrozen Cycle 6	BDL	BDL	3.8 ± 0.1	1.4 ± 0.1	0.0 ± 0.0	1.4 ± 0.5	BDL
	Frozen Cycle 1	BDL	0.3 ± 0.1	32.8 ± 16.1	1.2 ± 0.0	0.0 ± 0.0	6.1 ± 3.8	BDL
	Frozen Cycle 3	BDL	0.0 ± 0.0	7.1 ± 1.9	1.1 ± 0.0	0.1 ± 0.0	1.9 ± 0.1	BDL
	Frozen Cycle 6	BDL	0.0 ± 0.0	4.6 ± 1.0	1.4 ± 0.0	0.0 ± 0.0	1.6 ± 0.3	BDL
Overlying Water	Unfrozen Cycle 1	BDL	BDL	2.5 ± 0.1	0.5 ± 0.0	0.0 ± 0.0	1.1 ± 0.3	BDL
	Unfrozen Cycle 3	BDL	0.0 ± 0.0	2.8 ± 0.4	0.6 ± 0.0	0.0 ± 0.0	1.1 ± 0.1	0.0 ± 0.0
	Unfrozen Cycle 6	0.1 ± 0.0	0.1 ± 0.1	6.4 ± 3.7	0.4 ± 0.0	0.0 ± 0.0	1.3 ± 0.2	0.0 ± 0.0
	Frozen Cycle 1	BDL	BDL	2.9 ± 0.3	0.5 ± 0.0	0.0 ± 0.0	1.0 ± 0.1	0.0 ± 0.0
	Frozen Cycle 3	BDL	0.0 ± 0.0	2.1 ± 0.1	0.4 ± 0.0	0.0 ± 0.0	0.5 ± 0.1	0.0 ± 0.0
	Frozen Cycle 6	BDL	BDL	2.1 ± 0.4	0.8 ± 0.0	0.0 ± 0.0	0.9 ± 0.0	BDL

Appendix C continued

(a)	Treatment	Er	Eu	Fe	Ga	Gd	Ge	Hf
Pore Water	Unfrozen Cycle 1	BDL	BDL	175.8 ± 9.6	BDL	BDL	BDL	0.0 ± 0.0
	Unfrozen Cycle 3	BDL	BDL	121.2 ± 14.9	0.1 ± 0.0	BDL	0.1 ± 0.0	0.0 ± 0.0
	Unfrozen Cycle 6	0.0 ± 0.0	BDL	115.0 ± 17.1	BDL	BDL	BDL	0.0 ± 0.0
	Frozen Cycle 1	BDL	BDL	180.9 ± 28.4	BDL	BDL	0.1 ± 0.0	0.0 ± 0.0
	Frozen Cycle 3	BDL	BDL	214.5 ± 22.6	BDL	BDL	0.1 ± 0.0	0.0 ± 0.0
	Frozen Cycle 6	0.0 ± 0.0	BDL	186.6 ± 46.1	0.1 ± 0.0	BDL	0.1 ± 0.0	0.0 ± 0.0
Overlying Water	Unfrozen Cycle 1	BDL	BDL	108.5 ± 14.5	BDL	BDL	BDL	BDL
	Unfrozen Cycle 3	0.0 ± 0.0	BDL	85.6 ± 5.9	0.1 ± 0.0	BDL	BDL	BDL
	Unfrozen Cycle 6	0.0 ± 0.0	BDL	95.6 ± 10.5	0.1 ± 0.0	BDL	0.1 ± 0.0	BDL
	Frozen Cycle 1	BDL	BDL	79.1 ± 10.7	BDL	BDL	BDL	BDL
	Frozen Cycle 3	0.0 ± 0.0	BDL	91.2 ± 3.1	0.1 ± 0.0	BDL	0.1 ± 0.0	BDL
	Frozen Cycle 6	BDL	BDL	71.4 ± 8.9	0.1 ± 0.0	BDL	BDL	BDL

(b)	Treatment	Er	Eu	Fe	Ga	Gd	Ge	Hf
Pore Water	Unfrozen Cycle 1	BDL	BDL	254.6 ± 44.6	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0
	Unfrozen Cycle 3	BDL	BDL	183.4 ± 38.5	0.1 ± 0.0	BDL	0.1 ± 0.0	BDL
	Unfrozen Cycle 6	BDL	BDL	126.6 ± 10.0	0.1 ± 0.0	BDL	0.1 ± 0.0	BDL
	Frozen Cycle 1	0.0 ± 0.0	BDL	225.0 ± 47.4	BDL	0.1 ± 0.0	BDL	0.1 ± 0.0
	Frozen Cycle 3	0.0 ± 0.0	BDL	178.8 ± 37.3	0.1 ± 0.0	BDL	0.2 ± 0.0	BDL
	Frozen Cycle 6	0.0 ± 0.0	BDL	147.8 ± 18.4	BDL	BDL	0.1 ± 0.0	BDL
Overlying Water	Unfrozen Cycle 1	BDL	BDL	107.1 ± 14.1	0.1 ± 0.0	BDL	0.1 ± 0.0	BDL
	Unfrozen Cycle 3	BDL	BDL	118.6 ± 8.7	0.1 ± 0.0	BDL	0.1 ± 0.0	0.0 ± 0.0
	Unfrozen Cycle 6	BDL	BDL	118.6 ± 32.4	0.1 ± 0.0	BDL	BDL	0.0 ± 0.0
	Frozen Cycle 1	BDL	BDL	81.7 ± 8.7	BDL	BDL	BDL	BDL
	Frozen Cycle 3	BDL	BDL	61.5 ± 4.8	0.1 ± 0.0	BDL	BDL	BDL
	Frozen Cycle 6	BDL	BDL	76.2 ± 9.4	0.1 ± 0.0	BDL	BDL	BDL

Appendix C continued

(a)	Treatment	Hg	Ho	La	Li	Lu	Mg
Pore Water	Unfrozen Cycle 1	BDL	BDL	0.0 ± 0.0	28.0 ± 6.4	BDL	81933.0 ± 5236.2
	Unfrozen Cycle 3	BDL	BDL	0.0 ± 0.0	21.3 ± 3.0	BDL	57994.2 ± 1144.7
	Unfrozen Cycle 6	BDL	BDL	0.1 ± 0.0	14.7	BDL	55477.2 ± 1114.9
	Frozen Cycle 1	BDL	BDL	0.0 ± 0.0	22.7 ± 3.8	BDL	78683.4 ± 4158.9
	Frozen Cycle 3	BDL	0.0 ± 0.0	0.0 ± 0.0	33.9 ± 1.8	BDL	140503.1 ± 4034.5
	Frozen Cycle 6	BDL	0.0 ± 0.0	0.1 ± 0.1	15.4 ± 2.3	BDL	89690.4 ± 5319.1
Overlying Water	Unfrozen Cycle 1	BDL	BDL	0.0 ± 0.0	10.0 ± 0.0	BDL	50816.7 ± 1257.1
	Unfrozen Cycle 3	BDL	BDL	0.0 ± 0.0	11.2 ± 0.6	BDL	50789.4 ± 2120.3
	Unfrozen Cycle 6	BDL	0.0 ± 0.0	0.0 ± 0.0	13.5 ± 1.9	BDL	52363.1 ± 4879.4
	Frozen Cycle 1	BDL	BDL	0.0 ± 0.0	5.7 ± 0.5	BDL	46003.1 ± 1896.7
	Frozen Cycle 3	BDL	BDL	0.0 ± 0.0	8.7 ± 0.5	BDL	44257.8 ± 1771.1
	Frozen Cycle 6	BDL	BDL	0.0 ± 0.0	8.7 ± 0.5	BDL	45817.0 ± 1247.2

(b)	Treatment	Hg	Ho	La	Li	Lu	Mg
Pore Water	Unfrozen Cycle 1	BDL	0.0 ± 0.0	0.2 ± 0.1	25.0 ± 7.7	BDL	80846.7 ± 3367.7
	Unfrozen Cycle 3	BDL	BDL	0.1 ± 0.0	8.2 ± 1.9	BDL	49076.6 ± 1992.9
	Unfrozen Cycle 6	BDL	BDL	BDL	7.7 ± 0.5	0.0 ± 0.0	48001.0 ± 805.6
	Frozen Cycle 1	BDL	BDL	0.2 ± 0.1	16.7 ± 6.7	BDL	54727.7 ± 3950.0
	Frozen Cycle 3	BDL	BDL	0.0 ± 0.0	17.2 ± 2.1	BDL	133558.4 ± 8856.6
	Frozen Cycle 6	BDL	BDL	0.0 ± 0.0	11.3 ± 1.9	BDL	99806.4 ± 1081.2
Overlying Water	Unfrozen Cycle 1	BDL	0.0 ± 0.0	0.0 ± 0.0	2.7 ± 0.1	BDL	49100.3 ± 928.3
	Unfrozen Cycle 3	BDL	BDL	0.0 ± 0.0	6.5 ± 0.5	BDL	49084.0 ± 604.9
	Unfrozen Cycle 6	BDL	BDL	0.1 ± 0.0	6.8 ± 1.8	BDL	46690.2 ± 1064.8
	Frozen Cycle 1	BDL	BDL	0.0 ± 0.0	3.7 ± 0.4	BDL	45522.4 ± 474.9
	Frozen Cycle 3	BDL	0.0 ± 0.0	0.0 ± 0.0	5.1 ± 0.5	BDL	37250.4 ± 307.4
	Frozen Cycle 6	BDL	BDL	0.0 ± 0.0	6.8 ± 0.4	BDL	47005.4 ± 1357.6

Appendix C continued

(a)	Treatment	Mn	Mo	Nb	Nd	Ni	P
Pore Water	Unfrozen Cycle 1	6.2 ± 3.6	121.4± 13.4	0.5 ± 0.0	BDL	14.3 ± 1.4	353.7 ± 22.0
	Unfrozen Cycle 3	0.8 ± 0.3	71.7 ± 6.4	0.4 ± 0.0	BDL	7.9 ± 0.1	219.6 ± 13.7
	Unfrozen Cycle 6	6.6 ± 2.6	65.7 ± 9.1	0.4 ± 0.0	BDL	4.4 ± 0.6	214.2 ± 3.8
	Frozen Cycle 1	6.9 ± 2.2	112.1 ± 4.8	0.5 ± 0.0	BDL	9.8 ± 1.2	326.8 ± 22.8
	Frozen Cycle 3	1.8 ± 0.6	148.1 ± 39.3	0.5 ± 0.0	BDL	10.6 ± 0.2	524.0 ± 22.9
	Frozen Cycle 6	2.8 ± 1.1	58.0 ± 5.8	0.5 ± 0.0	0.3 ± 0.0	6.2 ± 0.4	318.2 ± 27.9
Overlying Water	Unfrozen Cycle 1	2.7 ± 0.2	17.7 ± 3.0	0.4 ± 0.0	BDL	7.6 ± 0.9	181.5 ± 15.5
	Unfrozen Cycle 3	0.3 ± 0.1	36.0 ± 2.7	0.5 ± 0.0	BDL	5.2 ± 0.2	195.9 ± 8.9
	Unfrozen Cycle 6	0.8 ± 0.1	52.8 ± 8.9	0.5 ± 0.1	BDL	3.6 ± 0.4	163.8 ± 14.0
	Frozen Cycle 1	4.9 ± 0.6	17.6 ± 0.9	0.5 ± 0.0	BDL	7.1 ± 0.8	161.9 ± 7.0
	Frozen Cycle 3	0.7 ± 0.2	31.3 ± 5.8	0.5 ± 0.0	BDL	2.9 ± 0.1	161.4 ± 4.9
	Frozen Cycle 6	0.6 ± 0.0	31.4 ± 0.7	0.4 ± 0.0	BDL	2.7 ± 0.1	149.4 ± 2.6

(b)	Treatment	Mn	Mo	Nb	Nd	Ni	P
Pore Water	Unfrozen Cycle 1	1254.9 ± 437.8	40.9 ± 2.5	0.4 ± 0.0	0.2 ± 0.0	163.4 ± 74.0	378.2 ± 30.6
	Unfrozen Cycle 3	363.2 ± 82.6	20.9 ± 2.5	0.4 ± 0.0	BDL	43.8 ± 16.0	196.0 ± 13.1
	Unfrozen Cycle 6	212.7 ± 13.0	21.9 ± 1.0	0.4 ± 0.0	BDL	14.2 ± 1.1	205.7 ± 4.4
	Frozen Cycle 1	970.8 ± 426.5	18.4 ± 3.3	0.4 ± 0.0	BDL	164.7 ± 83.6	249.7 ± 28.9
	Frozen Cycle 3	377.0 ± 125.7	61.6 ± 3.2	0.5 ± 0.0	BDL	22.5 ± 5.3	532.3 ± 42.8
	Frozen Cycle 6	344.6 ± 97.2	51.9 ± 4.8	0.4 ± 0.0	BDL	12.2 ± 2.0	395.6 ± 41.7
Overlying Water	Unfrozen Cycle 1	91.3 ± 6.7	6.3 ± 0.2	0.4 ± 0.0	BDL	10.4 ± 0.2	126.8 ± 3.4
	Unfrozen Cycle 3	162.8 ± 14.8	16.2 ± 1.0	0.4 ± 0.0	BDL	9.7 ± 0.5	150.2 ± 7.2
	Unfrozen Cycle 6	264.5 ± 117.0	19.9 ± 2.2	0.4 ± 0.0	BDL	26.8 ± 18.4	164.3 ± 6.9
	Frozen Cycle 1	87.6 ± 12.2	6.2 ± 0.3	0.4 ± 0.0	BDL	13.4 ± 1.4	129.4 ± 1.9
	Frozen Cycle 3	84.6 ± 11.0	13.1 ± 1.0	0.4 ± 0.0	BDL	7.9 ± 0.6	129.6 ± 4.4
	Frozen Cycle 6	137.5 ± 31.2	23.0 ± 0.2	0.4 ± 0.0	BDL	5.9 ± 0.7	165.9 ± 3.1

Appendix C continued

(a)	Treatment	Pb	Pr	Rb	Sb	Sc	Se
Pore Water	Unfrozen Cycle 1	0.1 ± 0.0	BDL	6.2 ± 0.9	0.3 ± 0.0	0.5 ± 0.0	2.3 ± 0.4
	Unfrozen Cycle 3	0.1 ± 0.0	BDL	6.4 ± 0.2	0.4 ± 0.0	0.4 ± 0.0	3.2 ± 1.3
	Unfrozen Cycle 6	0.1 ± 0.0	0.0 ± 0.0	4.9 ± 0.4	0.3 ± 0.0	0.4 ± 0.0	0.9 ± 0.3
	Frozen Cycle 1	0.1 ± 0.0	0.0 ± 0.0	7.3 ± 0.9	0.3 ± 0.1	0.4 ± 0.0	4.1 ± 1.7
	Frozen Cycle 3	0.1 ± 0.0	BDL	12.4 ± 0.5	0.6 0.1	0.5 ± 0.0	3.8 ± 0.0
	Frozen Cycle 6	0.1 ± 0.1	0.1 ± 0.0	5.9 ± 0.5	0.2 ± 0.0	0.4 ± 0.0	2.1 ± 0.7
Overlying Water	Unfrozen Cycle 1	0.0 ± 0.0	BDL	2.9 ± 0.3	0.1 ± 0.0	BDL	BDL
	Unfrozen Cycle 3	0.0 ± 0.0	BDL	4.3 ± 0.1	0.1 ± 0.0	0.2 ± 0.0	5.4 ± 0.0
	Unfrozen Cycle 6	0.0 ± 0.0	BDL	5.2 ± 0.3	0.2 ± 0.0	0.3 ± 0.0	BDL
	Frozen Cycle 1	0.0 ± 0.0	BDL	3.0 ± 0.1	0.0 ± 0.0	0.1 ± 0.0	BDL
	Frozen Cycle 3	0.0 ± 0.0	BDL	4.0 ± 0.2	0.1 ± 0.0	BDL	BDL
	Frozen Cycle 6	0.0 ± 0.0	BDL	3.9 ± 0.1	0.1 ± 0.0	0.1 ± 0.0	BDL

(b)	Treatment	Pb	Pr	Rb	Sb	Sc	Se
Pore Water	Unfrozen Cycle 1	0.1 ± 0.0	0.0 ± 0.0	2.9 ± 0.3	0.1 ± 0.0	0.2 ± 0.0	1.1 ± 0.0
	Unfrozen Cycle 3	0.1 ± 0.0	0.0 ± 0.0	1.5 ± 0.2	0.1 ± 0.0	0.1 ± 0.0	4.0 ± 0.0
	Unfrozen Cycle 6	0.1 ± 0.0	0.0 ± 0.0	1.4 ± 0.1	BDL	0.1 ± 0.0	BDL
	Frozen Cycle 1	0.1 ± 0.0	0.0 ± 0.0	1.7 ± 0.4	0.1 ± 0.0	0.2 ± 0.0	BDL
	Frozen Cycle 3	0.1 ± 0.0	0.0 ± 0.0	3.3 ± 0.3	0.1 ± 0.0	0.2 ± 0.0	3.4 ± 0.0
	Frozen Cycle 6	0.1 ± 0.0	0.0 ± 0.0	2.2 ± 0.2	0.1 ± 0.0	0.1 ± 0.0	BDL
Overlying Water	Unfrozen Cycle 1	0.0 ± 0.0	BDL	0.7 ± 0.0	BDL	BDL	BDL
	Unfrozen Cycle 3	0.1 ± 0.0	BDL	1.2 ± 0.1	BDL	0.1 ± 0.0	3.3 ± 0.0
	Unfrozen Cycle 6	0.1 ± 0.0	0.0 ± 0.0	1.3 ± 0.1	BDL	0.2 ± 0.0	BDL
	Frozen Cycle 1	0.1 ± 0.0	BDL	0.8 ± 0.0	BDL	BDL	BDL
	Frozen Cycle 3	0.0 ± 0.0	BDL	1.0 ± 0.0	BDL	0.1 ± 0.0	BDL
	Frozen Cycle 6	0.0 ± 0.0	BDL	1.3 ± 0.0	BDL	0.1 ± 0.0	0.5 ± 0.0

Appendix C continued

(a)	Treatment	Si	Sm	Sn	Sr	Ta	Th
Pore Water	Unfrozen Cycle 1	2170.6 ± 182.5	BDL	BDL	942.7 ± 181.2	BDL	BDL
	Unfrozen Cycle 3	2301.9 ± 49.7	BDL	0.1 ± 0.0	607.5 ± 41.8	0.0 ± 0.0	BDL
	Unfrozen Cycle 6	1939.0 ± 105.4	BDL	BDL	521.0 ± 67.1	BDL	0.0 ± 0.0
	Frozen Cycle 1	1712.2 ± 51.8	BDL	BDL	953.3 ± 204.8	BDL	0.0 ± 0.0
	Frozen Cycle 3	2295.4 ± 183.3	BDL	BDL	1259.8 ± 101.9	0.0 ± 0.0	0.0 ± 0.0
	Frozen Cycle 6	1687.7 ± 41.3	BDL	0.0 ± 0.0	590.6 ± 61.6	BDL	0.0 ± 0.0
Overlying Water	Unfrozen Cycle 1	BDL	BDL	BDL	400.8 ± 11.1	BDL	BDL
	Unfrozen Cycle 3	759.8 ± 49.0	BDL	BDL	448.7 ± 8.4	BDL	BDL
	Unfrozen Cycle 6	1236.4 ± 103.8	BDL	BDL	516.7 ± 50.5	BDL	0.0 ± 0.0
	Frozen Cycle 1	0.0 ± 0.0	BDL	BDL	399.0 ± 11.3	BDL	BDL
	Frozen Cycle 3	222.5 ± 0.0	BDL	BDL	395.5 ± 26.3	BDL	BDL
	Frozen Cycle 6	610.8 ± 16.3	BDL	0.1 ± 0.0	331.2 ± 23.8	BDL	0.0 ± 0.0

(b)	Treatment	Si	Sm	Sn	Sr	Ta	Th
Pore Water	Unfrozen Cycle 1	391.2 ± 63.8	0.1 ± 0.0	0.2 ± 0.0	558.1 ± 52.3	BDL	0.0 ± 0.0
	Unfrozen Cycle 3	378.7 ± 81.8	BDL	0.1 ± 0.0	346.9 ± 7.7	BDL	BDL
	Unfrozen Cycle 6	438.8 ± 10.7	BDL	BDL	324.9 ± 3.6	BDL	BDL
	Frozen Cycle 1	231.7 ± 76.8	BDL	BDL	450.4 ± 54.5	BDL	BDL
	Frozen Cycle 3	584.5 ± 55.1	BDL	0.2 ± 0.0	584.2 ± 70.8	BDL	0.0 ± 0.0
	Frozen Cycle 6	593.9 ± 50.2	BDL	BDL	471.4 ± 47.1	BDL	0.0 ± 0.0
Overlying Water	Unfrozen Cycle 1	BDL	BDL	BDL	327.1 ± 7.5	BDL	0.0 ± 0.0
	Unfrozen Cycle 3	105.7 ± 0.0	BDL	0.1 ± 0.0	328.2 ± 5.2	BDL	0.0 ± 0.0
	Unfrozen Cycle 6	468.6 ± 49.4	BDL	0.1 ± 0.0	328.0 ± 12.8	BDL	0.0 ± 0.0
	Frozen Cycle 1	0.0 ± 0.0	BDL	BDL	290.9 ± 11.2	BDL	BDL
	Frozen Cycle 3	0.0 ± 0.0	BDL	0.1 ± 0.0	185.3 ± 4.4	BDL	0.0 ± 0.0
	Frozen Cycle 6	212.7 ± 12.3	BDL	0.1 ± 0.0	220.7 ± 14.5	BDL	BDL

Appendix C continued

(a)	**Treatment**	**Ti**	**Tl**	**Tm**	**U**	**V**
Pore Water	Unfrozen Cycle 1	2.1 ± 0.2	0.0 ± 0.0	BDL	0.4 ± 0.1	86.3 ± 12.2
	Unfrozen Cycle 3	1.7 ± 0.2	BDL	BDL	0.7 ± 0.1	115.8 ± 19.0
	Unfrozen Cycle 6	2.1 ± 0.8	0.0 ± 0.0	BDL	0.6 ± 0.1	61.0 ± 12.5
	Frozen Cycle 1	2.1 ± 0.5	0.0 ± 0.0	BDL	0.5 ± 0.1	78.7 ± 15.3
	Frozen Cycle 3	2.2 ± 0.3	0.0 ± 0.0	BDL	2.7 ± 0.5	93.1 ± 5.5
	Frozen Cycle 6	2.5 ± 0.8	0.0 ± 0.0	BDL	1.1 ± 0.1	164.9 ± 10.5
Overlying Water	Unfrozen Cycle 1	1.8 ± 0.0	BDL	BDL	0.1 ± 0.0	47.0 ± 7.5
	Unfrozen Cycle 3	2.0 ± 0.0	BDL	BDL	0.2 ± 0.0	77.9 ± 5.4
	Unfrozen Cycle 6	1.6 ± 0.1	0.0 ± 0.0	BDL	0.3 ± 0.1	76.4 ± 10.8
	Frozen Cycle 1	BDL	BDL	BDL	0.1 ± 0.0	32.0 ± 5.4
	Frozen Cycle 3	BDL	BDL	BDL	0.4 ± 0.1	26.4 ± 1.7
	Frozen Cycle 6	0.9 ± 0.1	0.0 ± 0.0	BDL	0.5 ± 0.0	77.7 ± 7.7

(b)	**Treatment**	**Ti**	**Tl**	**Tm**	**V**	**U**
Pore Water	Unfrozen Cycle 1	2.9 ± 0.3	0.0 ± 0.0	BDL	21.4 ± 5.1	0.3 ± 0.0
	Unfrozen Cycle 3	1.6 ± 0.4	BDL	BDL	31.4 ± 2.3	0.1 ± 0.0
	Unfrozen Cycle 6	1.6 ± 0.2	BDL	BDL	34.5 ± 5.6	0.1 ± 0.0
	Frozen Cycle 1	2.7 ± 0.4	0.0 ± 0.0	BDL	13.6 ± 1.3	0.1 ± 0.0
	Frozen Cycle 3	2.2 ± 0.3	0.0 ± 0.0	BDL	55.1 ± 4.2	0.4 ± 0.0
	Frozen Cycle 6	2.1 ± 0.1	0.0 ± 0.0	BDL	46.2 ± 2.7	0.3 ± 0.0
Overlying Water	Unfrozen Cycle 1	1.1 ± 0.2	0.0 ± 0.0	BDL	13.6 ± 1.0	0.0 ± 0.0
	Unfrozen Cycle 3	1.6 ± 0.2	0.0 ± 0.0	BDL	33.7 ± 3.1	0.1 ± 0.0
	Unfrozen Cycle 6	2.0 ± 0.3	0.0 ± 0.0	BDL	32.0 ± 0.4	0.1 ± 0.0
	Frozen Cycle 1	0.9 ± 0.2	0.0 ± 0.0	BDL	10.2 ± 0.1	0.0 ± 0.0
	Frozen Cycle 3	0.9 ± 0.2	0.0 ± 0.0	BDL	13.6 ± 1.3	0.1 ± 0.0
	Frozen Cycle 6	1.4 ± 0.7	BDL	BDL	22.3 ± 3.2	0.1 ± 0.0

Appendix C continued

(a)	**Treatment**	**W**	**Y**	**Yb**	**Zn**	**Zr**
Pore Water	Unfrozen Cycle 1	BDL	2.6 ± 0.2	BDL	6.0 ± 1.2	0.1 ± 0.0
	Unfrozen Cycle 3	BDL	1.7 ± 0.0	BDL	8.9 ± 0.4	0.1 ± 0.0
	Unfrozen Cycle 6	BDL	1.4 ± 0.2	BDL	8.5 ± 1.5	0.2 ± 0.0
	Frozen Cycle 1	BDL	2.4 ± 0.4	0.0 ± 0.0	3.3 ± 0.7	0.1 ± 0.0
	Frozen Cycle 3	BDL	3.6 ± 0.5	0.0 ± 0.0	4.5 ± 0.6	0.2 ± 0.0
	Frozen Cycle 6	BDL	1.8 ± 0.1	0.1 ± 0.0	8.9 ± 0.3	0.4 ± 0.2
Overlying Water	Unfrozen Cycle 1	BDL	1.2 ± 0.1	0.0 ± 0.0	4.1 ± 1.2	0.0 ± 0.0
	Unfrozen Cycle 3	BDL	1.2 ± 0.0	BDL	2.6 ± 0.2	0.1 ± 0.0
	Unfrozen Cycle 6	BDL	1.2 ± 0.1	0.0 ± 0.0	3.5 ± 0.0	0.1 ± 0.0
	Frozen Cycle 1	BDL	1.1 ± 0.1	0.0 ± 0.0	3.4 ± 1.0	0.1 ± 0.0
	Frozen Cycle 3	BDL	1.2 ± 0.1	0.0 ± 0.0	2.8 ± 0.2	0.1 ± 0.0
	Frozen Cycle 6	BDL	0.9 ± 0.0	BDL	BDL	0.0 ± 0.0

(b)	**Treatment**	**W**	**Y**	**Yb**	**Zn**	**Zr**
Pore Water	Unfrozen Cycle 1	0.2 ± 0.0	1.6 ± 0.2	0.0 ± 0.0	11.9 ± 2.2	0.2 ± 0.0
	Unfrozen Cycle 3	BDL	1.1 ± 0.1	BDL	4.8 ± 0.7	0.1 ± 0.0
	Unfrozen Cycle 6	0.2 ± 0.0	0.8 ± 0.0	BDL	4.3 ± 0.8	0.1 ± 0.0
	Frozen Cycle 1	BDL	1.4 ± 0.1	0.0 ± 0.0	11.5 ± 5.8	0.1 ± 0.0
	Frozen Cycle 3	0.6 ± 0.0	1.6 ± 0.2	0.0 ± 0.0	2.6 ± 0.2	0.2 ± 0.0
	Frozen Cycle 6	0.3 ± 0.0	1.3 ± 0.1	0.1 ± 0.0	5.2 ± 0.7	0.1 ± 0.0
Overlying Water	Unfrozen Cycle 1	BDL	0.9 ± 0.0	BDL	BDL	0.1 ± 0.0
	Unfrozen Cycle 3	0.1 ± 0.0	0.9 ± 0.1	BDL	4.5 ± 0.0	0.0 ± 0.0
	Unfrozen Cycle 6	0.1 ± 0.0	1.0 ± 0.1	BDL	5.7 ± 2.0	0.1 ± 0.0
	Frozen Cycle 1	BDL	0.8 ± 0.0	BDL	BDL	0.0 ± 0.0
	Frozen Cycle 3	0.1 ± 0.0	0.5 ± 0.0	BDL	3.6 ± 0.0	0.0 ± 0.0
	Frozen Cycle 6	0.1 ± 0.0	0.6 ± 0.0	BDL	3.2 ± 0.6	0.0 ± 0.0

APPENDIX D: Mean ± SE metal concentrations (µg/L) from the accelerated weathering leaching experiment using Syncrude (a) and Suncor (b) cokes. (*n* = 3) (BDL = below detection limit)

(a)	Treatment	Ag	Al	As	Au	Ba	Ca
Pore Water	Untreated Day 0	BDL	1282.8 ± 293.8	0.4 ± 0.1	BDL	18.6 ± 2.0	109051.5 ± 2403.8
	Water Rinsed Day 0	0.0 ± 0.0	144.8 ± 38.1	0.4 ± 0.1	BDL	60.3 ± 0.5	57097.5 ± 7982.8
	Peroxide Treated Day 0	BDL	3421.8 ± 397.7	9.7 ± 0.6	BDL	23.7 ± 3.9	17098.6 ± 1849.2
	Untreated Day 15	BDL	252.3 ± 187.7	0.4 ± 0.0	0.0 ± 0.0	22.7 ± 0.5	102346.6 ± 12778.2
	Water Rinsed Day 15	BDL	16.1 ± 0.0	0.5 ± 0.0	0.0 ± 0.0	25.4 ± 0.5	61564.5 ± 3594.5
	Peroxide Treated Day 15	BDL	98.9 ± 27.6	0.3 ± 0.0	0.0 ± 0.0	53.7 ± 2.1	72603.4 ± 3951.4
	Untreated Day 30	BDL	12.7 ± 0.0	0.7 ± 0.1	BDL	18.9 ± 0.4	80988.6 ± 2931.5
	Water Rinsed Day 30	BDL	BDL	0.6 ± 0.1	BDL	28.5 ± 2.7	59843.9 ± 2162.8
	Peroxide Treated Day 30	BDL	79.5 ± 8.2	0.5 ± 0.3	0.0 ± 0.0	48.3 ± 5.3	69548.0 ± 4850.6
Overlying Water	Untreated Day 0	0.1 ± 0.0	206.5 ± 40.3	BDL	BDL	9.5 ± 0.5	70788.8 ± 2000.5
	Water Rinsed Day 0	BDL	91.6 ± 2.5	BDL	BDL	28.0 ± 0.4	67788.9 ± 4397.5
	Peroxide Treated Day 0	BDL	398.0 ± 24.5	1.3 ± 0.0	BDL	17.8 ± 0.7	23401.5 ± 539.3
	Untreated Day 15	0.1 ± 0.0	210.9 ± 163.4	0.5 ± 0.0	BDL	28.2 ± 1.6	78875.6 ± 3831.8
	Water Rinsed Day 15	BDL	BDL	0.4 ± 0.1	0.0 ± 0.0	33.6 ± 1.9	52183.2 ± 1429.2
	Peroxide Treated Day 15	BDL	531.3 ± 77.1	0.3 ± 0.0	0.0 ± 0.0	56.8 ± 3.3	53776.7 ± 616.3
	Untreated Day 30	BDL	7.7 ± 0.3	0.3 ± 0.0	BDL	25.4 ± 0.4	72231.9 ± 2039.7
	Water Rinsed Day 30	BDL	BDL	0.6 ± 0.0	BDL	37.1 ± 3.9	54134.9 ± 408.6
	Peroxide Treated Day 30	BDL	143.5 ± 71.2	0.5 ± 0.1	BDL	52.5 ± 4.3	60877.2 ± 5610.5

Appendix D continued

(b)	Treatment	Ag	Al	As	Au	Ba	Ca
Pore Water	Untreated Day 0	0.0 ± 0.0	115.5 ± 24.5	BDL	BDL	3.3 ± 0.6	88057.2 ± 2539.3
	Water Rinsed Day 0	BDL	20.8 ± 1.1	BDL	0.0 ± 0.0	10.3 ± 0.3	83972.8 ± 2426.2
	Peroxide Treated Day 0	BDL	27.6 ± 6.1	0.3 ± 0.0	BDL	4.0 ± 0.2	34743.7 ± 869.6
	Untreated Day 15	BDL	273.6 ± 201.9	0.7 ± 0.0	BDL	22.3 ± 1.2	96126.6 ± 7645.1
	Water Rinsed Day 15	BDL	99.9 ± 58.5	0.3 ± 0.0	BDL	13.0 ± 1.1	57628.6 ± 1835.8
	Peroxide Treated Day 15	BDL	546.2 ± 108.8	0.4 ± 0.1	BDL	11.2 ± 1.2	52176.4 ± 970.1
	Untreated Day 30	BDL	377.2 ± 180.1	0.3 ± 0.0	BDL	23.2 ± 1.3	79756.3 ± 3570.7
	Water Rinsed Day 30	BDL	126.8 ± 28.1	0.2 ± 0.1	BDL	11.8 ± 0.7	55909.0 ± 1081.2
	Peroxide Treated Day 30	BDL	511.7 ± 48.0	0.2 ± 0.0	BDL	9.8 ± 0.3	51258.8 ± 1414.5
Overlying Water	Untreated Day 0	BDL	31.4 ± 0.8	0.3 ± 0.1	BDL	7.8 ± 0.4	63713.6 ± 1044.4
	Water Rinsed Day 0	BDL	13.7 ± 1.8	0.4 ± 0.0	BDL	10.9 ± 0.2	71727.2 ± 1612.3
	Peroxide Treated Day 0	BDL	23.8 ± 1.8	BDL	0.0 ± 0.0	14.3 ± 0.6	32482.1 ± 200.9
	Untreated Day 15	BDL	225.0 ± 106.2	BDL	BDL	15.9 ± 0.6	67482.6 ± 501.9
	Water Rinsed Day 15	BDL	91.8 ± 14.9	0.3 ± 0.0	0.0 ± 0.0	12.9 ± 0.2	48599.4 ± 805.9
	Peroxide Treated Day 15	BDL	248.0 ± 16.6	BDL	0.0 ± 0.0	12.5 ± 0.8	45135.3 ± 939.6
	Untreated Day 30	BDL	293.1 ± 89/4	0.3 ± 0.1	BDL	19.3 ± 2.2	70032.2 ± 167.0
	Water Rinsed Day 30	BDL	164.3 ± 30.8	0.3 ± 0.1	BDL	13.3 ± 0.4	52781.9 ± 903.5
	Peroxide Treated Day 30	BDL	352.4 ± 29.8	0.2 ± 0.0	BDL	12.1 ± 1.0	47297.9 ± 1850.5

Appendix D continued

(a)	**Treatment**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**	**Cu**
Pore Water	Untreated Day 0	0.5 ± 0.1	1.9 ± 0.4	27.5 ± 2.3	BDL	0.4 ± 0.0	2.4 ± 0.1
	Water Rinsed Day 0	BDL	0.2 ± 0.1	22.3 ± 9.4	BDL	0.2 ± 0.0	1.6 ± 0.3
	Peroxide Treated Day 0	BDL	0.8 ± 0.2	19.3 ± 4.9	7.8 ± 0.5	0.3 ± 0.1	1.4 ± 0.2
	Untreated Day 15	BDL	0.4 ± 0.3	8.3 ± 7.6	BDL	0.1 ± 0.1	3.0 ± 0.4
	Water Rinsed Day 15	BDL	0.0 ± 0.0	0.5 ± 0.1	1.6 ± 0.0	0.0 ± 0.0	1.5 ± 0.5
	Peroxide Treated Day 15	BDL	0.3 ± 0.1	20.4 ± 1.5	BDL	0.1 ± 0.0	1.8 ± 0.5
	Untreated Day 30	0.1 ± 0.0	0.0 ± 0.0	0.5 ± 0.0	BDL	0.0 ± 0.0	1.7 ± 0.5
	Water Rinsed Day 30	BDL	BDL	0.7 ± 0.1	BDL	0.0 ± 0.0	0.9 ± 0.1
	Peroxide Treated Day 30	BDL	0.2 ± 0.0	15.1 ± 3.8	BDL	0.1 ± 0.0	1.4 ± 0.1
Overlying Water	Untreated Day 0	BDL	0.9 ± 0.2	3.8 ± 0.6	BDL	0.1 ± 0.0	1.6 ± 0.1
	Water Rinsed Day 0	BDL	0.2 ± 0.1	4.7 ± 1.0	BDL	0.1 ± 0.0	1.1 ± 0.2
	Peroxide Treated Day 0	BDL	0.1 ± 0.0	5.6 ± 0.3	1.8 ± 0.1	0.1 ± 0.0	1.0 ± 0.1
	Untreated Day 15	BDL	0.4 ± 0.3	4.0 ± 3.0	0.7 ± 0.0	0.1 ± 0.1	3.0 ± 0.7
	Water Rinsed Day 15	BDL	0.0 ± 0.0	1.1 ± 0.3	BDL	0.1 ± 0.0	1.1 ± 0.1
	Peroxide Treated Day 15	0.5 ± 0.1	0.9 ± 0.1	12.1 ± 0.4	1.5 ± 0.1	0.1 ± 0.0	1.9 ± 0.2
	Untreated Day 30	0.1 ± 0.0	BDL	0.2 ± 0.0	BDL	0.0 ± 0.0	1.1 ± 0.1
	Water Rinsed Day 30	BDL	0.0 ± 0.0	0.8 ± 0.4	BDL	0.0 ± 0.0	0.9 ± 0.1
	Peroxide Treated Day 30	0.2 ± 0.0	0.4 ± 0.2	10.8 ± 1.4	0.9 ± 0.0	0.1 ± 0.0	7.4 ± 5.8

Appendix D continued

(b)	Treatment	Ce	Cd	Co	Cr	Cs	Cu
Pore Water	Untreated Day 0	1.2 ± 0.2	BDL	6.2 ± 1.2	1.0 ± 0.0	BDL	4.1 ± 0.4
	Water Rinsed Day 0	0.4 ± 0.0	BDL	4.7 ± 0.1	0.6 ± 0.0	BDL	2.1 ± 0.0
	Peroxide Treated Day 0	0.0 ± 0.0	BDL	3.2 ± 0.4	1.4 ± 0.1	BDL	3.3 ± 0.3
	Untreated Day 15	3.3 ± 1.9	BDL	58.8 ± 10.5	BDL	0.1 ± 0.0	4.5 ± 1.3
	Water Rinsed Day 15	1.1 ± 0.5	0.1 ± 0.0	22.2 ± 1.9	BDL	0.0 ± 0.0	2.3 ± 0.7
	Peroxide Treated Day 15	3.6 ± 1.1	0.3 ± 0.1	28.1 ± 2.0	5.7 ± 1.0	0.0 ± 0.0	11.6 ± 3.3
	Untreated Day 30	3.1 ± 0.9	BDL	41.3 ± 4.5	1.3 ± 0.1	0.0 ± 0.0	5.7 ± 1.3
	Water Rinsed Day 30	1.4 ± 0.3	BDL	16.2 ± 2.1	0.9 ± 0.2	0.0 ± 0.0	2.3 ± 0.3
	Peroxide Treated Day 30	2.8 ± 0.2	BDL	19.2 ± 2.8	4.2 ± 0.8	0.0 ± 0.0	11.7 ± 0.8
Overlying Water	Untreated Day 0	0.4 ± 0.0	0.3 ± 0.0	1.5 ± 0.2	0.8 ± 0.0	BDL	3.1 ± 0.1
	Water Rinsed Day 0	0.3 ± 0.0	BDL	2.0 ± 0.1	0.9 ± 0.0	BDL	2.1 ± 0.2
	Peroxide Treated Day 0	BDL	BDL	1.6 ± 0.1	0.8 ± 0.2	BDL	3.3 ± 0.2
	Untreated Day 15	1.9 ± 0.7	BDL	9.2 ± 1.1	BDL	0.0 ± 0.0	5.3 ± 1.7
	Water Rinsed Day 15	0.8 ± 0.1	BDL	3.9 ± 0.0	BDL	BDL	2.7 ± 0.4
	Peroxide Treated Day 15	1.3 ± 0.3	BDL	6.5 ± 0.4	2.9 ± 0.7	0.0 ± 0.0	7.4 ± 0.8
	Untreated Day 30	2.6 ± 0.5	BDL	12.4 ± 1.4	0.8 ± 0.2	0.0 ± 0.0	5.9 ± 1.4
	Water Rinsed Day 30	1.3 ± 0.2	BDL	5.6 ± 0.2	0.9 ± 0.1	0.0 ± 0.0	2.8 ± 0.3
	Peroxide Treated Day 30	1.8 ± 0.0	BDL	7.9 ± 1.0	3.2 ± 0.5	0.0 ± 0.0	8.5 ± 0.8

Appendix D continued

(a)	**Treatment**	**Dy**	**Er**	**Eu**	**Fe**	**Ga**	**Gd**
Pore Water	Untreated Day 0	0.2 ± 0.0	0.1 ± 0.0	BDL	389.2 ± 26.8	BDL	0.2 ± 0.0
	Water Rinsed Day 0	BDL	BDL	BDL	245.7 ± 21.2	BDL	BDL
	Peroxide Treated Day 0	0.1 ± 0.0	0.1 ± 0.0	BDL	398.6 ± 50.5	0.8 ± 0.3	0.1 ± 0.0
	Untreated Day 15	BDL	0.0 ± 0.0	BDL	461.6 ± 33.3	BDL	BDL
	Water Rinsed Day 15	BDL	BDL	BDL	293.8 ± 13.2	BDL	BDL
	Peroxide Treated Day 15	0.1 ± 0.0	0.0 ± 0.0	BDL	355.0 ± 8.5	BDL	0.1 ± 0.0
	Untreated Day 30	BDL	BDL	BDL	403.0 ± 13.2	BDL	BDL
	Water Rinsed Day 30	BDL	BDL	BDL	316.0 ± 8.0	BDL	BDL
	Peroxide Treated Day 30	0.1 ± 0.0	BDL	BDL	389.0 ± 41.0	BDL	0.1 ± 0.0
Overlying Water	Untreated Day 0	0.1 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	272.4 ± 12.7	0.1 ± 0.0	0.1 ± 0.0
	Water Rinsed Day 0	BDL	0.1 ± 0.0	BDL	249.6 ± 24.5	BDL	0.0 ± 0.0
	Peroxide Treated Day 0	BDL	BDL	BDL	124.9 ± 0.5	BDL	BDL
	Untreated Day 15	BDL	BDL	BDL	303.2 ± 3.0	BDL	BDL
	Water Rinsed Day 15	BDL	BDL	BDL	227.2 3.7	BDL	BDL
	Peroxide Treated Day 15	0.2 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	556.0 ± 150.8	0.1 ± 0.0	0.2 ± 0.1
	Untreated Day 30	BDL	BDL	BDL	345.6 ± 20.2	BDL	BDL
	Water Rinsed Day 30	BDL	BDL	BDL	281.8 ± 4.3	BDL	BDL
	Peroxide Treated Day 30	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	415.0 ± 52.6	BDL	0.2 ± 0.0

Appendix D continued

(b)	**Treatment**	**Dy**	**Er**	**Eu**	**Fe**	**Ga**	**Gd**
Pore Water	Untreated Day 0	0.1 ± 0.0	BDL	BDL	433.1 ± 61.8	BDL	0.1 ± 0.0
	Water Rinsed Day 0	BDL	BDL	BDL	316.8 ± 18.2	BDL	BDL
	Peroxide Treated Day 0	BDL	BDL	BDL	154.9 ± 6.7	BDL	BDL
	Untreated Day 15	0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.0	494.4 ± 35.1	BDL	0.5 ± 0.2
	Water Rinsed Day 15	0.1 ± 0.0	0.1 ± 0.0	BDL	365.2 ± 47.1	BDL	0.1 ± 0.0
	Peroxide Treated Day 15	0.3 ± 0.1	0.2 ± 0.1	0.1 ± 0.0	2543.2 ± 897.9	0.1 ± 0.0	0.5 ± 0.1
	Untreated Day 30	0.3 ± 0.1	0.1 ± 0.0	0.1 ± 0.0	529.7 ± 23.7	0.1 ± 0.0	0.3 ± 0.1
	Water Rinsed Day 30	0.1 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	492.2 ± 19.5	0.0 ± 0.0	0.1 ± 0.0
	Peroxide Treated Day 30	0.3 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	905.8 ± 134.3	0.1 ± 0.0	0.3 ± 0.0

Overlying Water	Untreated Day 0	BDL	BDL	BDL	260.9 ± 10.1	BDL	0.1 ± 0.0
	Water Rinsed Day 0	BDL	BDL	BDL	298.2 ± 9.8	BDL	0.1 ± 0.0
	Peroxide Treated Day 0	BDL	BDL	BDL	148.7 ± 5.2	0.1 ± 0.0	0.1 ± 0.0
	Untreated Day 15	0.2 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	428.5 ± 60.5	BDL	0.3 ± 0.0
	Water Rinsed Day 15	0.1 ± 0.0	0.0 ± 0.0	BDL	420.7 ± 20.5	BDL	0.1 ± 0.0
	Peroxide Treated Day 15	0.2 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	2150.6 ± 674.3	BDL	0.2 ± 0.0
	Untreated Day 30	0.2 ± 0.0	0.2 ± 0.0	0.0 ± 0.0	439.0 ± 16.7	0.0 ± 0.0	0.2 ± 0.1
	Water Rinsed Day 30	0.1 ± 0.0	BDL	0.0 ± 0.0	438.8 ± 74.4	0.1 ± 0.0	0.1 ± 0.0
	Peroxide Treated Day 30	0.2 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	1218.0 ± 402.9	0.1 ± 0.0	0.2 ± 0.0

Appendix D continued

(a)	**Treatment**	**Ge**	**Hf**	**Hg**	**Ho**	**La**	**Li**
Pore Water	Untreated Day 0	BDL	BDL	BDL	0.0 ± 0.0	1.6 ± 0.4	116.7 ± 7.6
	Water Rinsed Day 0	BDL	BDL	BDL	0.0 ± 0.0	0.3 ± 0.1	30.5 ± 5.6
	Peroxide Treated Day 0	0.4 ± 0.0	0.3 ± 0.0	BDL	0.0 ± 0.0	0.4 ± 0.1	15.8 ± 2.0
	Untreated Day 15	BDL	BDL	BDL	BDL	0.2 ± 0.2	28.1 ± 12.0
	Water Rinsed Day 15	BDL	0.1 ± 0.0	BDL	BDL	0.0 ± 0.0	11.8 ± 0.0
	Peroxide Treated Day 15	BDL	BDL	BDL	BDL	0.2 ± 0.0	16.6 ± 2.2
	Untreated Day 30	0.1 ± 0.0	0.0 ± 0.0	BDL	BDL	0.0 ± 0.0	12.2 ± 1.4
	Water Rinsed Day 30	0.1 ± 0.0	0.0 ± 0.0	BDL	BDL	0.0 ± 0.0	8.0 ± 0.7
	Peroxide Treated Day 30	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0	0.1 ± 0.0	10.4 ± 2.7
Overlying Water	Untreated Day 0	BDL	BDL	BDL	BDL	0.7 ± 0.1	20.4 ± 8.6
	Water Rinsed Day 0	BDL	BDL	BDL	BDL	0.2 ± 0.0	BDL
	Peroxide Treated Day 0	BDL	BDL	BDL	0.0 ± 0.0	0.1 ± 0.0	BDL
	Untreated Day 15	BDL	0.0 ± 0.0	BDL	BDL	0.2 ± 0.2	21.4 ± 5.8
	Water Rinsed Day 15	BDL	BDL	BDL	BDL	0.0 ± 0.0	10.6 ± 0.0
	Peroxide Treated Day 15	BDL	BDL	BDL	0.0 ± 0.0	0.6 ± 0.1	BDL
	Untreated Day 30	0.1 ± 0.0	0.0 ± 0.0	BDL	BDL	0.0 ± 0.0	15.6 ± 0.6
	Water Rinsed Day 30	0.1 ± 0.0	BDL	BDL	BDL	0.0 ± 0.0	8.9 ± 1.8
	Peroxide Treated Day 30	0.2 ± 0.0	0.0 ± 0.0	BDL	0.0 ± 0.0	0.3 ± 0.1	6.1 ± 1.0

Appendix D continued

(b)	**Treatment**	**Ge**	**Hf**	**Hg**	**Ho**	**La**	**Li**
Pore Water	Untreated Day 0	BDL	BDL	BDL	BDL	0.6 ± 0.1	BDL
	Water Rinsed Day 0	BDL	BDL	BDL	BDL	0.3 ± 0.0	BDL
	Peroxide Treated Day 0	BDL	0.0 ± 0.0	BDL	BDL	0.0 ± 0.0	BDL
	Untreated Day 15	BDL	BDL	BDL	0.1 ± 0.0	1.9 ± 1.0	17.9 ± 2.2
	Water Rinsed Day 15	0.1 ± 0.0	0.0 ± 0.0	BDL	0.0 ± 0.0	0.7 ± 0.2	5.7 ± 1.5
	Peroxide Treated Day 15	BDL	0.0 ± 0.0	BDL	0.1 ± 0.0	1.6 ± 0.5	4.1 ± 1.5
	Untreated Day 30	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0	1.7 ± 0.4	10.2 ± 1.4
	Water Rinsed Day 30	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0	0.8 ± 0.1	5.0 ± 0.0
	Peroxide Treated Day 30	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0	1.3 ± 0.1	BDL
Overlying Water	Untreated Day 0	BDL	BDL	BDL	BDL	0.2 ± 0.0	BDL
	Water Rinsed Day 0	BDL	BDL	BDL	BDL	0.2 ± 0.0	BDL
	Peroxide Treated Day 0	BDL	BDL	BDL	BDL	0.0 ± 0.0	BDL
	Untreated Day 15	BDL	BDL	BDL	0.0 ± 0.0	0.8 ± 0.3	BDL
	Water Rinsed Day 15	BDL	BDL	BDL	BDL	0.4 ± 0.0	BDL
	Peroxide Treated Day 15	BDL	0.1 ± 0.0	BDL	0.0 ± 0.0	0.6 ± 0.1	BDL
	Untreated Day 30	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0	1.2 ± 0.2	6.0 ± 0.3
	Water Rinsed Day 30	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0	0.6 ± 0.1	BDL
	Peroxide Treated Day 30	BDL	0.0 ± 0.0	BDL	0.0 ± 0.0	0.8 ± 0.0	BDL

Appendix D continued

(a)	**Treatment**	**Lu**	**Mg**	**Mn**	**Mo**	**Nb**	**Nd**
Pore Water	Untreated Day 0	BDL	73303.8 ± 7741.3	595.5 ± 52.2	27.8 ± 7.0	0.4 ± 0.0	0.7 ± 0.2
	Water Rinsed Day 0	BDL	40828.3 ± 5319.2	281.1 ± 48.6	73.1 ± 10.6	0.5 ± 0.0	0.1 ± 0.0
	Peroxide Treated Day 0	BDL	10153.6 ± 710.7	240.7 ± 56.7	44.8 ± 1.8	0.5 ± 0.0	0.5 ± 0.1
	Untreated Day 15	BDL	81256.2 ± 9503.8	221.6 ± 210.3	327.2 ± 262.2	0.7 ± 0.1	0.3 ± 0.0
	Water Rinsed Day 15	BDL	60805.7 ± 2311.9	9.0 ± 2.6	71.7 ± 2.5	0.5 ± 0.0	BDL
	Peroxide Treated Day 15	BDL	61432.7 ± 4745.4	323.1 ± 8.5	1.4 ± 0.5	0.4 ± 0.0	0.2 ± 0.0
	Untreated Day 30	BDL	68771.6 ± 1379.3	10.8 ± 1.4	41.3 ± 2.4	0.1 ± 0.0	BDL
	Water Rinsed Day 30	BDL	58974.0 ± 2374.1	19.4 ± 4.5	52.1 ± 1.5	0.1 ± 0.0	0.1 ± 0.0
	Peroxide Treated Day 30	BDL	58684.3 ± 3301.6	237.7 ± 38.7	1.7 ± 0.6	BDL	0.1 ± 0.0
Overlying Water	Untreated Day 0	BDL	45709.2 ± 6357.9	68.9 ± 5.4	10.6 ± 3.2	0.5 ± 0.0	0.4 ± 0.0
	Water Rinsed Day 0	BDL	53961.5 ± 5398.6	56.5 ± 8.4	34.6 ± 6.4	0.5 ± 0.0	0.1 ± 0.0
	Peroxide Treated Day 0	BDL	13097.8	75.3 ± 4.4	11.3 ± 0.7	0.4 ± 0.0	0.2 ± 0.0
	Untreated Day 15	BDL	56931.1 ± 1813.0	79.5 ± 55.3	51.6 ± 21.8	0.5 ± 0.0	0.2 ± 0.0
	Water Rinsed Day 15	BDL	47210.1 ± 180.7	26.8 ± 5.2	14.5 ± 0.6	0.4 ± 0.0	BDL
	Peroxide Treated Day 15	BDL	48289.3 ± 230.3	128.3 ± 0.7	0.8 ± 0.1	0.4 ± 0.0	0.6 ± 0.1
	Untreated Day 30	BDL	59236.2 ± 1481.6	1.6 ± 0.7	23.6 ± 0.3	0.1 ± 0.0	BDL
	Water Rinsed Day 30	BDL	50137.4 ± 1200.0	18.7 ± 8.5	25.5 ± 1.4	0.1 ± 0.0	BDL
	Peroxide Treated Day 30	BDL	51653.7 ± 4267.6	133.4 ± 8.3	1.3 ± 0.3	0.0 ± 0.0	0.3 ± 0.0

Appendix D continued

(b)	**Treatment**	**Lu**	**Mg**	**Mn**	**Mo**	**Nb**	**Nd**
Pore Water	Untreated Day 0	BDL	39203.8 ± 1329.2	142.5 ± 28.7	0.7 ± 0.2	0.4 ± 0.0	0.5 ± 0.1
	Water Rinsed Day 0	BDL	58077.9 ± 1899.5	107.1 ± 3.5	1.7 ± 0.1	0.4 ± 0.0	0.2 ± 0.0
	Peroxide Treated Day 0	BDL	13393.1 ± 303.6	64.6 ± 8.0	10.5 ± 1.4	0.5 ± 0.0	0.1 ± 0.0
	Untreated Day 15	0.0 ± 0.0	55482.5 ± 3808.1	1278.1 ± 220.4	2.7 ± 1.1	0.4 ± 0.0	1.1 ± 0.7
	Water Rinsed Day 15	BDL	44719.4 ± 2334.7	481.6 ± 24.2	3.1 ± 0.7	0.0 ± 0.0	0.4 ± 0.2
	Peroxide Treated Day 15	0.0 ± 0.0	43356.4 ± 1319.3	563.0 ± 42.6	1.2 ± 0.3	0.0 ± 0.0	1.5 ± 0.5
	Untreated Day 30	BDL	55272.8 ± 3430.3	893.1 ± 103.7	1.3 ± 0.4	0.0 ± 0.0	1.1 ± 0.4
	Water Rinsed Day 30	BDL	48308.8 ± 476.9	369.4 ± 39.3	1.5 ± 0.3	0.0 ± 0.0	0.4 ± 0.1
	Peroxide Treated Day 30	BDL	45564.3 ± 1346.2	356.9 ± 54.3	0.6 ± 0.1	BDL	1.2 ± 0.0
Overlying Water	Untreated Day 0	BDL	33779.9 ± 824.5	39.9 ± 2.8	0.2 ± 0.0	0.4 ± 0.0	0.2 ± 0.0
	Water Rinsed Day 0	BDL	56307.3 ± 2129.9	59.2 ± 4.3	0.9 ± 0.1	0.4 ± 0.0	0.1 ± 0.0
	Peroxide Treated Day 0	BDL	12857.8 ± 370/1	33.6 ± 2.4	6.1 ± 0.4	0.5 ± 0.0	0.1 ± 0.0
	Untreated Day 15	BDL	52050.7 ± 1322.4	211.1 ± 15.6	1.1 ± 0.6	0.4 ± 0.0	0.8 ± 0.3
	Water Rinsed Day 15	BDL	43430.8 ± 863.3	84.8 ± 4.1	1.0 ± 0.2	0.4 ± 0.0	0.4 ± 0.1
	Peroxide Treated Day 15	BDL	43204.6 ± 949.6	126.3 ± 13.0	4.3 ± 0.6	0.4 ± 0.0	0.5 ± 0.1
	Untreated Day 30	BDL	54671.1 ± 607.0	302.1 ± 23.1	0.3 ± 0.1	0.0 ± 0.0	1.1 ± 0.3
	Water Rinsed Day 30	0.0	48436.1 ± 893.5	125.5 ± 3.7	0.6 ± 0.1	BDL	0.4 ± 0.1
	Peroxide Treated Day 30	BDL	45086.0 ± 1737.9	162.9 ± 24.5	0.9 ± 0.5	BDL	0.6 ± 0.0

Appendix D continued

(a)	Treatment	Ni	P	Pb	Pr	Rb	Sb
Pore Water	Untreated Day 0	2270.1 ± 160.0	484.5 ± 21.4	0.3 ± 0.1	0.2 ± 0.0	26.3 ± 2.4	0.1 ± 0.0
	Water Rinsed Day 0	854.6 ± 128.7	258.6 ± 16.8	0.4 ± 0.0	0.0 ± 0.0	11.0 ± 0.7	0.2 ± 0.0
	Peroxide Treated Day 0	711.0 ± 167.4	532.5 ± 55.2	0.4 ± 0.1	0.1 ± 0.0	6.5 ± 1.3	0.5 ± 0.0
	Untreated Day 15	524.3 ± 478.7	499.2 ± 37.4	0.2 ± 0.0	0.1 ± 0.0	9.2 ± 3.1	0.3 ± 0.0
	Water Rinsed Day 15	27.8 ± 0.6	367.6 ± 10.0	0.2 ± 0.1	BDL	4.9 ± 0.1	0.2 ± 0.0
	Peroxide Treated Day 15	165.3 ± 26.3	369.2 ± 14.4	0.2 ± 0.0	0.0 ± 0.0	7.0 ± 0.1	0.1 ± 0.0
	Untreated Day 30	20.9 ± 1.5	514.2 ± 24.6	0.4 ± 0.2	BDL	4.9 ± 0.3	0.2 ± 0.0
	Water Rinsed Day 30	22.1 ± 3.9	422.4 ± 16.2	0.2 ± 0.0	BDL	5.1 ± 0.2	0.2 ± 0.0
	Peroxide Treated Day 30	118.9 ± 44.3	411.0 ± 14.0	0.2 ± 0.0	0.0 ± 0.	6.7 ± 0.4	0.1 ± 0.0
Overlying Water	Untreated Day 0	278.5 ± 3.3	437.4 ± 19.4	0.4 ± 0.1	0.1 ± 0.0	4.6 ± 0.2	BDL
	Water Rinsed Day 0	218.2 ± 26.4	390.7 ± 41.3	0.1 ± 0.0	0.0 ± 0.0	3.9 ± 0.3	BDL
	Peroxide Treated Day 0	208.8 ± 9.6	241.9 ± 7.8	0.3 ± 0.0	BDL	2.3 ± 0.1	0.1 ± 0.0
	Untreated Day 15	246.5 ± 203.8	398.3 ± 10.9	0.2 ± 0.1	0.1 ± 0.0	7.5 ± 2.5	0.1 ± 0.0
	Water Rinsed Day 15	38.0 ± 3.2	329.9 ± 6.8	0.1 ± 0.0	BDL	3.8 ± 0.1	0.1 ± 0.0
	Peroxide Treated Day 15	131.0 ± 8.9	341.2 ± 1.1	0.3 ± 0.0	0.1 ± 0.0	4.4 ± 0.1	0.1 ± 0.0
	Untreated Day 30	22.5 ± 1.3	428.7 ± 12.6	0.2 ± 0.1	BDL	5.5 ± 0.1	0.1 ± 0.0
	Water Rinsed Day 30	27.5 ± 6.0	373.9 ± 18.8	0.1 ± 0.0	BDL	4.4 ± 0.1	0.1 ± 0.0
	Peroxide Treated Day 30	94.9 ± 30.0	383.6 ± 21.5	0.2 ± 0.0	0.1 ± 0.0	5.5 ± 0.6	BDL

Appendix D continued

(b)	**Treatment**	**Ni**	**P**	**Pb**	**Pr**	**Rb**	**Sb**
Pore Water	Untreated Day 0	31.7 ± 6.5	373.4 ± 14.7	0.8 ± 0.0	0.2 ± 0.0	0.7 ± 0.1	BDL
	Water Rinsed Day 0	25.1 ± 0.8	369.6 ± 9.6	0.2 ± 0.0	0.0 ± 0.0	0.9 ± 0.1	BDL
	Peroxide Treated Day 0	14.8 ± 1.8	183.8 ± 9.7	0.1 ± 0.0	0.0 ± 0.0	0.7 ± 0.0	BDL
	Untreated Day 15	258.5 ± 47.4	439.6 ± 30.8	0.2 ± 0.1	0.3 ± 0.2	2.9 ± 0.3	BDL
	Water Rinsed Day 15	91.9 ± 4.5	357.4 ± 12.1	0.2 ± 0.0	0.1 ± 0.0	1.6 ± 0.0	BDL
	Peroxide Treated Day 15	123.2 ± 8.4	336.6 ± 8.1	1.3 ± 0.5	0.4 ± 0.1	1.3 ± 0.1	BDL
	Untreated Day 30	180.3 ± 22.1	494.5 ± 8.4	0.3 ± 0.1	0.3 ± 0.1	2.3 ± 0.2	BDL
	Water Rinsed Day 30	71.1 ± 6.7	409.8 ± 5.1	0.2 ± 0.0	0.1 ± 0.0	1.4 ± 0.1	BDL
	Peroxide Treated Day 30	86.6 ± 11.2	411.0 ± 7.6	1.5 ± 0.3	0.3 ± 0.0	1.1 ± 0.1	BDL
Overlying Water	Untreated Day 0	8.4 ± 0.7	296.5 ± 2.1	0.8 ± 0.0	0.0 ± 0.0	0.4 ± 0.0	BDL
	Water Rinsed Day 0	11.8 ± 0.8	354.6 ± 15.1	0.3 ± 0.0	0.0 ± 0.0	0.4 ± 0.0	BDL
	Peroxide Treated Day 0	7.7 ± 0.7	187.7 ± 5.3	0.1 ± 0.0	BDL	0.4 ± 0.0	BDL
	Untreated Day 15	46.7 ± 3.9	393.8 ± 7.3	0.6 ± 0.3	0.2 ± 0.1	1.3 ± 0.1	BDL
	Water Rinsed Day 15	20.6 ± 0.8	322.2 ± 6.8	0.3 ± 0.1	0.1 ± 0.0	0.9 ± 0.0	BDL
	Peroxide Treated Day 15	34.3 ± 2.2	321.0 ± 6.4	1.6 ± 0.4	0.2 ± 0.0	0.8 ± 0.0	BDL
	Untreated Day 30	60.8 ± 4.9	454.6 ± 6.4	0.6 ± 0.2	0.3 ± 0.1	1.5 ± 0.1	BDL
	Water Rinsed Day 30	28.8 ± 1.1	392.7 ± 11.8	0.3 ± 0.0	0.1 ± 0.0	1.2 ± 0.1	BDL
	Peroxide Treated Day 30	43.9 ± 3.4	399.9 ± 8.2	1.6 ± 0.2	0.2 ± 0.0	0.9 ± 0.1	0.0 ± 0.0

Appendix D continued

(a)	Treatment	Sc	Se	Si	Sm	Sn	Sr
Pore Water	Untreated Day 0	0.9 ± 0.1	BDL	8396.7 ± 1710.5	0.2 ± 0.0	BDL	1256.5 ± 71.1
	Water Rinsed Day 0	0.5 ± 0.0	BDL	BDL	BDL	BDL	669.9 ± 81.3
	Peroxide Treated Day 0	1.7 ± 0.1	BDL	11350.9 ± 213.4	0.2 ± 0.0	0.3 ± 0.0	151.9 ± 6.1
	Untreated Day 15	1.3 ± 0.6	BDL	BDL	0.1 ± 0.0	BDL	942.9 ± 82.8
	Water Rinsed Day 15	0.6 ± 0.0	BDL	BDL	BDL	BDL	473.9 ± 27.2
	Peroxide Treated Day 15	1.7 ± 0.1	BDL	168822.7 ± 0.0	0.1 ± 0.0	BDL	469.6 ± 20.9
	Untreated Day 30	0.6 ± 0.0	1.9 ± 0.4	BDL	BDL	0.2 ± 0.0	681.7 ± 8.8
	Water Rinsed Day 30	0.5 ± 0.0	BDL	BDL	BDL	0.2 ± 0.1	500.7 ± 29.4
	Peroxide Treated Day 30	1.1 ± 0.2	2.9 ± 0.4	4507.6 ± 0.0	BDL	BDL	447.4 ± 9.5
Overlying Water	Untreated Day 0	0.2 ± 0.0	BDL	BDL	BDL	0.3 ± 0.0	602.1 ± 37.6
	Water Rinsed Day 0	0.2 ± 0.0	BDL	BDL	BDL	0.3 ± 0.0	472.7 ± 49.8
	Peroxide Treated Day 0	BDL	BDL	BDL	BDL	0.5 ± 0.1	158.5 ± 1.0
	Untreated Day 15	0.4 ± 0.1	BDL	4760.3 ± 0.0	0.1 ± 0.0	BDL	612.5 ± 3.5
	Water Rinsed Day 15	0.2 ± 0.0	BDL	BDL	BDL	BDL	391.4 ± 9.1
	Peroxide Treated Day 15	0.5 ± 0.1	BDL	BDL	0.1 ± 0.0	BDL	374.6 ± 8.4
	Untreated Day 30	0.3 ± 0.0	BDL	23129.4 ± 5851.4	0.0 ± 0.0	0.1 ± 0.0	612.0 ± 20.1
	Water Rinsed Day 30	0.3 ± 0.0	3.2 ± 0.0	22813.7 ± 3239.1	BDL	0.1 ± 0.0	420.8 ± 5.8
	Peroxide Treated Day 30	0.6 ± 0.0	1.7 ± 0.0	6967.9 ± 0.0	0.1 ± 0.0	0.8 ± 0.0	400.0 ± 5.3

Appendix D continued

(b)	Treatment	Sc	Se	Si	Sm	Sn	Sr
Pore Water	Untreated Day 0	0.1 ± 0.0	BDL	BDL	0.1 ± 0.0	0.3 ± 0.0	482.9 ± 5.4
	Water Rinsed Day 0	BDL	BDL	BDL	0.1 ± 0.0	BDL	482.8 ± 4.4
	Peroxide Treated Day 0	0.2 ± 0.0	4.0 ± 0.0	BDL	BDL	BDL	190.4 ±1.5
	Untreated Day 15	0.3 ± 0.1	4.8 ± 0.6	BDL	0.4 ± 0.1	0.1 ± 0.0	518.9 ± 32.2
	Water Rinsed Day 15	BDL	2.6 ± 0.6	BDL	0.1 ± 0.0	0.1 ± 0.0	382.7 ± 9.3
	Peroxide Treated Day 15	0.4 ± 0.1	1.4 ± 0.0	BDL	0.3 ± 0.1	0.1 ± 0.0	355.0 ± 2.3
	Untreated Day 30	0.3 ± 0.0	1.7 ± 0.0	2244.3 ± 482.1	0.2 ± 0.1	0.2 ± 0.0	479.9 ± 12.0
	Water Rinsed Day 30	0.2 ± 0.0	BDL	3601.7 ± 192.1	0.1 ± 0.0	0.4 ± 0.0	360.7 ± 4.2
	Peroxide Treated Day 30	0.4 ± 0.0	1.0 ± 0.0	6520.5 ± 1038.3	0.2 ± 0.0	0.2 ± 0.0	333.3 ± 7.2
Overlying Water	Untreated Day 0	BDL	BDL	BDL	BDL	BDL	460.3 ± 3.0
	Water Rinsed Day 0	BDL	BDL	BDL	0.1 ± 0.0	BDL	464.1 ± 4.1
	Peroxide Treated Day 0	0.3 ± 0.0	BDL	BDL	BDL	0.4 ± 0.1	197.6 ± 5.4
	Untreated Day 15	0.1 ± 0.0	BDL	BDL	0.2 ± 0.1	BDL	415.7 ± 6.0
	Water Rinsed Day 15	0.1 ± 0.0	BDL	BDL	0.1 ± 0.0	BDL	339.4 ± 7.9
	Peroxide Treated Day 15	0.2 ± 0.1	BDL	BDL	0.1 ± 0.0	0.1 ± 0.0	315.0 ± 9.7
	Untreated Day 30	0.2 ± 0.0	2.2 ± 0.5	7037.6 ± 392.2	0.2 ± 0.0	0.2 ± 0.0	450.7 ± 6.3
	Water Rinsed Day 30	0.2 ± 0.0	0.5 ± 0.0	3449.6 ± 1384.9	0.1 ± 0.0	BDL	357.3 ± 4.7
	Peroxide Treated Day 30	0.3 ± 0.0	BDL	3115.9 ± 212.8	0.1 ± 0.0	0.3 ± 0.0	316.2 ± 7.0

Appendix D continued

(a)	Treatment	Ta	Th	Ti	Tl	Tm	U
Pore Water	Untreated Day 0	BDL	BDL	2.8 ± 0.3	BDL	BDL	BDL
	Water Rinsed Day 0	BDL	0.0 ± 0.0	BDL	BDL	BDL	0.0 ± 0.0
	Peroxide Treated Day 0	BDL	0.1 ± 0.0	21.1 ± 1.8	BDL	BDL	0.0 ± 0.0
	Untreated Day 15	0.0 ± 0.0	0.0 ± 0.0	4.3 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	Water Rinsed Day 15	BDL	0.0 ± 0.0	2.0 ± 0.0	BDL	0.0 ± 0.0	0.0 ± 0.0
	Peroxide Treated Day 15	BDL	0.1 ± 0.0	3.3 ± 0.8	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Untreated Day 30	BDL	0.0 ± 0.0	2.2 ± 0.4	BDL	BDL	0.0 ± 0.0
	Water Rinsed Day 30	BDL	0.0 ± 0.0	2.1 ± 0.3	BDL	BDL	0.0 ± 0.0
	Peroxide Treated Day 30	BDL	0.0 ± 0.0	2.6 ± 0.1	0.1 ± 0.0	BDL	0.0 ± 0.0
Overlying Water	Untreated Day 0	BDL	BDL	2.7 ± 0.0	0.1 ± 0.0	BDL	0.0 ± 0.0
	Water Rinsed Day 0	BDL	0.0 ± 0.0	2.1 ± 0.2	0.0 ± 0.0	BDL	BDL
	Peroxide Treated Day 0	BDL	0.0 ± 0.0	9.3 ± 0.3	BDL	BDL	BDL
	Untreated Day 15	BDL	BDL	1.6 ± 0.1	0.1 ± 0.0	BDL	BDL
	Water Rinsed Day 15	BDL	0.0 ± 0.0	1.8 ± 0.0	BDL	BDL	BDL
	Peroxide Treated Day 15	BDL	0.0 ± 0.0	3.1 ± 0.2	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Untreated Day 30	BDL	BDL	1.7 ± 0.3	BDL	BDL	0.0 ± 0.0
	Water Rinsed Day 30	BDL	BDL	1.2 ± 0.2	BDL	BDL	BDL
	Peroxide Treated Day 30	BDL	0.0 ± 0.0	2.2 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

Appendix D continued

(b)	**Treatment**	**Ta**	**Th**	**Ti**	**Tl**	**Tm**	**U**
Pore Water	Untreated Day 0	BDL	0.0 ± 0.0	2.4 ± 0.1	BDL	BDL	0.1 ± 0.0
	Water Rinsed Day 0	BDL	0.0 ± 0.0	1.8 ± 0.1	BDL	BDL	BDL
	Peroxide Treated Day 0	BDL	BDL	1.9 ± 0.3	BDL	BDL	0.0 ± 0.0
	Untreated Day 15	BDL	0.0 ± 0.0	4.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Water Rinsed Day 15	BDL	BDL	1.9 ± 0.2	BDL	0.0 ± 0.0	BDL
	Peroxide Treated Day 15	BDL	0.0 ± 0.0	2.0 ± 0.2	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	Untreated Day 30	BDL	0.0 ± 0.0	3.1 ± 0.7	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Water Rinsed Day 30	BDL	0.0 ± 0.0	1.8 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	BDL
	Peroxide Treated Day 30	0.0 ± 0.0	0.0 ± 0.0	2.2 ± 0.3	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
Overlying Water	Untreated Day 0	BDL	0.0 ± 0.0	1.8 ± 0.0	BDL	BDL	0.0 ± 0.0
	Water Rinsed Day 0	BDL	BDL	2.3 ± 0.6	BDL	BDL	BDL
	Peroxide Treated Day 0	BDL	BDL	1.7 ± 0.1	BDL	BDL	BDL
	Untreated Day 15	BDL	0.0 ± 0.0	2.7 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	Water Rinsed Day 15	BDL	0.0 ± 0.0	1.7 ± 0.0	0.0 ± 0.0	BDL	0.0 ± 0.0
	Peroxide Treated Day 15	BDL	0.0 ± 0.0	4.6 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
	Untreated Day 30	BDL	BDL	2.1 ± 0.3	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Water Rinsed Day 30	BDL	BDL	1.5 ± 0.4	BDL	0.0 ± 0.0	0.0 ± 0.0
	Peroxide Treated Day 30	BDL	0.0 ± 0.0	2.3 ± 0.3	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0

Appendix D continued

(a)	Treatment	V	W	Y	Yb	Zn	Zr
Pore Water	Untreated Day 0	549.4 ± 109.2	BDL	4.2 ± 0.5	0.1 ± 0.0	158.9 ± 21.7	BDL
	Water Rinsed Day 0	868.7 ± 84.9	BDL	1.8 ± 0.2	BDL	64.0 ± 14.4	BDL
	Peroxide Treated Day 0	277.9 ± 14.5	BDL	1.0 ± 0.2	0.1 ± 0.0	74.2 ± 21.0	10.7 ± 0.8
	Untreated Day 15	786.4 ± 397.3	0.1 ± 0.0	2.6 ± 0.1	BDL	39.4 ± 27.8	0.1 ± 0.0
	Water Rinsed Day 15	87.4 ± 5.8	BDL	1.3 ± 0.1	BDL	6.9 ± 1.0	0.1 ± 0.0
	Peroxide Treated Day 15	4.7 ± 0.9	BDL	1.9 ± 0.1	BDL	61.4 ± 11.8	0.4 ± 0.0
	Untreated Day 30	54.6 ± 5.7	BDL	1.9 ± 0.0	BDL	9.3 ± 2.8	0.1 ± 0.0
	Water Rinsed Day 30	72.5 ± 12.7	BDL	1.2 ± 0.0	BDL	6.3 ± 1.1	BDL
	Peroxide Treated Day 30	2.8 ± 0.9	BDL	1.7 ± 0.2	BDL	38.9 ± 10.9	0.3 ± 0.0
Overlying Water	Untreated Day 0	200.9 ± 45.4	BDL	2.2 ± 0.3	BDL	29.5 ± 2.1	BDL
	Water Rinsed Day 0	371.4 ± 42.2	BDL	1.3 ± 0.1	BDL	24.7 ± 5.5	BDL
	Peroxide Treated Day 0	212.9 ± 29.0	BDL	0.4 ± 0.1	BDL	25.8 ± 1.0	BDL
	Untreated Day 15	385.6 ± 207.8	BDL	1.9 ± 0.2	BDL	22.3 ± 11.9	0.0 ± 0.0
	Water Rinsed Day 15	52.7 ± 0.9	BDL	1.3 ± 0.0	BDL	8.7 ± 1.3	0.0 ± 0.0
	Peroxide Treated Day 15	22.2 ± 1.7	BDL	2.5 ± 0.2	BDL	49.3 ± 1.3	0.6 ± 0.2
	Untreated Day 30	63.1 ± 2.6	BDL	1.5 ± 0.2	BDL	6.7 ± 0.5	BDL
	Water Rinsed Day 30	63.2 ± 6.6	BDL	1.2 ± 0.1	BDL	7.1 ± 1.3	BDL
	Peroxide Treated Day 30	7.3 ± 3.0	BDL	1.8 ± 0.2	BDL	35.9 ± 7.8	0.3 ± 0.0

Appendix D continued

(b)	**Treatment**	**V**	**W**	**Y**	**Yb**	**Zn**	**Zr**
Pore Water	Untreated Day 0	3.6 ± 0.9	BDL	1.9 ± 0.1	BDL	12.4 ± 2.2	0.1 ± 0.0
	Water Rinsed Day 0	2.7 ± 0.2	BDL	1.6 ± 0.1	BDL	9.9 ± 0.5	BDL
	Peroxide Treated Day 0	50.2 ± 10.2	0.4 ± 0.0	0.6 ± 0.0	BDL	44.8 ± 18.1	0.1 ± 0.0
	Untreated Day 15	2.2 ± 0.4	BDL	3.1 ± 1.0	0.1 ± 0.0	74.0 ± 20.7	0.1 ± 0.0
	Water Rinsed Day 15	3.3 ± 0.5	BDL	1.8 ± 0.2	BDL	37.0 ± 8.0	BDL
	Peroxide Treated Day 15	2.0 ± 0.9	BDL	2.9 ± 0.6	0.2 ± 0.0	72.1 ± 1.8	0.2 ± 0.0
	Untreated Day 30	1.4 ± 0.2	BDL	2.9 ± 0.4	0.1 ± 0.0	59.2 ± 7.6	0.1 ± 0.0
	Water Rinsed Day 30	1.8 ± 0.2	BDL	1.6 ± 0.2	0.0 ± 0.0	27.6 ± 1.7	BDL
	Peroxide Treated Day 30	1.5 ± 0.4	BDL	2.5 ± 0.1	0.1 ± 0.0	46.6 ± 3.8	0.1 ± 0.0
Overlying Water	Untreated Day 0	0.8 ± 0.1	BDL	1.4 ± 0.1	0.1 ± 0.0	12.4 ± 0.0	BDL
	Water Rinsed Day 0	1.3 ± 0.1	BDL	1.3 ± 0.1	BDL	13.2 ± 1.5	0.0 ± 0.0
	Peroxide Treated Day 0	29.3 ± 2.9	0.2 ± 0.0	0.6 ± 0.0	BDL	26.5 ± 0.5	0.0 ± 0.0
	Untreated Day 15	2.4 ± 0.7	BDL	1.9 ± 0.3	0.2 ± 0.0	25.6 ± 3.8	0.1 ± 0.0
	Water Rinsed Day 15	3.5 ± 0.6	BDL	1.3 ± 0.1	BDL	17.6 ± 1.1	0.1 ± 0.0
	Peroxide Treated Day 15	38.6 ± 1.9	BDL	1.6 ± 0.1	0.1 ± 0.0	32.5 ± 2.7	0.3 ± 0.0
	Untreated Day 30	1.0 ± 0.0	BDL	2.4 ± 0.2	0.1 ± 0.0	36.5 ± 3.7	0.1 ± 0.0
	Water Rinsed Day 30	1.6 ± 0.4	BDL	1.5 ± 0.1	0.1 ± 0.0	23.4 ± 1.0	0.1 ± 0.0
	Peroxide Treated Day 30	3.8 ± 2.4	BDL	1.8 ± 0.1	0.1 ± 0.0	31.3 ± 2.7	0.1 ± 0.0