CONTAMINATED SEDIMENTS IN THE KINGSTON INNER HARBOUR: ASSESSING ECOLOGICAL EFFECTS, EVALUATING AND MINIMIZING REMEDIATION IMPACTS

SÉDIMENTS CONTAMINÉS DANS L'ARRIÈRE-PORT DE KINGSTON : DÉTERMINATION DES EFFETS ÉCOLOGIQUES, ÉVALUATION ET RÉDUCTION DES IMPACTS D'UNE DÉPOLLUTION

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This thesis is dedicated to the memory of my mother, who had insisted since my youth that I acquire a university education, and, after I had achieved this and subsequently joined the Canadian Forces, had encouraged me to one day return to academics.

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ABSTRACT

Burbridge, David Jon; M.Sc.; Royal Military College of Canada; June 2010; Contaminated Sediments in the Kingston Inner Harbour: Assessing Ecological Effects, Evaluating and Minimizing Remediation Impacts; Dr. Kenneth J. Reimer.

Sediments within the Great Cataraqui River in Kingston, Ontario are contaminated with various metals and organic contaminants, particularly chromium and PCBs, resulting from historical industrial activities within the Kingston Inner Harbour. Since risk to human health and benthic invertebrates has been established in previous studies, this thesis first utilized conventional ecological risk assessment methodology to determine whether risk was also present to higher-trophic-level wildlife receptors. It was established that risk is present to some wildlife receptors; therefore, there were sufficient lines of evidence of biological impacts to warrant a remediation options analysis. This options analysis, which included consideration of the natural characteristics of the Kingston Inner Harbour, as well as speciation analysis of sediment pore water for the presence of hexavalent chromium, established that dredging is feasible and is the most appropriate remediation strategy for long-term human health and ecological risk reduction. Finally, a life cycle assessment (LCA) was conducted on alternatives within the dredging strategy to determine the option with the lowest environmental burden. An emerging tool for application in remediation decision-making, this LCA compared two options for the dewatering and disposal of dredged sediments and determined that soil washing technology is favored for dredged volumes above approximately 33,000 m^3. The results of this thesis will provide government and private-sector decision-makers with information relevant to potential future remediation efforts.

Keywords: sediment remediation, chromium speciation analysis, aquatic ecological risk assessment, life cycle assessment, Kingston Inner Harbour

RÉSUMÉ

Burbridge, David Jon; M.Sc.; Collège militaire royal du Canada; juin 2010; Sédiments contaminés dans l'arrière-port de Kingston: détermination des effets écologiques, évaluation et réduction des impacts d'une dépollution; Dr. Kenneth J. Reimer.

Les sédiments dans la rivière Great Cataraqui à Kingston, Ontario, sont contaminés par divers métaux et polluants organiques, en particulier le chrome et les PCB, en raison des activités industrielles passées dans l'arrière-port de Kingston. Le risque pour la santé humaine et pour les invertébrés benthiques a été établi dans des études antérieures; nous avons donc utilisé d'abord dans cette thèse des méthodes classiques d'évaluation du risque écologique pour déterminer s'il existait également un risque pour les récepteurs fauniques de niveau trophique supérieur. Il a été démontré que certains récepteurs fauniques courent un risque; il y avait suffisamment d'éléments de preuve à l'appui des impacts biologiques pour justifier une analyse des options de dépollution. Cette analyse des options, qui incluait l'examen des caractéristiques naturelles de l'arrière-port de Kingston, de même qu'une analyse de spéciation de l'eau interstitielle pour détecter la présence de chrome hexavalent, a montré qu'un dragage est faisable et constitue la stratégie de dépollution la plus appropriée pour protéger la santé humaine et réduire le risque écologique à long terme. Enfin, une analyse du cycle de vie (ACV) a été effectuée pour différentes solutions dans le cadre de la stratégie de dragage afin de déterminer l'option dont le fardeau environnemental était le moins lourd. Ce type d'ACV est un outil de plus en plus utilisé dans la prise de décisions en matière de dépollution; il nous a permis de comparer deux options pour l'extraction de l'eau et l'élimination des sédiments dragués et a révélé que la technologie de lavage des sols est préférable pour les volumes dragués supérieurs à environ 33 000 m^3. Les résultats de cette thèse fourniront aux décideurs des secteurs public et privé des renseignements intéressants pour les efforts futurs de dépollution.

Mots clés : dépollution des sédiments, analyse de spécification du chrome, évaluation du risque pour l'écologie aquatique, analyse du cycle de vie, arrière-port de Kingston

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LIST OF ABBREVIATIONS AND ACRONYMS

ADD	average daily dose
AOC	area of concern
As	arsenic
ASWG	Aquatic Sites Working Group
AVS	acid volatile sulphide
BCS	basic chromium sulphate
BW	body weight
CCME	Canadian Council of Ministers of the Environment
CoPC	contaminant of potential concern
Cr	chromium
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
CRSG	Cataraqui River Stakeholders Group
CTRG	Canadian Tissue Residue Guideline
Cu	copper
DALY	disability-adjusted life years
DDT	dichlorodiphenyltrichloroethane
dw	dry weight
EC	Environment Canada
EDTA	ethylenediaminetetraacetic acid
EPC	exposure point concentration
ERA	ecological risk assessment
ESG	Environmental Sciences Group
FCSAP	Federal Contaminated Sites Action Plan
FIR	food ingestion rate
GLWQA	Great Lakes Water Quality Agreement
HDPE	high-density polyethylene
Hg	mercury
HPLC	high performance liquid chromatography
HQ	hazard quotient
ICP-MS	inductively coupled plasma – mass spectrometer
IJC	International Joint Commission
ISO	International Organization for Standardization
ISQG	interim sediment quality guideline
KIH	Kingston Inner Harbour
LCA	life cycle assessment
LCIA	life cycle impact assessment
LEL	lowest effect level
LLDPE	linear low-density polyethylene
LOD	limit of detection
LOQ	limit of quantitation
MeHg	methyl mercury
MNR	monitored natural recovery
MSWP	mobile soil washing plant
NEL	no effect level
NOAEL	no observed adverse effect level

NRC	National Research Council
OMoE	Ontario Ministry of the Environment
OPA	Ontario Power Authority
PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCB	polychlorinated biphenyl
ppb	parts per billion
ppm	parts per million
PSQG	provincial sediment quality guidelines
Pt	points
QC	quality control
RPD	relative percent difference
SEL	severe effect level
t	ton
TEF	toxic equivalency factor
TEQ	toxic equivalency unit
TOC	total organic content
TRV	toxicological reference value
UCL95	95-percent upper confidence level of the mean
UHP	ultra-high purity
UNESCO	United Nations Environmental, Scientific and Cultural Organization
USEPA	United States Environmental Protection Agency
VEC	valued ecosystem component
ww	wet weight
YLD	years of healthy life lost due to disability
YLL	years of life lost due to mortality
Zn	zinc

CHAPTER 1: INTRODUCTION

A historically significant port, the city of Kingston has been the site of numerous industrial activities over the past two centuries. The Kingston Inner Harbour comprises the final 2.5 km of the Great Cataraqui River, between Highway 401 and Lake Ontario, and its western shore has been the site of various industries including tanneries, a lead smelter, manufacturing and fabrication companies, a woolen mill, a grist mill, a brewery, boat-building facilities, fuel depots, and a railway transport corridor (Malroz Engineering Inc., 2003). These historical industrial activities within the Kingston Inner Harbour have resulted in the contamination of sediments within the Great Cataraqui River. This environmental legacy is presenting human and ecological health risks (Environmental Sciences Group (ESG), 2010a; 2010b), and is complicating the redevelopment of adjacent brownfield properties.

The water quality throughout the Kingston Inner Harbour is generally good (ESG, 2009a). However, within a portion of the river that is south of Belle Island, the concentration of contaminants within the underlying sediments is particularly high and exceeds guidelines published by the Canadian Council of Ministers of the Environment (CCME) for the following: arsenic (As), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), zinc (Zn), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and dichlorodiphenyltrichloroethane (DDT) (ESG, 2009a). The area of the Kingston Inner Harbour containing most of the anthropogenic contamination will be referred to in this thesis as the impacted area (or impacted site).

Numerous studies have shown that even in the absence of contamination within surface waters, potential exists for adverse effects on aquatic organisms that reside or forage in and near contaminated sediments (Apitz *et al.*, 2005). Ecological risk assessment (ERA) is a process for estimating the likelihood of adverse ecological effects to biological organisms (receptors) that may occur, or are occurring, from exposure to contaminants or other stressors (United States Environmental Protection Agency (USEPA), 1992; Chapman and Wang, 2000). For example, evidence of potential ecological risk can be established if a receptor's average daily dose (ADD) of a contaminant exceeds a critical threshold, called a toxicological reference value (TRV), which represents the highest average daily intake of a contaminant that does not result in

adverse health effects for that particular receptor (CCME, 1996). Additional evidence of ecological effects can come from a variety of other sources, such as field observations (USEPA, 1992a).

Chromium has been identified as one of the most pervasive and widespread contaminants of potential concern (CoPCs) within the sediments of the impacted area; in some locations, concentrations of chromium in surface sediments exceed the CCME guideline by four orders of magnitude (ESG, 2009a; 2009b). The highest sediment concentrations of chromium (maximum 83,000 parts per million (ppm)) are located within the Orchard Street Marsh, which subsequently drains into the Great Cataraqui River. The Davis Tannery operated between 1903 (Davis and Davis, 1937) and 1973, and discharged untreated chromium-contaminated effluent into the marsh (located north of the property) over a 55-year period (Ontario Ministry of the Environment (OMoE), 1978). Chromium contamination within sediments that are adjacent to industrialized areas is an environmentally important, globally pervasive problem and tanneries are amongst the primary sources of chromium contamination to surface freshwaters (Pawlikowski, 2006).

Chromium exists in two primary species – trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)); while Cr(III) is an essential micronutrient for many higher organisms (Lau *et al.,* 2008), Cr(VI) is toxic, and has much greater mobility, solubility, and bioavailability than Cr(III) (Megharaj *et al.,* 2003). However, chromium speciation in sediment pore water related to untreated tannery effluent discharge is virtually unstudied (Dominik *et al.,* 2007). If remediation of a contaminated site is determined to be necessary, it is important that efforts do not result in unacceptable consequences. The necessity to determine the chromium speciation within the pore water of the impacted area sediments is crucial not only to increase the accuracy of assessing potential ecological impacts, but it is also highly relevant for potential dredging operations. Dredging chromium-contaminated sediments can become complicated if sediment pore water is found to be high in Cr(VI), as it can potentially be released into the water column and/or mobilized after sediment disposal (Bufflap and Allen, 1995a).

While an ERA is clearly relevant to remediation decision-making, other types of assessments and decision-making tools, such as life cycle assessment (LCA), can be

complementary and therefore collectively aid decision-makers (Suter, 2006). Life cycle assessment (LCA) is a tool that can aid in adding, analyzing, and minimizing the environmental burdens associated with a product or service over its entire life cycle (Diamond *et al.,* 1999). While traditionally applied to industrial production processes, LCA has recently emerged as an informative source of data for environmental remediation decision-making (Lemming *et al.,* 2010). Preliminary leachate tests conducted on samples of impacted area sediment have determined that they can be disposed of in a non-hazardous waste landfill (MacMillan and Presley, 2010); however, to reduce the cost associated with transport and disposal to this final destination, the dredged sediments must first be dewatered and multiple options exist to accomplish this. The novel approach of using LCA to help assess the suitability of remediation alternatives (*i.e.* with regard to their environmental impacts) is particularly relevant in the City of Kingston, as the city's municipal council has declared its intent to become "Canada's Most Sustainable City" (Foster, 2009).

This thesis has been divided into six chapters. Chapter 2 is a literature review that examines the natural and historical setting of the impacted site and identifies significant contributors of contamination. This chapter also reviews information relevant to the understanding of sediments and sediment remediation, ecological risk assessment, chromium species, and life cycle assessment.

Chapter 3 is a semi-quantitative aquatic ERA that has been conducted in accordance with literature guidance from the CCME (1996). Sediment, plant, and fish samples were collected and analyzed to determine the concentration of CoPCs within these environmental media, as well as to model the effect that ingestion of these contaminated media would have on higher-trophic-level receptors. As they are the most dominant and widespread contaminants within the impacted area, the seven CoPCs whose ecological impacts will be evaluated in this chapter are: As, Cr, Cu, Pb, Hg, Zn, and PCBs. This ERA assesses the potential for risk to representatives of various receptor classes whose diet consists mostly or entirely of aquatic biota, including herbivorous mammals, piscivorous mammals, piscivorous birds, and non-piscivorous birds. This ERA also compares modeled and actual whole-body fish tissue concentrations to various

criteria, as well as considering field observations, to assess the presence and magnitude of risk to fish.

Chapter 4 is a sediment remediation options and feasibility analysis, which includes a chromium speciation analysis that was undertaken to determine if Cr(VI) is present within the sediment pore water of the impacted area. The latter study used equilibrium dialysis cells, or "peepers", which were designed and deployed to sample contaminated pore water.

Chapter 5 is a LCA that compares the environmental burden of two alternatives for the dewatering and disposal of potentially dredged sediments from the impacted site. The first option is to use mechanical grain size separation and dewatering (mechanical processing), which allows the reuse of uncontaminated grain size fractions while disposing of contaminated fractions in a non-hazardous waste landfill. The second option is to transport the dredged sediments to a large, open-air storage area, to allow the natural processes of evaporation, evapotranspiration, and soil infiltration to dewater the sediments (natural dewatering), after which the dried contaminated sediments would be transported to a non-hazardous waste landfill.

Chapter 6 is a general summary of thesis conclusions, as well as recommendations that may be useful to those making decisions regarding potential future remediation efforts for the impacted area.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

2.1.1 Historical, Geographical, and Meteorological Setting

Established in 1673 as Fort Frontenac and being the oldest city in Ontario (Osborne and Swainson, 1988), Kingston is a historic city of approximately 117,000 people (Statistics Canada, 2006) and is located at the eastern end of Lake Ontario, at the southern terminus of the historic Rideau Canal. It was initially established for its location as a port for the exploitation of the fur trade and as a fort for the defence of New France (Preston, 1954). In modern times, Kingston's economy has relied on the presence of public-sector institutions and establishments such as education, military, and correctional services. Kingston was formerly a much more industrialized city, being home to many manufacturing firms such as a large locomotive works and various shipbuilding companies (Osborne and Swainson, 1988). Kingston has a temperate climate (January, -7.7°C; July, 20.3°C) with an average annual precipitation of approximately 960 mm (National Climate Data and Information Archive, 2009).

2.1.2 Geological Setting

The Kingston area is a region characterized by nearly flat-lying Cambro-Ordovician sandstones and Middle Ordovician limestones and shaly limestones that overlie Precambrian rock (Liberty, 1971; Creasy, 1981; Baker, 1916). This Precambrian basement, part of the Grenville Province of the Canadian Shield, is found at the surface in the Frontenac Axis. Where traversed by the St. Lawrence River, its quality as a resistant bedrock sill is responsible for the creation of the Thousand Islands archipelago (Helmstaedt *et al.,* 1987). A thin veneer of glacial and alluvial deposits, as well as soils, cover areas around Kingston where rock outcroppings are not present (Helmstaedt and Godin, 2008). Kingston has long been referred to as "The Limestone City", a moniker which refers to the widespread utilization of Black River limestone (of the Middle Ordovician period) in older buildings (Jolliffe, 1965).

2.1.3 Hydrological Setting

The Great Cataraqui River originates in the Canadian Shield in the vicinity of Newboro, and flows south (Crysler and Latham Ltd., 1977), reaching Lake Ontario at the bottom of the Kingston Inner Harbour at 75 m above sea level (Coakley and Karrow, 1994). The Great Cataraqui River watershed drains approximately 930 km^2 of adjacent land, has a mean depth of 1.2 m, and has an average width of approximately 1,000 m (Crysler and Latham Ltd., 1977). Most of the river's course is located in the Canadian Shield; only the southernmost 10 percent of the river is located on limestone or clay plains (Paine, 1983). It is estimated that the Great Cataraqui River exchanges its total volume approximately 76 times annually (Paine, 1983). The final 2.5 km of the Great Cataraqui River, flowing between Highway 401 and the LaSalle Causeway, is known as the Kingston Inner Harbour. Beyond the LaSalle Causeway is the Kingston Outer Harbour and Lake Ontario, the latter of which empties into the St. Lawrence River, east of Kingston. Figure 2.1 is an overview view of the southern Kingston Inner Harbour, between Belle Island and Lake Ontario, labeled with past and present land uses on its shores.

The Great Cataraqui Marsh is a coastal marsh located along the western shoreline of the Kingston Inner Harbour between Highway 401 and Belle Island, and is considered by the Ontario Ministry of Natural Resources to be a Provincially Significant Wetland (OMoE, 2004). Current velocities under maximum river flow at the narrow portion of the channel adjacent to the Great Cataraqui Marsh are estimated to be approximately 0.18 $m \cdot s^{-1}$ (Paine, 1983), and 0.4 $m \cdot s^{-1}$ in the portion of the river north of Belle Island (Hall, 1999).

Figure 2.1: Map of the Southern Kingston Inner Harbour (ESG, 2009a). Selected geographic features and former, current, and proposed land uses. See over for legend.

Geographic Features	
31	Anglin Bay
7	Barker's Point
13	Belle Island
14	Butternut Creek
4	John Counter Street
3	Gore Road
27	Green Bay Park
17	Orchard Street Marsh
16	South Stream
5	West Stream
Former Uses	
19	Arcom Waste Disposal Facility
12	Belle Island Landfill/Cataraqui Park
10	Federal Dredged Sediments Disposal Site
20	Former Davis Tannery
21	Former Frontenac Lead Smelter
35	Former Kingston Coal Gasification Plant
28	Former Kingston Cotton Mill (Woolen Mill)
Current Uses	
26	Buried sewage force main and water main
18	Canadian Forces Base Kingston
9	Constructed wetland test plot
29	Douglas Fluhrer Park
23	Emma Martin Park
36	Fort Frontenac
33	Frontenac Village Residential Development
32	HMCS Cataraqui Facility
15	Kingscourt Storm Sewer
30	Kingston Marina
38	Kingston Outer Harbour
25	Kingston Rowing Club
34	LaSalle Causeway
1	Music Marina
8	Phreatophyte tree species test plot
6	Rideau Canal
11	Rideau Marina
22	River Street Pumping Station
24	Underground Combined Sewer Outflow Storage Tank
Proposed Uses	
2	Proposed bridge crossing

Figure 2.1 (continued)

2.2 Industrial History of the Kingston Inner Harbour

The early growth and prosperity of Kingston was because it was a significant port, largely owing to the opening of the Rideau Canal in 1832 (Preston, 1954) and its prominence as a garrison town (Mika and Mika, 1969). The steep limestone banks on the eastern shore of the Great Cataraqui River limited this portion of land to residential and rural uses, but beginning in the mid-1800s, the gentle slopes of the western shore of the Kingston Inner Harbour, particularly in the southern portion of the harbour between Anglin Bay and Belle Island, began a period of significant industrial and commercial development. A variety of companies emerged over the following decades, including tanneries, a lead smelter, manufacturing and fabrication companies, a woolen mill, a grist mill, a brewery, boat building facilities, fuel depots, and a railway transport corridor (Malroz Engineering Inc., 2003). Figure 2.2 displays a photograph of the west side of the Kingston Inner Harbour in 1924.

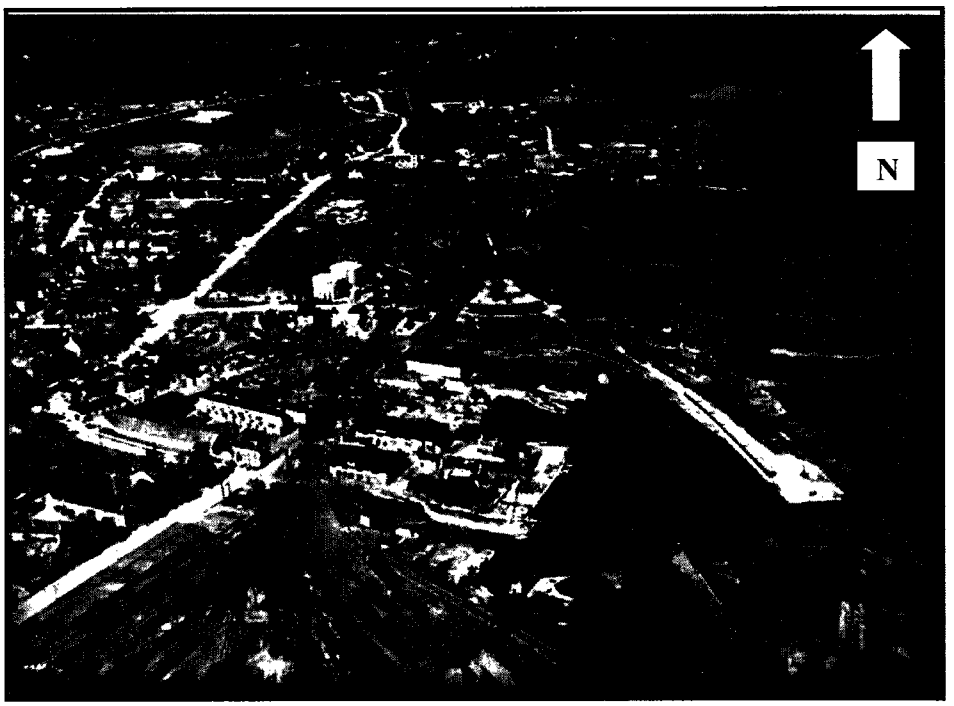

Figure 2.2: West Side of the Kingston Inner Harbour in 1924 (National Air Photo Gallery, 1924a). This photograph was taken approximately above Fort Frontenac, looking northwards along the Great Cataraqui River. Note the numerous rail lines that moved through the downtown, the shipbuilding facilities in Anglin Bay, the fuel storage facilities, and the scuttled ships in the water.

By the 1970s, most industry on the western shore of the Kingston Inner Harbour had ceased operations, although the legacy of contamination from many of these industries has continued to persist into the present day. ESG (2009) lists and describes previous environmental studies that have been conducted on the Kingston Inner Harbour, many of which have been conducted within the impacted area. As detailed in ESG (2009), laboratory analysis of surface water has shown that negligible levels of contaminants are present in these samples in comparison to Canadian Water Quality Guidelines for the Protection Aquatic Life, as published by the CCME. As these guidelines are very conservative, surface water can be effectively ruled out as an exposure pathway. Within the sediments of the impacted area, numerous contaminants have been found to be present above the CCME Freshwater Sediment Quality Guidelines (ESG, 2009a; 2009b) including: As, Cr, Cu, Pb, Hg, Zn, PCBs, PAHs, and DDT (ESG, 2009b). Of these CoPCs, Cr and PCBs are the most abundant and widespread. Chemical and toxicological backgrounds for these CoPCs are presented in CCME (1999a) and are also summarized in ESG (2009a, 2009b). Particularly notable historical sources of contamination are a former lead smelter, the former Davis Tannery, and the former Belle Island Landfill.

2.2.1 Lead Smelter

Operating as early as 1878 (Engineering and Mining Journal, 1878), the Frontenac Lead Smelting Works was built to treat galena from the company's mine in Loughborough at Perth Road, located approximately 25 km north of the city (Ontario Bureau of Mines, 1904). Initially considered an ambitious endeavor, the mine and smelting works ran only intermittently for approximately three years, and was abandoned by 1882 (Ontario Bureau of Mines, 1904). The total quantity of galena smelted was approximately 100,800 lbs, and the quantity of lead produced was 61,549 lbs (Ontario Department of Agriculture, 1885). Figure 2.3 displays the location of the Frontenac Lead Smelting Works.

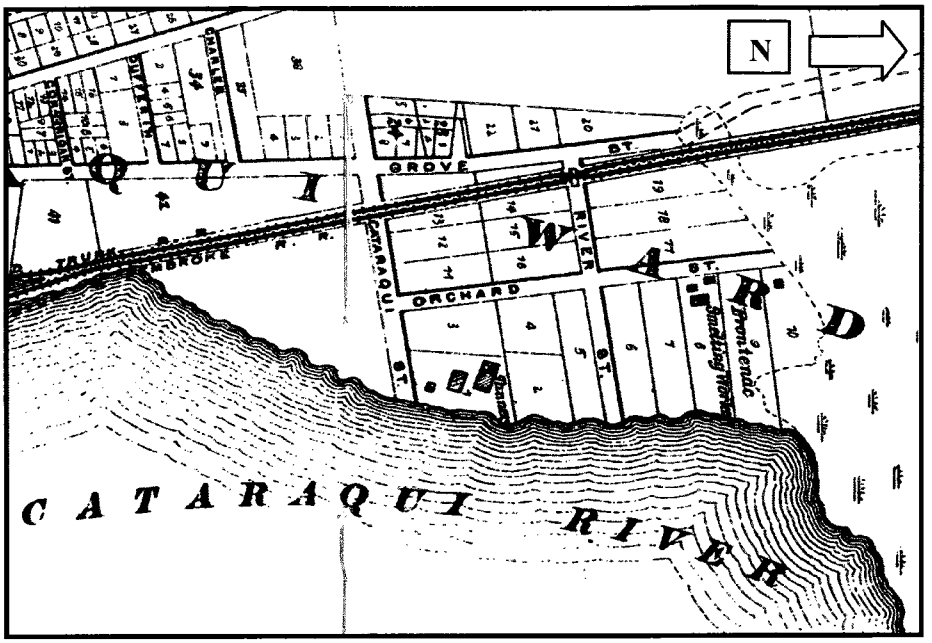

Figure 2.3: Location of the Frontenac Lead Smelting Works in 1878 (Meecham (JH) and Company, 1878). North points approximately to the right of map; the works was located east of Orchard Street and north of River Street. The thoroughfare annotated on the map as Grove Street is now Rideau Street. The Kingston Cotton Mill (now known locally as the Woolen Mill) is not present as it was not constructed until the early 1880s.

Dormant for almost 30 years, the North American Smelting Company purchased the Frontenac Lead Smelting Works and associated mine in 1911. By December, 1912, the smelter had been rebuilt and was treating scrap and lead dross, as well as domestic and American ores, including concentrates from the mine in Loughborough (Department of Mines, 1919; 1913). This plant closed on November 1, 1913. In the latter part of 1916, operations resumed under the Kingston Smelting Company (Department of Mines, 1919), only to cease in December 1917 (Canadian Mining Journal, 1918). Reopening for the final time on February 14, 1919, under the name of Kingston Smelters (Ontario Bureau of Mines, 1919), this company would also be short lived and the property was sold to the Davis family in 1922 to facilitate the expansion of their burgeoning tanning business (Davis and Davis, 1937). In general, the lead smelting industry in Ontario languished during this period because the smelters could not acquire sufficient tonnage of ore, and because of the significant freight and duty expenses associated with shipping to the United States (Newnam, 1917).

2.2.2 Davis Tannery

A. Davis and Son Ltd., locally referred to as the Davis Tannery, opened in 1903 after purchasing the Kingston Tannery property from its proprietor, J.J. Carrington. Amongst the first companies in Canada to use such techniques, the Davis Tannery began to use chromium tanning methods in 1912 (Davis and Davis, 1934), and continued to do so until its closure in 1973 (OMoE, 1978). In 1914, the factory constructed a direct rail connection with the Canadian National Rail line to expedite the traffic of goods, and it produced a "considerable" amount of footwear for use by the soldiers overseas during The Great War (Davis and Davis, 1937). By the 1920s, the tannery had become one of the largest in Canada, and by 1955 it was turning six million pounds of hides per year into leather (Kingston Whig-Standard, 1955). Until 1967, all chromium-contaminated effluents from the tannery were discharged into the marsh and creek north of the property, which subsequently flowed into the Great Cataraqui River. In addition, solid wastes appeared to have been dumped along the edges of the marsh and various other locations on the property (OMoE, 1978). Figure 2.4 displays an oblique overhead view of the Davis Tannery and former lead smelter. Though it is not certain whether the photo actually displays a release of chromium-contaminated effluent, Figure 2.5 nevertheless shows how the marsh drains into the Great Cataraqui River.

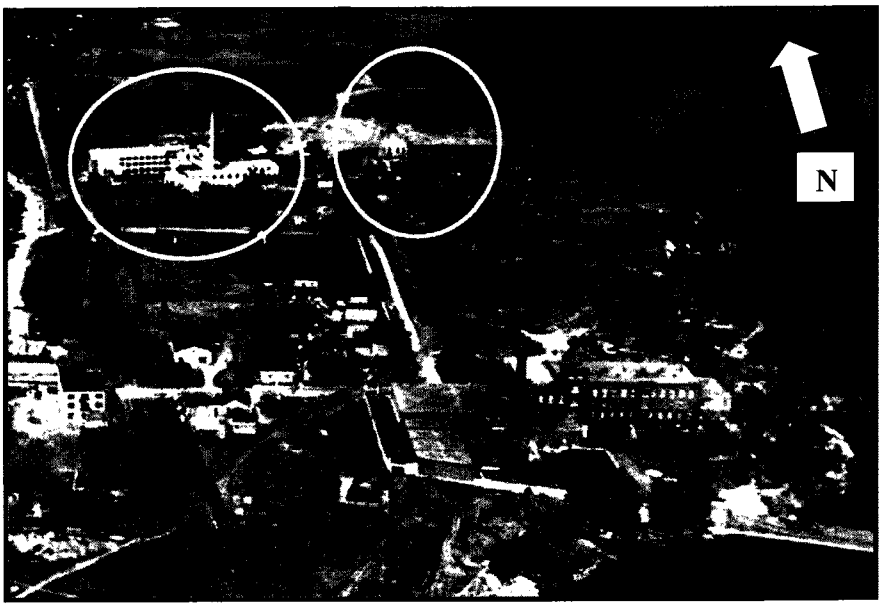

Figure 2.4: Davis Tannery and the Former Lead Smelter Buildings in 1924 (National Air Photo Gallery, 1924b). Note the Woolen Mill in the bottom right-hand corner. The Davis Tannery was comprised of the buildings surrounding the smokestack in the top left-hand corner. The smokestack to the right of the Davis Tannery was the smelter of the lead smelting firms that occupied the property, and these firms had buildings situated to the fore of the smelter.

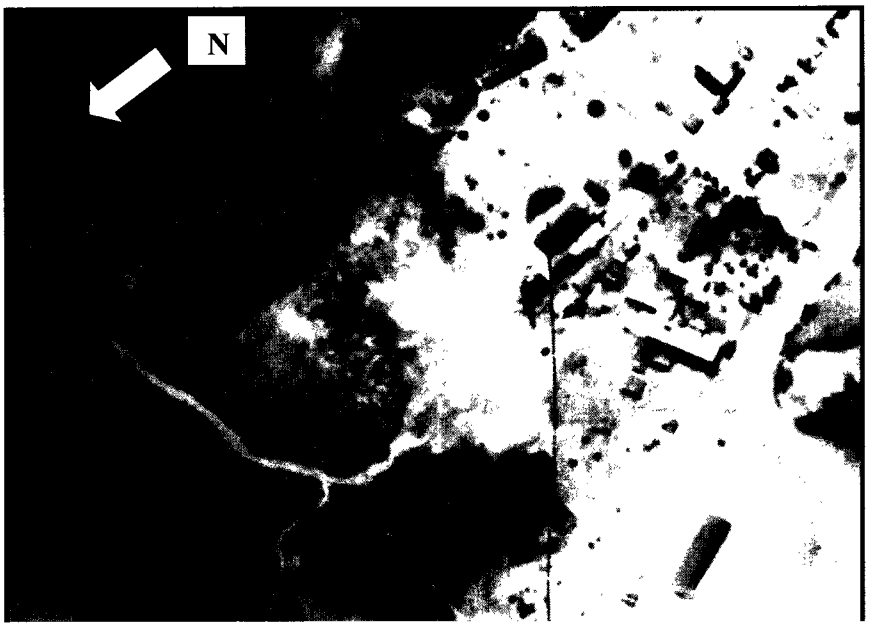

Figure 2.5: Davis Tannery and Former Lead Smelter in 1937 (National Air Photo Library, 1937). From 1912 to 1967, all chromium-contaminated effluents from the Davis Tannery were discharged, untreated, directly into the Orchard Street Marsh. Although it is not certain if the photo actually displays such a release, the photo nevertheless makes clear the flow of the marsh into the Great Cataraqui River.

2.2.3 Belle Island Landfill

The site upon which Cataraqui Park now exists was originally a shallow marsh between the west side of Belle Island and the mainland. In 1916, while the LaSalle Causeway was being constructed, dredged sediments were deposited into this marsh, making it even shallower. From 1952 until its closure in 1974, before government regulations had been established for waste disposal, this marsh was the location of a municipal landfill (Wright and Welbourne, 2002) and the 44-hectare marsh was completely filled in (Figure 2.6). As a result, and ever since, an artificial peninsula has existed between Belle Island and the mainland and water is restricted to flowing only on the east.

In the mid-1990s, after leachate was observed at numerous points along the shore, water, soil, and sediment testing revealed that numerous contaminants were seeping from the former landfill, including Cu, Pb, PCBs, and PAHs (Wright and Welbourne, 2002). A subsequent sub-surface investigation of the landfill property revealed household garbage, paper, rags, plastic, wire, wood, asphalt, cinders, brick, glass, metal, and railways ties. Wastes from a tannery, potentially from the Davis Tannery, were also unearthed (Malroz Engineering Inc., 1999). To mitigate leachate migration from the site, the city adopted various remedial measures, which includes active groundwater pumping (Rose *et al.*, 2004). However, a recent report detailing the results of water sampling near the southeast corner of the former Belle Park Landfill identified that this location "remained a potential ongoing source of [PCB] contamination that could not be attributed to fluxes in suspended solids alone", but that this particular area itself may be contaminated by an "ongoing source of PCB contamination" (Benoit and Burniston, 2010). Upon the closure of the landfill, the site was converted into a multiple use recreational park, known as Cataraqui Park, which includes a 9-hole golf course, tennis courts, and walking paths. It is important to note that no landfill dumping ever occurred on Belle Island, only in the marsh between the island and the western shore of the river (Wright and Welbourne, 2002).

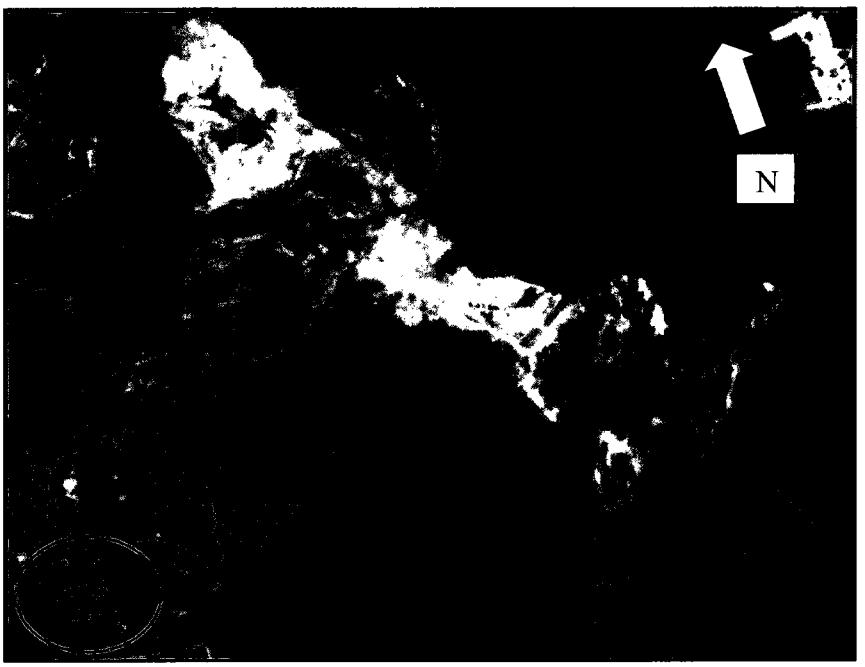

Figure 2.6: Belle Island Landfill in 1974 (National Air Photo Library, 1974). Originally the site of a marsh that loosely connected Belle Island to the west shore of the Great Cataraqui River, the landfill was in operation from 1952 to 1974. Note the semi-circular outcrop on the north end of the landfill, which is a federal waste disposal site that contains sediments that were dredged from the Rideau Canal (Malroz Engineering Inc., 1999). The buildings of the former Davis Tannery, which had closed by 1973, are visible in the lower left-hand corner of the photograph.

2.3 Cultural Significance of the Kingston Inner Harbour

The Great Cataraqui River comprises the southern third of the historic 202 km Rideau Canal that connects Ottawa to Kingston (Crysler and Latham Ltd., 1977). In 2007, the United Nations Environmental, Scientific, and Cultural Organization (UNESCO) added the Rideau Canal, and associated fortifications along its route, to the World Heritage List of less than 900 properties that are deemed to have "outstanding universal value" (UNESCO, 2009). Constructed in the early nineteenth century, it was built to aid the British in defending the colony of Canada. Presently, it is the best preserved example of a slackwater canal in North America (UNESCO, 2009).

There are two identified pre-contact archeological sites in the Kingston Inner Harbour, namely the Kingston Outer Station located just south of the Great Cataraqui Marsh and aboriginal burial sites on Belle Island, but it is recognized that all locations

along the shores of the Cataraqui River hold potential for additional archeological sites of this nature (Archeological Services Inc., 2008).

The southern Kingston Inner Harbour is the site of a marine graveyard, or "boneyard" (Moore, 1995a) and since the 1930s has been the subject of numerous archeological surveys (Moore, 1995b). Lying between the Kingston Rowing Club and the LaSalle Causeway (see Figure 2.1), there are fourteen identified vessels that lie submerged or partially submerged along the western shore (Moore, 1995b). Dating from the late nineteenth and early twentieth century, these include both sail and steam vessels (Moore, 1995b). Upon the capture of Fort Frontenac by the British in 1758, French vessels were believed to have potentially been burned at the anchorage north of Fort Frontenac (Moore, 1995b), though historical records from this period are scant (Moore, 2009). Four wooden vessels were unearthed during excavation for the building of Normandy Hall in 1953, though at least one of these is now believed to date from approximately 1820 (Moore, 1995b). Though it is difficult to hypothesize about exact locations, it is possible that the southern Kingston Inner Harbour may contain remnants of these French vessels (Moore, 2009); if discovered, these vessels would have "extreme historical significance" (Moore, 2009). No archeological surveys have been conducted within the southern Kingston Inner Harbour since 1995 (Moore, 2009), and due to the presence of contamination, divers would only enter these water "very reluctantly" (Hill, 2009).

2.4 Municipal Significance of the Kingston Inner Harbour

Kingston's historical importance, as well as its scenic downtown waterfront, is a significant draw for local tourism; in 2008, 2.5 million tourists came to Frontenac County, and they spent over $333 million (Tourism Kingston, 2010). As far back as 1984, the city's Master Plan for the waterfront described the property on the western shore of the Great Cataraqui River, from Anglin Bay to Cataraqui Park, as primarily industrial land that was providing little benefit to the city. The land was described as "ripe for redevelopment and the city should not allow this opportunity to escape unattended" (Totten Sims Hubicki Associates, 1984). Presently, Kingston continues to plan for future redevelopment on this land, though none has occurred up to this time.

Present plans for the former industrial properties include the establishment of assisted housing for special needs groups (rent-geared-to-income, etc) and dedicated parkland (City of Kingston, 2006).

In January 2000, Kingston City Council created the Kingston Environmental Advisory Forum (KEAF), the impetus of which was community concerns over the leaching of contamination from the former Belle Island Landfill (City of Kingston, 2007). KEAF is composed of municipal civil servant, academic, conservation authority, and municipal health representatives charged with identifying environmental issues and priorities in Kingston, and assisting the city council in preparing its environmental strategy (City of Kingston, 2008). KEAF immediately established the Inner Harbour Working Group to aid in the adoption of a comprehensive plan for the area (City of Kingston, 2008). A public workshop sponsored by KEAF in 2002 determined that the Kingston Inner Harbour should be redeveloped in a sustainable fashion. As the City of Kingston has signaled its intent to become "Canada's Most Sustainable City" (Foster, 2009), it is important to consider that any future remediation actions for the Kingston Inner Harbour reflect the notions of environmental stewardship and sustainability.

2.5 The International Joint Commission and the Canada-Ontario Agreement

The Kingston Inner Harbour fall within the jurisdiction of the Great Lakes International Joint Commission (IJC) treaty, an agreement that defines the Great Lakes System as "all streams, rivers, lakes, and other bodies that are within the drainage basin of the St. Lawrence River at or upstream from the point at which the river becomes the international boundary between Canada and the United States" (IJC, 1987). The mission of the IJC is to prevent and resolve disputes between the United States and Canada under the *1909 Boundary Waters Treaty* (IJC, 2009). Signed in 1972 and renewed in 1978, the *Great Lakes Water Quality Agreement* (GLWQA) defines areas of concern (AOCs) as locations in the Great Lakes that are deemed to be severely ecologically degraded. The presence of heavily contaminated sediments from anthropogenic discharges in the Great Lakes is a major environmental concern because of their effects on benthic life, other aquatic biota, and the water column (Great Lakes Water Quality Board, 1985). The

GLWQA seeks to restore and protect the chemical, physical, and biological integrity of the Great Lakes Basin Ecosystem, and includes a number of targets and guidelines to achieve these objectives (Environment Canada (EC), 2009).

In 2002, to help Canada achieve its commitments under the GLWQA, the Canada-Ontario Agreement (COA) committed the Government of Canada and the Ontario provincial government to develop a framework for assessing and managing contaminated sediments within AOCs (OMoE, 2008). The resulting *Canada-Ontario Decision Making Framework for Assessment of Great Lakes Contaminated Sediment* (EC and OMoE, 2008) is founded specifically on ecological risk assessment principles, and is based on a weight of evidence approach that considers the following four lines of evidence (LOE):

i. sediment chemistry;
ii. sediment toxicity to benthic invertebrates;
iii. benthic community structure alteration; and
iv. potential for contaminant biomagnification.

In 2006, the Cataraqui River Stakeholders Group (CRSG) was formed, consisting of representatives from ESG, OMoE, EC, Fisheries and Oceans Canada, Transport Canada, Parks Canada, Canadian Forces Base Kingston, and Rideau Renewal Limited. Although the Kingston Inner Harbour is not an AOC under COA, the COA framework for contaminated sediments has been used by the CRSG to provide a robust and accepted architecture for management and decision-making.

Figure 2.7 is a flow diagram outlining the steps and decision points in the COA framework. Based on a framework that is conceptually founded on increasing complex tiers of ERA as defined by CCME (1997) (and are discussed in Section 2.7.1), Steps 1-3 and Decisions 1-2 correspond to a Screening ERA, Steps 4-5 and Decisions 3-4 correspond to a Preliminary Quantitative ERA, and Steps 6-7 and Decisions 5-6 correspond to a Detailed Quantitative ERA (EC and OMoE, 2008).

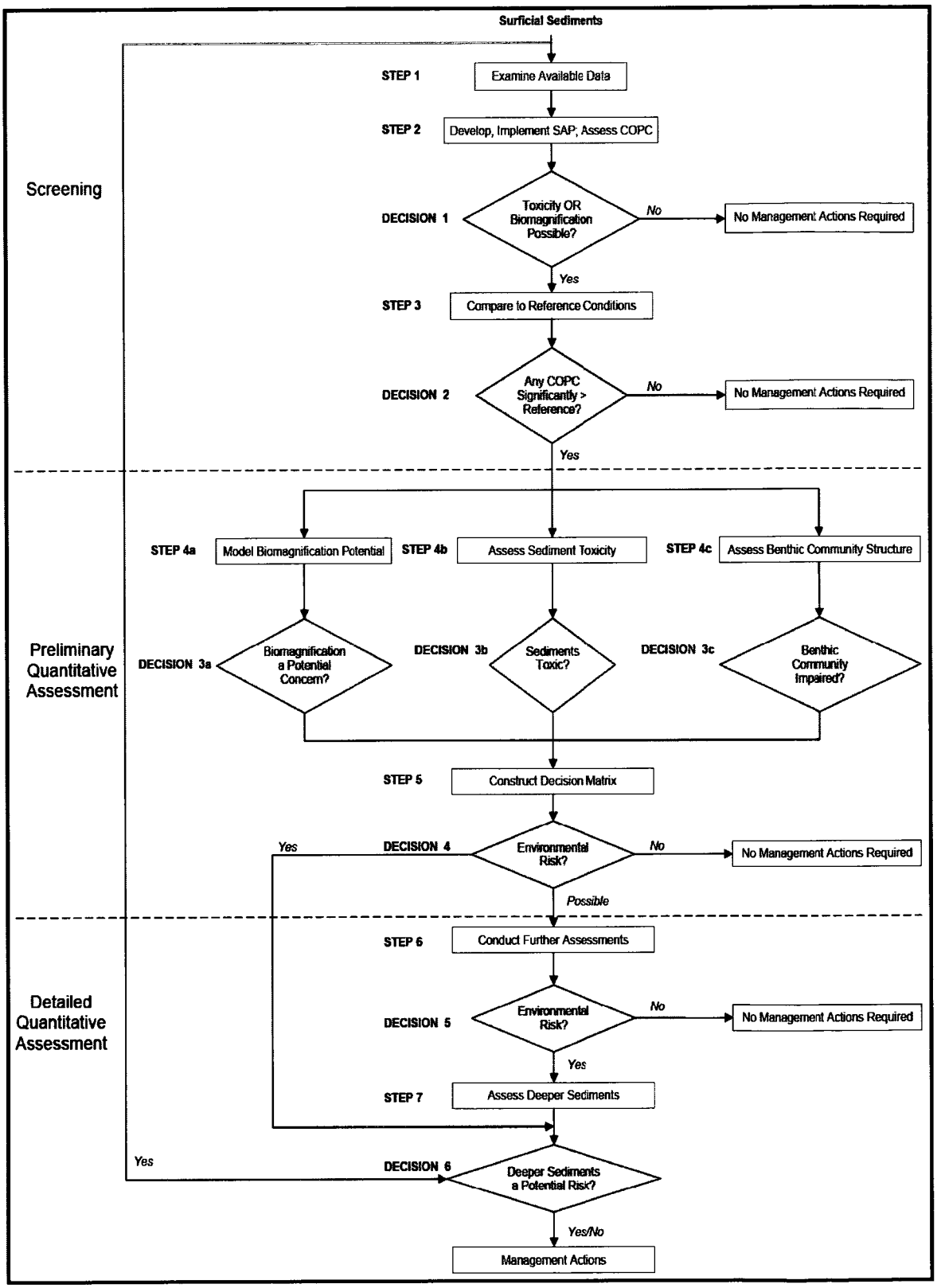

Figure 2.7: Canada-Ontario Decision-Making Framework for Assessment of Great Lakes Contaminated Sediments (EC and OMoE, 2008)

2.6 Sediments

2.6.1 Introduction

Sediment can be defined as "suspended or deposited solids, of mineral as well as organic material, acting as a main component of a matrix which has been or is susceptible to being transported by water" (Owens, 2008). Sediments are frequently found to have been contaminated by past industrial activities; this historical legacy can complicate the redevelopment of harbour and waterfront areas for residential or commercial uses (Breedveld, 2008), and may act as a potential non-point-contamination source that could influence the quality of surface waters (Rodrigues and Formoso, 2005). Of those contaminants originating from industrial sources, the most destructive to fluvial systems are metals, synthetic organic compounds (*e.g.* PCBs), and radionuclides. Contaminants are not necessarily permanently fixed in the sediments, and remobilization can occur by numerous pathways of physical (*e.g.* flooding), chemical (*e.g.* change in pH, degradation of some organic compounds into a more mobile form), and biological (*e.g.* oxidation of anoxic sediments by bioturbation) origin (Zoumis *et al.*, 2001).

Two qualities, grain size and total organic content (TOC, a measure of the amount of organic matter within a sample), have a significant effect on the capacity for contaminants to adsorb to sediments. Fine grain sizes and high TOC allow contaminants to bind to sediments much more strongly than sediments of coarse grain sizes and low TOC (Apitz *et al.*, 2005). Table 2.1 contains a basic classification of sediments based on grain size.

Table 2.1: Basic Grain Size Classification for Sediments

State	Classification[1]	Grain size diameter[1]	Constituents[2]
Sediments	Coarse-grained	> 63 μm	Boulders, cobbles, gravels, sands
	Fine-grained	0.45 to 63 μm	Silts, coarse and medium clay
Dissolved	In-solution/dissolved	< 0.45 μm	Fine clay, colloidal

[1] Taylor *et al.* (2008)
[2] Owens (2008)

2.6.2 Sediment Guidelines

CCME, comprised of federal, provincial and territorial environment ministers, is the primary body in Canada for intergovernmental discussion on environmental matters of both national and international relevance (CCME, 1999d). The Canadian Sediment Quality Guidelines for the Protection of Aquatic Life were developed by CCME (2001) to provide reference points for an aquatic system in which to assess the potential for adverse biological effects. Within these guidelines, CCME has published Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Levels (PELs). ISQGs are the presently accepted levels at which contaminants are expected to result in adverse effects in less than 25 percent of receptors; PELs are the concentrations at which adverse effects are expected to be observed in more than 50 percent of receptors (CCME, 1999a). ISQGs may be used as remediation targets, but CCME cautions that ISQGs are to be used alongside other information that supports the sediment quality assessment, such as unique site background (reference) levels and ecological assessments. Within the impacted area of the Kingston Inner Harbour, chromium is the most abundant and widespread contaminant, followed by PCBs, Hg, and Pb. Taken from ESG (2010), Table 2.2 lists CCME guidelines for the CoPCs that are considered in this thesis, the mean and range of CoPCs in surface sediments within the impacted area, and background concentrations. The unit of measurement for these values is parts per million (ppm), which is equivalent to $mg \cdot kg^{-1}$.

Table 2.2: Comparison of CCME Freshwater ISQGs and PELs to Impacted Site Means, Ranges, and Background Values

Contaminant	CCME ISQG[3] (ppm)	CCME PEL[3] (ppm)	Impacted site mean[4] (ppm)	Impacted site range[4] (ppm)	Back-ground[4] (ppm)
Arsenic	5.9	17.0	38	2.0 - 477	2.7
Chromium (total)[1]	37.3	90.0	1127	16 - 9,900	67
Copper	35.7	197	58	340 - 5.0	33
Lead	35.0	91.3	157	10 - 840	51
Mercury	0.17	0.486	2.0	0.21 - 9.0	N/A
Zinc	123	315	201	23 - 720	123
Polychlorinated biphenyls					
Aroclor 1254[2]	0.060	0.340	N/A	N/A	N/A
Total PCBs	0.0341	0.277	0.520	0.00 - 3,000	0.035

[1] No specific guidelines exist for Cr(III) or Cr(VI)
[2] Aroclor 1254 is the only individual Aroclor for which CCME publishes a guideline
[3] CCME (1999a)
[4] ESG (2010)

2.6.3 Stratigraphy, Grain Size Distribution, and Organic Content of Kingston Inner Harbour Sediments

Asquini *et al.* (2007) determined that the three types of sediment found in the impacted area are gyttja, clay, and peat, and the two predominant grain size fractions are clays and fine to medium organic-rich silts (gyttja). Gyttja is a soft, generally water-rich mud (greater than 80 percent of wet weight), dark brown to black in color, which is found throughout a wide range of organic content (20 to 70 percent). Peat is a type of sediment commonly found in wetlands and marshes that contains more than 70 percent organic detritus (Dalrymple and Carey, 1990). Asquini *et al.* (2007) found that the top layer of sediment in the Kingston Inner Harbour, extending to a depth of 25 to 40 cm, is composed of gyttja. The layer below the gyttja was found to be clay, except in the western portion of the impacted area (adjacent to the Davis Tannery property and marshy in nature), in which peat is predominant below the gyttja and no clay layer was present.

Tinney (2006) determined that sediments within the impacted area are chiefly composed of clays and fine silts, with 95 percent of grain sizes being fine-grained. Tinney (2006) and Goodberry *et al.* (2006) each found that surficial sediments within the impacted area are high in TOC. Due to the presence of fine grain sizes and high TOC, and a relatively low average water depth (1.2 m), it is likely that any recreational boating

or weather-induced water turbulence within the impacted area (and the Kingston Inner Harbour in general) could easily facilitate the suspension and redistribution of contaminated sediments (ESG, 2006b). Results of Pb-210 testing of sediments support the conclusion that the sediments within the Kingston Inner Harbour have a tendency for re-suspension and redistribution (ESG, 2006b). As an example, the results of Benoit and Burniston (2010) identify that PCB concentrations in water samples were "highly correlated with suspended solid concentrations", leading them to the conclusion that PCB concentrations in the water column were "generally driven by sediment resuspension." Located in Appendix A, Figure A.2 is a map that displays the grain size distribution within, and surrounding, the impacted site. Figure A.3 is a map that displays TOC levels, and surface sediment plume maps showing concentrations and distributions, found in Figure A.4 to Figure A.10, have been generated for each of the CoPCs considered in this thesis. All maps have been taken from ESG (2009b). The map depicting the concentration and distribution of chromium in surface sediments is also found in Figure 2.8.

ESG (2009a) includes a detailed account of previous studies on sediment quality, and contains a summary of studies researching associated biological effects, which have been conducted for the Kingston Inner Harbour. These previous studies predominantly surveyed available research and information, and gathered data on characteristics of the Kingston Inner Harbour including contaminant sources, concentrations, distribution, fate, and transport within the impacted area, all of which would correspond variously between Step 1-4a, and inform Decisions 1-3a, of the COA framework. It is these studies that have established the foundation upon which the list of CoPCs for the impacted site have been selected.

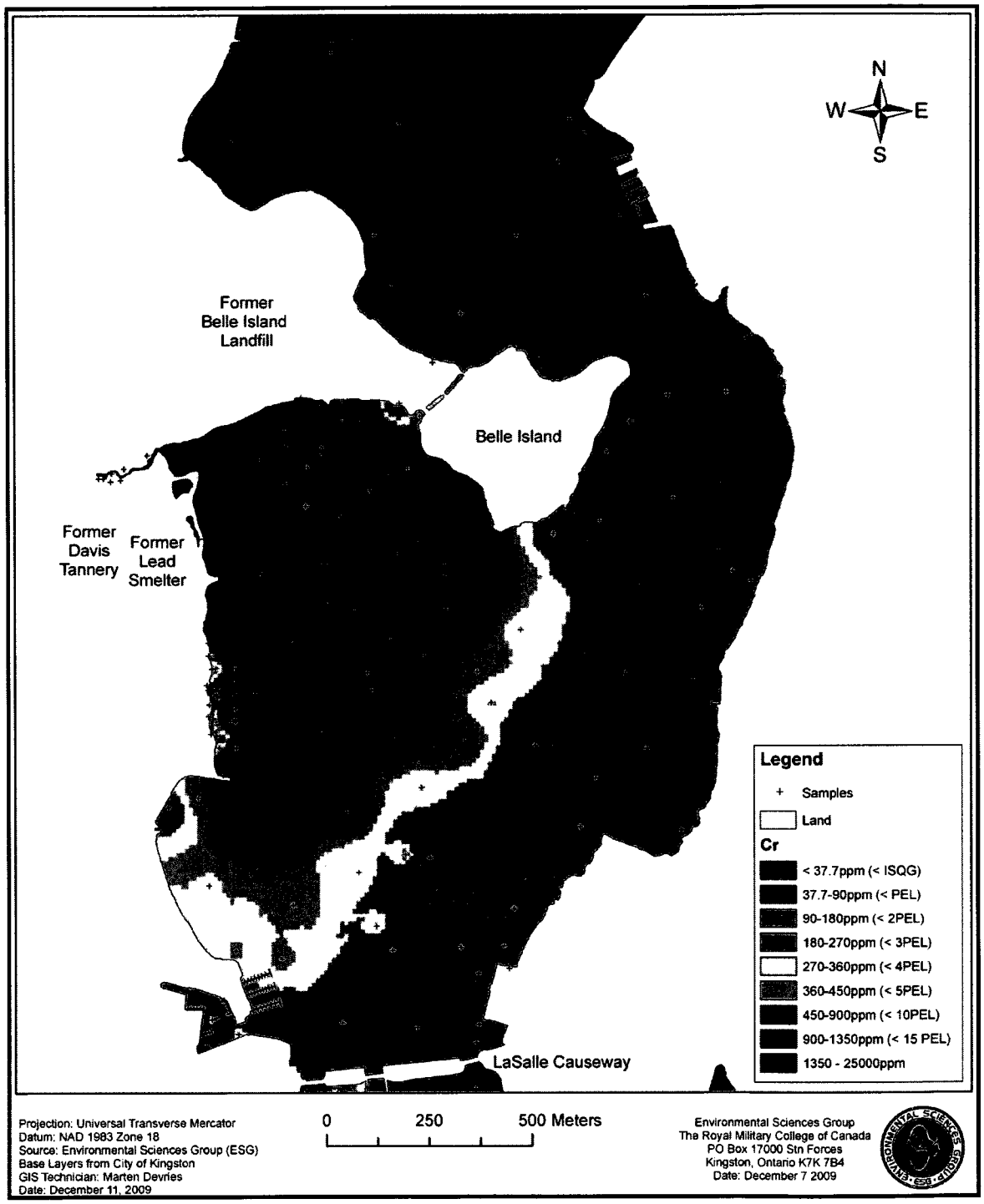

Figure 2.8: Distribution of Chromium in Surface Sediments of the Kingston Inner Harbour (ESG, 2009b).

2.7 Biological Effects from Contaminated Sediments within the Impacted Area

ESG (2010a) is a comprehensive study of biological effects associated with contaminated sediments from the impacted area. Specifically, ESG (2010a) assimilates data for the three lines of evidence, (ii) to (iv), listed in Section 2.5.

Under the criteria defined within COA, eight locations within the river portion of the impacted area (specifically southwest of Belle Island, adjacent to the Orchard Street Marsh) have demonstrated toxicity effects to benthic invertebrates, although most locations within the impacted area do not demonstrate these effects (ESG, 2010a). However, no toxicity effects have been detected to benthic invertebrates when exposed to sediments sampled from outside the impacted area (ESG, 2010a). Although sediment toxicity test results for the impacted area as a whole are inconsistent, the results for the area southwest of Belle Island demonstrate a clear toxicity to benthic invertebrates (ESG, 2010a).

ESG (2010a) determined that benthic invertebrate species that are tolerant of organic pollution predominate throughout the impacted area. A benthic community structure assessment tool, BEnthic Assessment of SedimenT (BEAST) analysis, was used to compare benthic community structure at the impacted site to similar test sites from within the Great Lakes system. The result of the BEAST analysis concluded that, for most locations within the impacted area, benthic invertebrate communities are "severely stressed" (ESG, 2010a). Multivariate analysis showed that benthic communities at reference sites were significantly different from impacted sites, and environmental variables explaining the benthic community structure were related to both natural environmental gradients (*e.g.* grain size, alkalinity) and contaminant gradients (*e.g.* Cr) concentrations (ESG, 2010a).

ESG (2010a) examined various types of biota samples (cattails and other macrophytes, benthic invertebrates, and fish) from within the impacted area, concluding that they all consistently exhibit bioaccumulation of contaminants such as Cr, PCBs, and Hg. Samples of these same types of biota from outside the impacted area did not demonstrate evidence for bioaccumulation of these contaminants. In comparison to tissue residue guidelines for the protection of wildlife consumers of aquatic biota, benthic

invertebrate samples from within the impacted area regularly exceeded the associated guidelines, while samples of benthic invertebrates taken from outside the impacted area did not accumulate these contaminants to the same level (ESG, 2010a)

ESG (2010a) has established that three lines of evidence (sediment toxicity, benthic community structure alteration, and bioaccumulation) consistently demonstrate ecological effects. Additionally, ESG (2010b) contains a risk assessment that has established the presence of risk to humans, predominantly due to ingestion of contaminated fish. However, to date, no research has studied the potential for adverse effects to higher-trophic-level wildlife receptors from contaminated sediments within the impacted area, which would further support evidence of biomagnification (Decision 4a).

2.8 Ecological Risk Assessment

Wildlife receptors can be exposed to contamination by many different pathways, including direct contact with contaminated sediments and consumption of organisms that have accumulated contaminants originating from the sediments (National Research Council (NRC), 2007). A stressor is any physical, chemical, or biological substance or object that may produce an adverse effect (Suter, 2006), and can be of natural or anthropogenic origin (Diamond and Serveiss, 2001). ERA is a methodical process for estimating the likelihood that adverse ecological effects may result, or are resulting, as a consequence of exposure to one or more stressors (USEPA, 1992a). The objectives of the ERA will determine the nature of the sampling, as well as the degree of detail required within the assessment (CCME, 1997). The ERA process is used to arrange and analyze data, information, assumptions, and uncertainties to aid decision-makers in evaluating and anticipating the relationship between stressors and ecological effects (USEPA, 1998). In essence, ERA is the estimation of the probability of unwanted effects (van de Guchte, 1995), and is a well-established and recognized tool for determining whether a contaminated site warrants remedial action (Förstner and Apitz, 2007).

It is necessary to distinguish the terms "hazard" and "risk" to understand both the process and result of an ERA (Chapman and Wang, 2000). Hazard is the intrinsic capability of a stressor to create an adverse effect on a receptor. However, the mere presence of a stressor is not sufficient to cause adverse effects; exposure, by way of

inhalation, ingestion, or dermal contact, must occur. Risk is the likelihood that a stressor will cause an adverse effect on a receptor (Chapman and Wang, 2000). In essence, hazard addresses *possibilities* while risk addresses *probabilities*. The degree to which an adverse effect will occur is the product of the concentration of the stressor in the receptors environment, and the duration of the exposure to the stressor of the receptor (Chapman and Wang, 2000).

CCME recognizes a tiered approach to the conduct of ERA, and is composed of the following three levels: screening assessment, preliminary quantitative ERA, and detailed quantitative ERA (CCME, 1996). If a screening assessment sufficiently characterizes risk at a contaminated site within a tolerable level of complexity, the subsequent levels of complexity are not required; however, if the screening assessment does not adequately characterize risk, subsequent levels of ERA are undertaken until an acceptable degree of complexity is achieved (CCME, 1996). With each subsequent level, the ERA process moves from being predominantly qualitative and descriptive, to an increasingly quantitative and predictive nature. The following is a brief description of each ERA level (CCME, 1996):

i. Screening assessment: largely descriptive in nature, this level of ERA relies on simple, qualitative, and/or comparative methods. This level has a strong reliance on literature information and previously gathered data. Screening assessments are always undertaken before any subsequent level of ERA.

ii. Preliminary quantitative ERA: intermediate between the other two levels, increasing importance is placed on data collection, particularly with respect to significant issues identified in the screening assessment.

iii. Detailed quantitative ERA: the most rigorous level, it is characterized by its quantitative results that are generated from site-specific data and predictive modeling. Results of this level of assessment may attempt to explain complex ecosystem responses.

The three tiers of ERA are comprised of four identical steps: receptor characterization, exposure assessment, hazard assessment, and risk characterization (CCME, 1996). The CRSG has identified the need for a semi-quantitative ERA, which incorporates the screening assessment with aspects of the preliminary quantitative ERA. In the conduct of this semi-quantitative ERA, the four steps of the ERA process can be characterized by (CCME, 1996):

i. Receptor characterization: identify exposed habitats and populations, with particular emphasis on sensitive or endangered wildlife; gather qualitative site information; conduct a literature review on receptors of concern; establish a conceptual model for the ecosystem; and determine assessment and measurement endpoints of the ERA.

ii. Exposure assessment: identify the CoPCs, exposure media, and exposure pathways to be assessed, as well as any major data gaps or uncertainties. In addition, it is necessary to identify the most probable pathways of exposure for each species of concern and develop a simple food chain model.

iii. Hazard assessment: locate CoPC toxicity data from the literature for applicable receptors; if necessary, extrapolate toxicity information from species of which toxicological data does exist for use on species of concern; consider mixtures of chemicals; and identify regulatory information.

iv. Risk characterization: make semi-quantitative risk estimates using the quotient method; characterize risk as high, intermediate, or negligible; compare CoPC concentrations to available criteria; and identify important uncertainties and data gaps.

In the conduct of an ERA, locations providing a means of comparing the concentration of contaminants in the impacted site to the concentrations that are naturally

present are carefully selected. These reference sites are ideally situated as geographically close to the impacted site as possible (CCME, 1996).

2.9 Sediment Remediation Strategies

The COA framework clearly indicates the need for a management decision, and if the ERA indicates risk to higher-trophic-level receptors, there will be a need for sediment remediation. However, determining remediation solutions is complex, and this difficulty is exacerbated by underwater conditions, the presence of sensitive receptors and habitats, water currents, and access difficulties (Zeller and Cushing, 2006). Within populated areas, an appropriate sediment risk management strategy must not only identify environmental risks associated with contaminated sediments, but consider fitting and adapted remediation options for use in an urban scenario (Breedvelt, 2008). Three generic active response alternatives are presently employed in contaminated sediment management strategies:

i. Monitored natural recovery (MNR): involves allowing the contaminated sediment to remain in place, permitting the continuing natural aquatic processes to "contain, destroy, or otherwise reduce the bioavailability of the contaminants" (NRC, 1997). The effectiveness of MNR relies on physical, chemical, and biological process such as burial of contaminated sediments resulting from natural sedimentation, limited contaminant mobility resulting from binding processes such as adsorption and precipitation, and contaminant transformation to less toxic forms through chemical or biological processes (Zeller and Cushing, 2006). The decision to adopt MNR as a sediment management strategy is not a "no-action decision" (Magar and Wenning, 2006), it is founded on the belief that while the contaminated sediments do pose a measure of risk to the surrounding ecosystem, the risk is sufficiently low to rely on natural processes to reduce this risk over time in an acceptably safe manner (Apitz and Power, 2002).

ii. Capping: a subaqueous remediation option in which a covering, or cap, is placed over a deposit of contaminated sediment. This cap may be comprised of clean sediments, sand, gravel, or may involve a more complex design with geotextiles, liners, and multiple layers (Palermo, 1998). There are two types of capping: *in-situ* capping and *ex-situ* capping. *In-situ* capping is performed by placing the capping material directly onto the contaminated sediments, in their original location, thereby sequestering contaminants from pelagic and benthic receptors until natural degradation processes occur (Thoma *et al.,* 1993). *Ex-situ* capping is achieved by first dredging the contaminated sediments from the affected water body, and then transporting them to the capping location (another aquatic environment), where the cap is then deposited on the submerged sediments (Liu *et al.,* 2001). Capping reduces the flux of contaminants into the overlying aquatic ecosystem by increasing the time for diffusive and advective processes to occur, inhibiting pore water processes through adsorption, and by ceasing the re-suspension and desorption of contaminants into the water column (Thoma *et al.,* 1993). However, capping may result in a sudden and substantial restructuring of biogeochemical mechanisms within the sequestered sediments, which are dependent on natural redox conditions, thereby negatively impacting biological processes responsible for natural contaminant attenuation processes (Himmelheber *et al.,* 2008).

iii. Dredging (and Excavation): an *ex-situ* method that involves the physical removal of sediments from a water body, either while still immersed in water (dredging) or after the water has been rechanneled or drained (excavation). As opposed to *maintenance* dredging, which is conducted for the purpose of removing accumulated sediments from navigation channels, harbors, etc., *environmental* dredging is conducted for the purpose of removing contaminated sediment for remediation purposes (Zeller and Cushing, 2006). Environmental dredging activities strive to

remove sediments that have contamination at a level above a specified criterion, while minimizing the re-suspension and release of contaminants to the surrounding ecosystem (Zeller and Cushing, 1996). For the remainder of this document, "dredging" will mean environmental dredging.

Identifying and eliminating the source of contamination is of paramount importance before undertaking any remediation actions, to achieve long-term contamination mitigation goals: contaminated sediment management cannot be disassociated from that of soil and water, as these three environmental mediums are linked hydrodynamically (Apitz and White, 2003). Identifying and understanding unique site characteristics are critical in determining which sediment remediation alternative to employ (Förstner and Apitz, 2007), and no particular method is ideal or problem-free in all situations (Azcue *et al.,* 1998). Ultimately, sediment remediation analysis must acknowledge the limitations and uncertainties in each alternative, and achieve a balance between three primary goals:

i. minimizing contamination risks to human and environmental receptors (Apitz *et al.,* 2005);

ii. minimizing risks associated with the remediation actions, such as detrimental effects on habitats or human injury (Zeller and Cushing, 2006); and

iii. minimizing the cost of remediation (Apitz *et al.,* 2005).

2.10 The Presence of Chromium (VI) in Pore water: Assessing the Potential for Negative Impacts from Remediation Action

2.10.1 General

Of the four guidance rules of the COA framework (EC and OMoE, 2008), one asserts that the impacts of remediation actions should not outweigh the benefits. In the event that dredging is favored as the remediation strategy for the impacted area, silt

curtains placed around the area being dredged allow the predominant or complete containment of fine sediments that will inevitably become suspended during such operations. However, these silt curtains do not have the ability to contain *dissolved* deleterious substances, which can produce negative water quality effects beyond the impacted area. Due to the presence of high concentrations of chromium in sediments within the impacted area, it must be determined whether the particularly toxic form of chromium, Cr(VI), is present in sediment pore water. While this contaminant has not been found in surface waters (ESG, 2009a; 2009b), the necessity to determine the speciation of chromium in the pore water of the impacted site is crucial not only to increase the accuracy of assessing potential ecological impacts, but it is also highly relevant for potential dredging operations. If sediment pore water is high in Cr(VI), dredging operations can become complex as the Cr(VI) can potentially be released into the water column and/or mobilized after sediment disposal (Bufflap and Allen, 1995a).

2.10.2 Distinguishing Trivalent and Hexavalent Chromium

There are nine different oxidation states of chromium, ranging from -2 to +6 (CCME, 2006); however, under most surficial conditions, only the +3 and +6 oxidation states are stable (Fendorf and Zasoski, 1992). The toxicity and mobility of chromium is highly dependent on its oxidation state (Megharaj *et al.,* 2003; Graham *et al.,* 2009). Therefore, it is inadequate to consider only the total chromium in predicting sediment toxicity; instead, individual concentrations of both Cr(III) and Cr(VI) must be detected to determine contaminant bioavailability and toxicity (Chapman *et al.,* 1998). The detection and study of chromium species is of considerable interest, and is therefore a permanent and significant responsibility for analytical chemists in fields such as environmental science (Gómez and Callao, 2006; Barnowski *et al.,* 1997).

Cr(III) strongly adsorbs to surfaces such as sediments, forms salts that are relatively less soluble in water than salts of Cr(VI) (CCME, 2006), and is 100 times less toxic than Cr(VI) (Megharaj *et al.,* 2003). Cr(III) is an essential micronutrient in many higher organisms, and has for decades been recognized as required in the human body for glucose level regulation. More recently, Cr(III) has also been identified as potentially beneficial in the treatment of cardiovascular disease and as an antidepressant agent

(Pattar *et al.,* 2006). Conversely, most salts formed by Cr(VI) are soluble and highly mobile (CCME, 2006). Cr(VI) is highly toxic to all life (Megharaj *et al.,* 2003) due to these qualities, in concert with its high oxidizing potential and its ease of passage through biological membranes (CCME, 2006). Though the carcinogenicity of Cr(III) is still in contention, there is no doubt about the carcinogenic nature of Cr(VI) (Lau *et al.,* 2008). Cr(VI) is an irritant and a corrosive that can be taken-up by biota through inhalation, dermal contact, and ingestion (Fendorf and Zasoski, 1992). However, it is misleading to refer to Cr(III) as safer because it can be converted to Cr(VI) at any point that chemical conditions allow (Sirajuddin *et al.,* 2007), thus the hazard of Cr(III) is equivalent to that of Cr(VI) if oxidizing conditions can occur (Fendorf and Zasoski, 1992).

2.10.3 Pore water

Sediments commonly contain approximately 20 to 50 percent water, and the chemistry of this pore water can be dramatically different from waters above the sediment (Teasdale *et al.,* 1995). Determination of the actual dissolved fraction of a trace element that occurs in two oxidation states (*e.g.* Cr(III) and Cr(VI)) necessitates the identification of the concentrations of individual species (Dominik *et al.,* 2007). It is imperative that samples be collected meticulously, such that original chemical conditions are maintained and chemical species are not transformed (Teasdale *et al.,* 1995). Dissolved metals in pore water can be a primary bioavailable source to some benthic organisms (Serbst *et al.,* 2003), and may be the exclusive source for others (Vink, 2009). Despite the fact that aqueous-phase speciation can influence bioavailability, limited research has been conducted to determine metal speciation in pore waters (Fairbrother *et al.,* 2007).

2.10.4 Qualities of Tannery Effluents

Chromium is a metal that has been used extensively in the metallurgic, refractory, chemical, electroplating, and tanning industries (Apte *et al.,* 2005). Effluents originating from tanneries are noted for their high salinity, organic loading, and pH, as well their high concentrations of sulfide and chromium (Tunay *et al.,* 1999; Song *et al.,* 2000). Typically, the source of chromium used for tanning is a Cr(III) salt called basic

chromium sulphate (BCS) (Thorstensen, 1984), and wastewaters that originate from the soaking, liming, and tanning steps are responsible for less than 50 percent of the volume, but 90 percent of the pollution effects (Bajza and Vrcek, 2000). When these effluents are discharged into river systems, serious environmental ramifications can result (Mwinyihija *et al.,* 2006). Toxic chemical discharge from leather tanning establishments are the inevitable result of the manufacturing process and, over time, an excessive accumulation of these chemicals in the surrounding soil and water will have an adverse effect on vegetation and biota (Tariq *et al.,* 2006). Although the perception of the environmental consequences of chromium contamination has evolved in the tanning industry (United Nations Environment Programme, 1991) and modern wastewater treatment processes have improved the water-quality of effluents, older tanneries incorporated little or no treatments before discharge into water bodies (Walsh and O'Halloran, 1997). The fact that the tanning industry has a deleterious effect on the environment is now well-known (Cooman *et al.,* 2002) and has become a serious issue of worldwide discussion (Tariq *et al.,* 2006).

Dominik *et al.,* (2007) determined that Cr(III) originating from tannery effluent, in the absence of elevated current velocity, is quickly deposited in the sediments by two mechanisms: precipitation and adsorption to colloidal and particulate fractions. Poor storage and waste-disposal practices for materials and effluents can also be source of Cr(VI) to surface water and groundwater (Zazo *et al.,* 2008). Under reducing and mildly oxidizing conditions, Cr(VI) reduction to Cr(III) can occur in minutes to days (Magar *et al.,* 2007). Once Cr(VI) has been reduced, Cr(III) is stable in aquatic environments and oxidation to Cr(VI) is improbable, even when dissolved oxygen is present (Martello *et al.,* 2007), as Cr(VI) reductants are more abundant than Cr(III) oxidants in natural sediments (Martello *et al.,* 2007; Magar *et al.,* 2008). The two primary environmental electron donors to Cr(VI) are Fe(II) and sulfide species (S^{2-}, HS^-, and H_2S) (Palmer and Wittbrodt, 1991; Magar *et al.,* 2008; Zazo *et al.,* 2008). The reduction of Cr(VI) to Cr(III) is enhanced when discharged into wetland sediments due to the presence of Cr(VI)-reducing humic substances. Additionally, the presence of plants affect wetland geochemistry through subsurface to surface movement of pore water via evapotranspiration, as well as the presence of root exudates in pore water (Zazo *et al.,*

2008). The only environmental oxidants of Cr(III) at pH < 9 are hydrogen peroxide (H_2O_2) and manganese oxide (Mn oxides, MnO_2) (Magar *et al.,* 2007). Masscheleyn *et al.,* (1992) found that in wetland soils, reduction of Cr(VI) is highly favored over the oxidation of Cr(III), even when high concentrations of MnO_2 are present.

In many sediment systems, a region exists that releases H_2S if treated with acid, and the materials that produce this sulphide are termed acid-volatile sulfide (AVS) (Rickard and Morse, 2005). AVS can be used as a predictor of the toxicity of sediments for cationic metals such as Cu, Pb, and Zn, as when AVS is in greater concentration than the concentration of all metals extractable by AVS, no adverse biological effects are found (Berry *et al.,* 2004). Though not forming an insoluble sulfide like other AVS-extractable metals, Cr(VI) is not stable in anoxic sediments where AVS is formed. In such an environment, only Cr(III) will be present in sediments and little chromium will be found in pore water (Berry *et al.,* 2004).

The specifics regarding the environmental fate, transport, and speciation of chromium from tannery effluents in freshwater systems is still not well understood (Dominik *et al.,* 2007). Moreover, of the research that has been conducted on chromium speciation, relatively little is known about the speciation of chromium from tanneries in freshwater environments, including associated pore water (Dominik *et al.,* 2007). This represents a significant knowledge gap as many rivers and streams worldwide are polluted with chromium-contaminated effluents from tanneries.

2.11 Potential End-Destination Options for Dredged Sediments

If the impacted area of the Kingston Inner Harbour were dredged, an end-destination strategy must be developed for contaminated sediments. Preliminary leachate tests conducted on samples of impacted area sediment have determined that they may be disposed of in a non-hazardous waste landfill (MacMillan and Presley, 2010). However, before disposal, dredged sediments must be dewatered and two potential alternatives are explored in this thesis: the first option is to use mechanical grain size separation and dewatering (*mechanical processing*); the second option is to store the dredged sediments in a large open area to allow the natural processes of evaporation, evapotranspiration, and

soil infiltration to dewater the sediments (*natural dewatering*), and then transport the dried sediments to the landfill.

A dredging company has been identified as a potential supplier of mechanical sediment processing technology, having employed their Mobile Soil Washing Plants (MSWPs) internationally to process contaminated soils and sediments. The current location of the North American MSWP is Stuart, FL (Mann, 2009); however, a project using this MSWP will be undertaken and completed in Toronto prior to the commencement of the proposed remediation project in Kingston (Tejani, 2010). Therefore, if the MSWP was to be used in the Kingston project, it would be shipped from Toronto.

The MSWP is composed of a total of 45 portable units, each on skid-mounted and containerized equipment, and weighs a total of 500 tonnes (Mann, 2009; Boskalis Dolman, 2009). The portable units use a water-based volume reduction process involving grain size and density separation (Boskalis Dolman, 2009). The process used by the MSWP is based on a number of in-line process steps that can be considered separate plant modules (Boskalis Dolman, 2009). These process steps include screening and separation units, a polymer dosing unit, plant automation and control equipment, and "plug and play" belt filter processes (Boskalis Dolman, 2009). The MSWP process is based on the principle that contaminants adhere most to soils and sediments that have small grain sizes and are high in organic content (Boskalis Dolman, 2009). Grain size separation is achieved using hydrocyclones, and flocculation is initiated using polymers. At full production speed, the MSWP can process approximately 76 $m^3 \cdot hr^{-1}$ (Mann, 2009).

Mechanical sediment processing has the advantage of separating fine-grained sediments that are high in contamination from the sand fractions that have low contamination concentrations. This separation allows the low-contamination sand fractions to be reused, while the fine fractions are disposed of in a landfill or otherwise. Another attractive quality of this process is that the MSWP includes a mechanical dewatering process that makes the sediments that are destined for disposal much lighter, reducing the environmental impact of transportation to landfill. However, acquiring the MSWP for use on Kingston Inner Harbour sediments incurs environmental impacts associated with transporting the equipment to Kingston.

Natural dewatering includes transporting the dredged sediments to a dewatering location, where they are placed into specially constructed holding pits to dry for approximately two years. Upon completion of the drying phase, the sediments would then be transported to a landfill. A location for natural dewatering of sediments was constructed north of Kingston in 2004 for a previous sediment dredging project. The site is composed of holding pits, which are constructed by excavating soils and compacting the bottom and sides of the pit to reduce the possibility of water movement into the subsurface. The project for which this dewatering location was originally constructed required a total volume of 60,000 m^3 of holding space. As of April 2010, these sediments remain in that location, although the City of Kingston is currently developing a plan to dispose of them (MacLatchy, 2010). Unless another strategy is developed, this disposal will likely be in a municipal non-hazardous waste landfill as these sediments have met the requirements of applicable leachate tests (MacLatchy, 2010). Once removed, the dewatering location would likely need to be expanded to accommodate the Kingston Inner Harbour sediments. The natural dewatering option does not allow the separation of cleaner from more contaminated grain sizes, and will result in heavier impacts from transporting sediments from the dredging site to the dewatering location, as the sediments will not have undergone any weight reduction from water extraction. In addition, this option necessitates an extra handling step as dewatered sediments that are located at the dewatering location must be reloaded onto trucks for transport to the landfill.

2.12 Life Cycle Assessment for Sediment Remediation Projects

2.12.1 Sustainable Development in Remediation

As exemplified, for instance, by the energy use patterns of western nations, many people live in excess of what the natural world can sustainably provide. Sustainable development has been defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (World Commission on Environment and Development, 1987). The concept of sustainability necessitates that environmental and social factors not be excluded from economic factors in management and decision-making processes (Arevalo *et al.,* 2007). Remediation of contaminated sites is regarded as a sustainable practice because it permits the reuse of

natural spaces by human and natural receptors (Harbottle *et al.,* 2008). However, although remediation is directed towards minimizing risk to human and ecological receptors, remediation activities themselves produce environmental burdens that differ according to the method selected (Diamond *et al.,* 1999). These negative environmental impacts can include global warming, depletion of natural resources, and health effects to human and ecological receptors (Suèr *et al.,* 2004).

2.12.2 Life-cycle Assessment

Life cycle assessment (LCA) is "a compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle" (International Organization for Standardization (ISO), 2006b). First used in packaging and waste management studies in the late 1960s, its use subsequently spread to manufacturing and product development purposes (Baumann and Tillman, 2004). Only beginning very recently, LCA is now becoming an increasingly popular tool in support of environmental decision-making for remediation of contaminated sites (Lemming *et al.,* 2010). The framework, requirements, and guidelines for an LCA are published by ISO in the international standards ISO 14040 and ISO 14044 (ISO, 2006a; 2006b).

Product systems can be broken down into unit processes, which are the smallest elements for which input and output data are available (ISO, 2006a). Input and output flows of unit processes can generally be classified as belonging to either the *ecosphere*, which are inputs and outputs directly to and from nature, including resources inputted directly from nature such as logs and water, and emissions to air, water, and soil; and the *technosphere*, which are inputs and outputs of products and services, to and from other unit process. There are four phases of an LCA study, the relationship between which is illustrated in Figure 2.9:

i. Goal and scope definition: in stating the goal of the study, such items as the intended application of the study, the intended audience, and the reasons for carrying out the study are explicitly stated. In defining the scope, one indicates such items as the product system to be studied and its function, the functional unit, system boundaries, data requirements, and

assumptions and limitations of the study (ISO, 2006a). The functional unit is a quantified measure of the performance of a product system that can serve as a reference unit; system boundaries are criteria that designate which unit processes will be considered a part of the product system under study (ISO, 2006a). Properly defining the goal and scope of an LCA is crucial in establishing the context within which the comparison is being undertaken (Morais and Delerue-Matos, 2010) and it must fulfill the requirements of the decision to be supported. Depending on the intent of the LCA, the goal and scope definition can be very focused or very broad.

ii. Life cycle inventory analysis (LCI): the phase of the LCA in which all inputs, outputs, and potential environmental impacts throughout the life cycle of the product system are compiled and evaluated (ISO, 2006a).

iii. Life cycle impact assessment (LCIA): the phase of the LCA in which the magnitude and significance of the potential environmental impacts of the product system are recognized and evaluated (ISO, 2006a).

iv. Interpretation: the phase of the LCA in which the results of the LCI and/or LCIA are evaluated with respect to the goal and scope definition of the study, to reach conclusions and recommendations (ISO, 2006a).

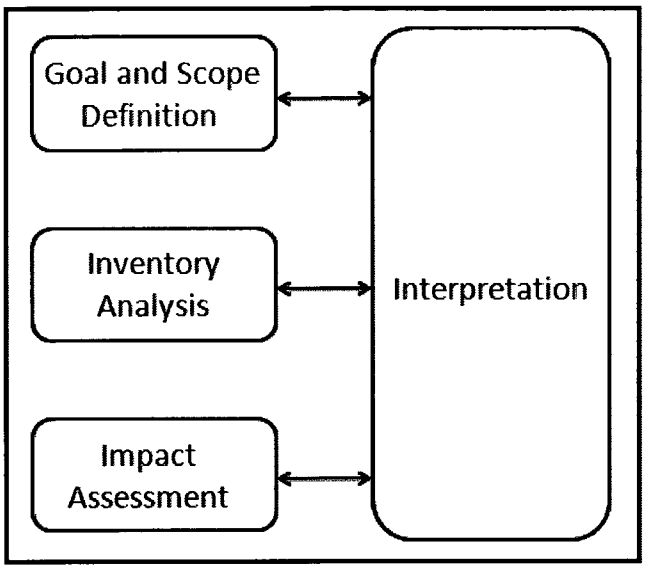

Figure 2.9: The Life Cycle Assessment Framework (ISO, 2006a)

Most LCA practitioners use off-the-shelf computer software for their data requirements and analysis (Cooper and Fava, 2006). As of 2006, 31 percent of practitioners use SimaPro software, the second most popular software package (Cooper and Fava, 2006). LCA software provides input and output data for individual unit processes, and the ecoinvent database is available within SimaPro. The ecoinvent database is an amalgamation of ecosphere and technosphere data generated by different Swiss institutes, and currently is comprised of over 4000 unit processes from industries such as agriculture, energy supply, transport, biofuels and biomaterials, bulk and speciality chemicals, construction materials, packaging materials, basic and precious metals, metals processing, ICT and electronics as well as waste treatment (Swiss Centre for Life Cycle Inventories, 2010). As with any LCA database, unit process data may not be available for every product or service that is a component of a given system process. In this situation, one may choose the next best material as a proxy, and this substitution should be noted in the LCA report.

Once ecosphere and technosphere inputs and outputs of a product system have been identified in the LCI, a number of impact assessment methods are available for the calculation of LCIA results. Different impact assessments methods are comprised of unique impact categories to which LCI results are assigned, with each individual method

having unique parameters for calculating these impacts (PRé Consultants, 2008a). Impact categories are classifications that represent environmental issues of concern to which LCIA results may be assigned (ISO, 2006a). To be compliant with ISO standards, an LCA report must include a characterization assessment, and may include normalization, grouping, and weighting (ISO, 2006b):

i. Characterization: is the process of converting LCI results to common units, through use of characterization factors, and the gathering of similar effects into impact categories (ISO, 2006b).

ii. Normalization: is the process of establishing the significance of impact category results, relative to reference information, for the purpose of determining the relative magnitude of each (ISO, 2006b). The impact category result is divided by a reference, called a normal value. The normal value for an impact category is most commonly established by determining the sum of effects for that impact category for a region, throughout the course of an entire year, and dividing by the number of inhabitants (PRé Consultants, 2008a). The purpose of normalization is to determine which impact categories contribute the greatest environmental effects (high-leverage categories), which can be considered negligible, and what the relative order of magnitude the impacts of a product system have in comparison to the normal value (PRé Consultants, 2008a).

iii. Grouping: is the amalgamation of impact categories into one or more sets, and may include ranking and sorting (ISO, 2006b). Ranking is the process of determining the priority of consideration to particular impact categories (*i.e.* establishing a hierarchy). Sorting is the process of ordering the presentation of impact categories on the basis of similarity in geographical scale (local, regional, global) or the nature of inputs and outputs. Grouping will not be used in this thesis.

iv. Weighting: is the process of multiplying the results of different impact categories by different numerical values (ISO, 2006b). These numerical values are establish through subjective value choices and are scientifically-based. Weighting will not be used in this thesis.

Damage assessment is a relatively recent step that has been introduced in LCA (PRé Consultants, 2008b). Using this methodology, impact categories (now called midpoint categories) are combined to form damage categories (PRé Consultants, 2008b). One such impact assessment method that utilizes the mid-point/damage category approach is IMPACT 2002+. This method considers 14 midpoint categories: human toxicity, respiratory effects (due to inorganics), ionizing radiation, ozone layer depletion, photochemical oxidation, aquatic ecotoxicity, terrestrial ecotoxicity, aquatic acidification, aquatic eutrophication, terrestrial acidification/nitrification, land occupation, global warming, non-renewable energy consumption, and mineral extraction. Human toxicity can be separated into two separate midpoint categories, namely carcinogenic and non-carcinogenic effects, giving IMPACT 2002+ fifteen midpoint categories (Humbert *et al.*, 2005). All midpoint categories are expressed in terms of units of a reference substance, and each of these midpoint categories are associated with one or more of the four damage categories: human health, ecosystem quality, climate change, and resources (Figure 2.10).

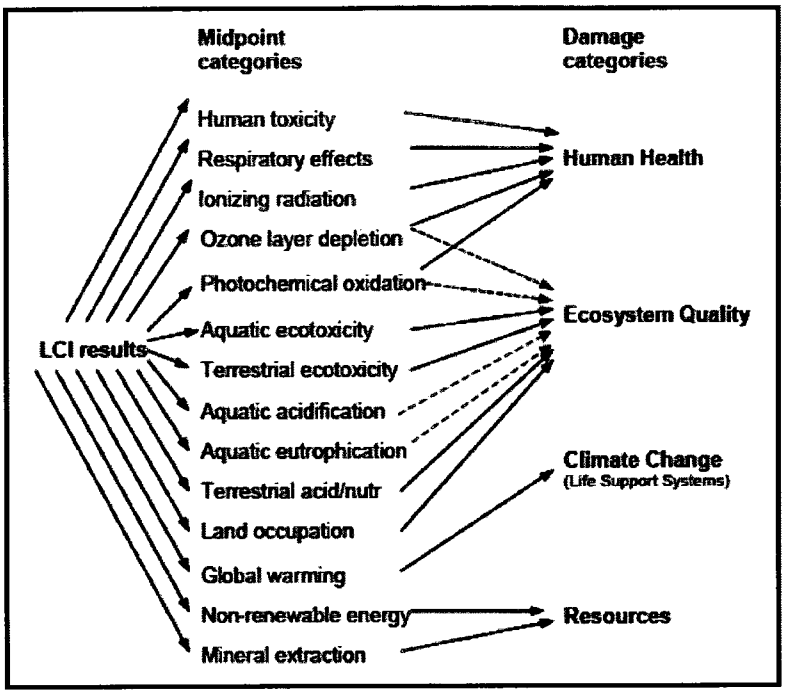

Figure 2.10: Overall Scheme of the IMPACT 2002+ Framework (PRé Consultants, 2008b; based on Jolliet *et al.*, 2003a). The framework links LCI results via the midpoint categories to damage categories.

At the level of characterization of midpoint categories, the units: kg-equivalent of reference substance *x* (kg_{eq} substance *x*), expresses the amount of a reference substance that equates to the impact of the contaminant under consideration (Humbert *et al.*, 2005). Once at the damage category level, the units of these four damage categories are:

i. Disability-adjusted life years (DALY): is the metric used to measure impacts on human health. DALYs express mortality and loss of health that can be disaggregated into disease and injury causes and risk factors, and are the sum of: (1) years of life that have been lost due to premature mortality (YLL) due to the a cause, and (2) years of healthy life lost resulting from disability (YLD) from the health condition (Lopez *et al.*, 2006). A single DALY can therefore be thought of as a year of healthy living lost due to the combination of mortality (compared to global standard of life expectancy) and/or disability resulting from a human health impact (Lopez *et al.*, 2006).

ii. Potentially disappeared fraction of species per m^2 per year ($PDF \cdot m^{-2} \cdot yr^{-1}$): is the metric for impacts on ecosystem quality. This unit is an expression of the fraction of species disappeared on 1 m^2 of terrestrial surface during one year. For example, a product system having an ecosystem quality score of 0.5 $PDF \cdot m^2 \cdot yr^{-1}$ is estimated to cause the loss of 50 percent of species on 1 m^2 of earth surface during one year.

iii. Equivalent kilograms of CO_2 (kg_{eq}-CO_2): is the common metric for impacts resulting in climate change. For example, considered on a time scale of 100 years, the contribution of 1 kg of CH_4 to global warming is 42 times higher than 1 kg of CO_2 contributes (PRé Consultants, 2008a). Therefore, the characterization factor for CH_4 is 42, and is 1 for CO_2.

iv. Megajoules of primary non-renewable energy (MJ): is the common metric for impacts resulting in resources damage, as this category is largely monopolized by non-renewable energy consumption (Humbert *et al.*, 2005).

At the level of assessing normalized damage, results are expressed in points (Pt), which are equal to person-years (pers-yrs). For each specific category, a point represents the average impact that a European inhabitant causes over the span of a year (Humbert *et al.*, 2005). This average impact of a typical European is calculated by integrating the total annual impacts from emissions and extractions across Europe, and then dividing by the European population (Humbert *et al.*, 2005). A tabular summary of midpoint and damage categories, reference substances, and units is given in Table 2.2; for a more detailed account of these and other components of IMPACT 2002+, the reader is encouraged to consult Humbert *et al.*, (2005), Jolliet *et al.*, (2003b), and visit (http://www.epfl.ch/impact) for the most current values of normalization factors. In this thesis, SimaPro 7 was used and the current normalization factors at the time of writing are also presented in Table 2.3.

Table 2.3: Midpoint Categories and Associated Reference Substances, Damage Categories and Associated Units, Normalization Factors, and Normalized Damage Units Used in IMPACT 2002+ (adapted from Humbert *et al.*[1] (2005) with information from PRé Consultants[2] (2008b))

Midpoint category[1]	Midpoint reference substance[1]	Damage category[1]	Damage unit[1]	Normalization factors[2]	Normalized damage unit[1]
Human toxicity (carcinogens and non-carcinogens	kg_{eq} chloroethylene into air	Human health	DALY	0.0071 DALY·pers^{-1}·yr^{-1}	Pt
Respiratory (inorganics)	kg_{eq} $PM_{2.5}$ into air	Human health			
Ionizing radiations	Equivalent-Becquerel (Bq_{eq}) carbon-14 into air	Human health			
Ozone layer depletion	kg_{eq} CFC-11 into air	Human health			
		Ecosystem quality	N/A	N/A	N/A
Aquatic ecotoxicity	kg_{eq} triethylene glycol into air	Ecosystem quality	PDF·m^2·yr	13,700 PDF·m^2·yr·pers^{-1}·yr^{-1}	Pt
Terrestrial ecotoxicity	kg_{eq} triethylene glycol into air	Ecosystem quality			
Terrestrial acidification/nitrification	kg_{eq} SO_2 into air	Ecosystem quality			
Aquatic acidification	kg_{eq} SO_2 into air	Ecosystem quality	N/A	N/A	N/A
Aquatic eutrophication	kg_{eq} PO_4^{3-} into water	Ecosystem quality	N/A	N/A	N/A
Land occupation	m^2_{eq} organic arable land per year	Ecosystem quality	PDF·m^2·yr	13,700 PDF·m^2·yr·pers^{-1}·yr^{-1}	Pt
Global warming	kg_{eq} CO_2 into air	Climate change	kg_{eq} CO_2 into air	9,950 kg_{eq} CO_2·pers^{-1}·yr^{-1}	Pt
Non-renewable energy	MJ of total primary non-renewable or kg_{eq} crude oil (860 kg·m^3)	Resources	MJ	152,000 MJ·pers^{-1}·yr^{-1}	Pt
Mineral extraction	MJ of total primary non-renewable or kg_{eq} crude oil (860 kg·m^3)	Resources			

2.13 Thesis Objectives

A human health risk assessment, sediment toxicity tests, and benthic community structure analysis have concluded that sediment contamination in the Kingston Inner Harbour is having adverse biological effects. This thesis includes three distinct studies that will inform potential future actions for the impacted area:

i. an ecological risk assessment, to evaluate the effect of the contaminated sediments on higher-trophic-level receptors;

ii. a remediation options and feasibility analysis, to assess which sediment remediation strategy is most appropriate for potential action on impacted area sediments, and to evaluate the influence of pore water constituents on this choice; and

iii. a life cycle assessment, comparing two potential remediation alternatives for the impacted area.

CHAPTER 3: ECOLOGICAL RISK ASSESSMENT

3.1 Methodology

This chapter describes a semi-quantitative ERA that has been performed in accordance with guidance literature from CCME (1996) and from the Aquatic Sites Working Group (ASWG) of the Federal Contaminated Sites Action Plan (FCSAP) (Chapman, 2010). Sediment, plant, and fish samples were collected and analyzed to determine the concentration of CoPCs within these environmental media, as well as to model the effect ingestion of these contaminated media would have on higher-trophic-level receptors. Because they are the most dominant and widespread contaminants within the Kingston Inner Harbour, the seven CoPCs to be evaluated for their risk to receptors in this ERA are As, Cr, Cu, Pb, MeHg, Zn, and PCBs (see Chapter 2 of this report). Although many ERAs will estimate fish contaminant concentrations based on sediment concentrations, this ERA uses fish-tissue analysis as it provides a more accurate estimate of risk to piscivorous wildlife. To establish a local baseline, sediment, plant, and fish samples were collected from upstream reference sites in the Kingston Inner Harbour that have not been affected by contamination. All data used in this ERA are contained within Appendix B, Tables B1 to B10.

This ERA assesses the potential risk to wildlife representatives of various receptor classes whose diet consists mostly or entirely of aquatic biota, including herbivorous mammals, piscivorous mammals, piscivorous birds, and non-piscivorous birds. For each receptor, an average daily dose (ADD) is estimated for each CoPC, a toxicological reference value (TRV) is identified from the literature, and a hazard quotient (HQ) is calculated. ADDs are determined by measuring the concentrations of CoPCs in sampled biota that the individual receptors are known to ingest, as well as considering additional receptor characteristics and exposure factors. TRVs, being unique to a receptor species or species class for each respective CoPC, are estimates of no-observed-adverse-effect-levels (NOAELs). A NOAEL represents the maximum dose at which no adverse biological effects are expected to occur in a receptor related to exposure to a specific chemical. The HQ is calculated by taking the quotient of each respective ADD and TRV pair. An HQ of less than 1.0 implies that risk is negligible and no remediation action is

required. An HQ close to a value of 1.0 can make judgment regarding risk uncertain, and will usually require more data will usually be required to establish the likelihood of risk (CCME, 1996). An HQ greater than 1.0 indicates that risk may be intermediate or high and that remediation action may be required: the greater the HQ, the greater the likelihood of risk being present at a contaminated site (CCME, 1996). Appendix E.1 contains a sample of all calculations that have been performed in this ERA.

3.2 Receptor Characterization

3.2.1 Receptor Characteristics

Selection of appropriate receptors is a crucial aspect of conducting an effective ERA, as the ERA should ideally provide insight into the health of the entire ecosystem being studied (Seston *et al.,* 2009). Valued ecosystem components (VECs) are environmental elements, such as resources or features, which have ecological significance, are important to human populations, and can act as a basis for assessing the impact of contamination (CCME, 1996). In particular, so-called "sentinel species" are those species that "can be used to identify potential health hazards to other animals or humans" (NRC, 1991). Among other characteristics, sentinel species should have high trophic status, a restricted home range, well-known biology, and be sensitive to pollutants (Basu *et al.,* 2007). Receptor characterization is the process of identifying VECs that are most likely to be affected by contamination present at the site (CCME, 1996).

Classes of VECs that have been selected for inclusion within this ERA include fish (brown bullhead, yellow perch, and northern pike), herbivorous mammals (muskrat), piscivorous mammals (mink), non-piscivorous birds (red-winged blackbird), and piscivorous birds (osprey, great blue heron). In recognition of their importance to the ecology of the impacted area, reptiles and amphibians were also included within the conceptual model; however, it is not possible to calculate HQs for these species as TRVs are currently not available in toxicology literature.

3.2.2 Brown Bullhead

The brown bullhead (*Ameiurus nebulosus*) is a nocturnal feeder known to inhabit warmer temperature waters that are slow moving, have abundant aquatic vegetation, and have sediments composed of mud or sand (Scott and Crossman, 1973; Sinnot and Ringler, 1987). Aside from its high population in the Kingston Inner Harbour, the brown bullhead is an ideal VEC for many reasons. First, its home range is very small. In habitats that are conducive to spawning, which includes shallow water, low flow, and natural shelter such as logs and vegetation (all of which are characteristic of the impacted area), a study along the Anacostia River, Washington, DC, found that the average annual linear home range was less than 1 km (Sakaris and Jesian, 2005). Second, brown bullheads are bottom-dwelling fish that feed on benthic invertebrates throughout their life. As such, they are a crucial link between the benthic community and piscivorous wildlife. Third, brown bullhead bury themselves in sediment, with this behavior occurring more frequently and for longer periods as water temperature drops (Loeb, 1964; cited in Cranshaw *et al.,* 1982). Loeb (1964; cited in Cranshaw *et al.,* 1982) found that when the temperature dropped below 8°C, fish would often remain buried for periods exceeding 24 hours. Based on the climate of southeastern Ontario, the brown bullhead will therefore spend a large portion of the year buried in sediment, and thus its health could potentially be greatly affected by the sediment quality within its habitat. The limited home range of the brown bullhead, along with its intimate relationship to the sediment through diet and cold weather dormancy, makes it a good indicator of biological effects of local contamination (Rafferty *et al.,* 2009; Logan, 2007). For the past quarter-century the brown bullhead has often been used as an indicator of environmental contamination, and it has regularly been referred to as a sentinel species (Iwanowicz *et al.,* 2009).

3.2.3 Yellow Perch

Yellow perch (*Perca flavescens*) are known to inhabit small to medium sized rivers as well as lakes and ponds (Page and Burr, 1991). These fish have long had importance to both commercial and recreational fishing, especially in the Great Lakes region (Scott and Crossman, 1973), and are found in abundance in the Kingston Inner Harbour. They have a preference for clear water near vegetation (Page and Burr, 1991;

Fish and Savitz, 1983), a quality characteristic of the impacted area, and are seldom found in open water (Fish and Savitz, 1983). Yellow perch are highly adaptable, can use a variety of habitats from warm to cooler temperatures, and are inactive at night and rest on the bottom (Scott and Crossman, 1973). Yellow perch remain active during the winter months and can be found under the ice in both shallow and deeper water (Scott and Crossman, 1973). The home range of yellow perch has been reported to be 0.54 to 2.20 ha (Fish and Savitz, 1983). The yellow perch has a high appetite, and although its foraging habits vary depending on its size and the season, its diet will consist mostly of immature insects, larger invertebrates, and other fish (Scott and Crossman, 1973). The yellow perch was chosen as a suitable VEC for this ERA because of its limited home range and benthic feeding habits, as well as its economic and recreational relevance.

3.2.4 Northern Pike

The top predator with large populations in the Kingston Inner Harbour (Malroz Engineering Inc., 2003), the northern pike (*Esox lucius*) lives in habitats characterized by is clear, vegetated lakes and small to medium rivers (Page and Burr, 1991). The northern pike is a carnivore that feeds predominantly on vertebrates, and generally behaves as an opportunist with no particular species primarily selected as prey (Scott and Crossman, 1973). Prey is approximately 90 percent fish, but will also include frogs, crayfish and even mice or ducklings (Scott and Crossman, 1973). Northern pike have been noted to lack a well-defined home range (Cook and Bergensen, 1988). Diana *et al.* (1977) noted that while linear movements varied from zero to 4,000 m per day, fish would sometimes move within confined areas as small as 0.5 km, and other times travel to distant locations. The northern pike was selected as a VEC because of its position as top predator in the aquatic food chain, as well as its relative importance as a sport fish.

3.2.5 Muskrat

Only two herbivorous mammals were identified at the impacted site: muskrat (*Ondatra zibethica*) and beaver (*Castor canadensis*) (Ecological Services, 2008). Between these two species, the muskrat has a greater suitability as a VEC because its home range is much smaller (making it more vulnerable to local conditions), it is the

most aquatic of the two mammals (USEPA, 1993), data regarding its feeding and living habits was more readily available than for the beaver, and they are typically held in a high ecological regard (Juhlin and Halbrook, 1997). Muskrats inhabit marshes, lakes, and streams and feed principally on aquatic plants (USEPA, 1993). In many aquatic ecosystems, muskrats are the dominant herbivore (Erb and Perry, 2003). Primarily foraging at night, muskrats show a preference for cattails and usually feed on the roots and basal portions, although they are also known to consume other parts of the plant (USEPA, 1993). In a study of an Ontario marsh, Proulx and Gilbert (1983) found that muskrats spent most of their time within 17 to 33 m of their den. They extended their home range as marsh water levels declined, and cattails were the most important food item.

3.2.6 Mink

Mink (*Mustela vison*) is a member of the weasel family and is found throughout North American forested regions, especially those that contain wetlands (Basu *et al.*, 2007). These mammals are active, solitary, opportunistic predators (Basu *et al.*, 2007). Primarily nocturnal hunters, mink are the most numerous and widespread carnivorous mammal in North America (USEPA, 1993). Fish often comprise a considerable fraction of the mink's diet (Hinck *et al.*, 2009), but they are also known to prey on aquatic invertebrates, as well as birds and mammals (USEPA, 1993). In a study of mink inhabiting a Michigan river, 85 percent of their year-round diet was found to be fish, while the remainder was composed mainly of crustaceans, amphibians, birds, and mammals (USEPA, 1993). Many organizations, including EC and the USEPA, consider mink a sentinel species because of its high susceptibility to many pollutants (Basu *et al.*, 2009). Research has shown that methylmercury (MeHg) and PCBs are especially toxic to mink, and that these contaminants act synergistically in this receptor (Wren *et al.*, 1987a; 1987b). Mink are regarded to be among the most sensitive mammals to PCBs (Bleavins *et al.*, 1981). Because of the proximity of the impacted site to urban development, mink populations may be unlikely in this area (Ecological Services, 2008). However, the extensive riparian areas throughout other areas of the Kingston Inner Harbour are likely home to mink; therefore, for conservatism mink are included as a VEC in this ERA.

Additionally, the particular sensitivity of this species to certain contaminants in the impacted area will generate conservatism in this ERA and therefore be protective of other piscivorous mammals.

3.2.7 Red-Winged Blackbird

The red-winged blackbird (*Agelaius phoeniceus*) is one of the most numerous and ubiquitous avian species in North America (Mosimann and James, 1979), and is the most abundant species in the marsh of the impacted area (Ecological Services, 2008). Red-winged blackbirds have frequently been studied by ornithologists not only because of their large populations, but because of their strongly expressed polygyny. Contrary to the behavior of most birds, which breed monogamously, male red-winged blackbirds can attract 15 or more mates per year to their exclusive territories (Beletsky, 1996). Roosts of red-winged blackbirds are usually found in wetland habitats, especially cattail marshes, as the combination of water and dense vegetation provides safety from predators (Beletsky, 1996). The main diet of these non-piscivorous birds, when in a non-agricultural area, is seeds and insects (McNicol *et al.,* 1982), both of which are found in the impacted area. Red-winged blackbirds have been chosen as a VEC because of their close association with the aquatic marsh environment, their representation of non-piscivorous birds, and their high recognizability and scientific importance.

3.2.8 Great Blue Heron

The great blue heron (*Ardea herodias*) is a colonial nester. They can be considered a sentinel species because of their predominantly piscivorous feeding habits and their placement at the top of the aquatic food chain (Baker and Sepúlveda, 2009). They are commonly found in wetland areas and have a preference for eating fish, though they will also consume other prey such as amphibians, reptiles, and insects (USEPA, 1993). When great blue herons are looking for fish they generally seek shallow areas where smaller fish are numerous (USEPA, 1993). Two studies on the composition of the diet of great blue herons in Michigan reported that 98 percent and 94 percent of the diet, respectively, was fish (USEPA, 1993). Great blue herons have been found to be poor predators of healthy fish yet good predators of unhealthy fish (Kushlan and Hancock,

2005), perhaps causing them to have a propensity to consume fish with higher levels of contamination. Great blue herons have many characteristics that make them an ideal VEC in this ERA: their high consumption of aquatic prey yields a high potential for exposure to contaminants, particularly for bioaccumulative contaminants (Seston *et al.,* 2009), data concerning their eating and behavior are readily available (USEPA, 1993), and they are widely recognized and appreciated by the public, who would have an interest in ensuring their preservation (Seston *et al.,* 2009; Kushlan and Hancock, 2005).

3.2.9 Osprey

A once-endangered species, the osprey (*Pandion haliaetus*) is highly recognized by the general public and has been the recipient of efforts to provide suitable nesting locations with anti-raccoon guards to boost its populations (EC, 2005). There is only one nesting pair of osprey known to inhabit the impacted area, and it currently lives on the south side of Belle Park, adjacent to the impacted site, on an artificial nesting platform (Kristensen, 2010). Ospreys are large birds of prey and are found close to water bodies. These birds feed almost exclusively on fish (more than 99 percent of their diet) and are adapted to hovering over water bodies before capturing fish with their talons (USEPA, 1993). In particular, osprey have a preference for hunting fish that inhabit shallow waters, are slow-moving, and eat benthic organisms (USEPA, 1993), such as the brown bullhead. In the Great Lakes basin ecosystem, osprey have been observed to consume a variety of fish, with an average of almost 35 percent brown bullhead, approximately 12 percent yellow perch, and approximately 5 percent northern pike (EC, 2005). Local availability will affect the actual proportions in an osprey's diet (EC, 2005). After catching a fish, the osprey will consume the entire fish except for the large bones. Because of their high fish consumption, osprey can be exposed to especially high levels of bioaccumulative contaminants (Linkov *et al.,* 2001). Of all toxins, the organochlorine compounds have had the most harmful effect on osprey populations (Poole, 1989). The osprey is a sentinel species and has been included as a VEC because of the need to help populations recover, their prominence and vulnerability at the top of the aquatic food chain, and their wide recognition by the public, who have an interest in seeing this species preserved. Although piscivorous birds are represented by both the osprey and great blue heron, redundancy at

the highest trophic level is favorable because of these species' vulnerability to aquatic contamination, particularly bioaccumulative contamination.

3.2.10 Reptiles

Numerous reptiles have been documented to inhabit the impacted site including the northern water snake (*Nerodia sipedon*), garter snake (*Thamnophis sirtalis*), painted turtle (*Chrysemys picta marginalis*), and snapping turtle (*Chelydra serpentina*) (Ecological Services, 2008). Also known to inhabit the impacted site is the map turtle (*Graptemys geographica*), a provincial species of concern, as well as the stinkpot turtle (*Sternotherus odoratus*), a provincially threatened species. These reptiles are all recognized as very important constituents of the impacted area ecosystem. Although reptile species are generally widespread in wildlife habitats, relatively few toxicological studies have been conducted on them (Salice *et al.,* 2009) and there presently exists no data to permit quantitatively including them in this ERA. However, the high level of contact that these reptiles have with the sediment, by burrowing in the summer and hibernating in the winter, may make these species susceptible to adverse biological impacts related to sediment toxicity.

3.2.11 Amphibians

Three species of amphibians are known to habitat the impacted area: the bullfrog (*Rana catesbeiana*), the green frog (*Rana clamitans*), and the leopard frog (*Rana pipiens*) (Ecological Services, 2008). None of these species are listed by OMoE as a provincial species of concern or as an endangered species. Similar to the reptiles, there is little toxicological information to generate TRVs and there exists no data from the impacted site on these species to allow them to be considered in the quantitative calculation of risk. Nevertheless, and again similar to the reptiles, because of the extensive contact these species have with the sediments, they may have a predisposition to adverse biological impacts related to sediment toxicity.

3.2.12 Conceptual Model

Subsequent to identifying VECs, it is necessary to develop a conceptual model to represent the ecosystem. Conceptual models can include such details as contaminated media, receptors, and pathways of exposure (CCME, 1996). The complexity of a conceptual model is influenced by the inherent complexity of the ecosystem being studied, as well as the availability of data to support the risk assessment. The conceptual model for this ERA, based on the receptors identified above, is found in Figure 3.1. The exposure pathways identified in the conceptual model for each of these receptors are not exhaustive, but reflect those that are dominant and are thus considered in this ERA. Numerous trophic levels are represented in the conceptual model, with sediment ingestion and food consumption being the main exposure pathways considered. Benthic invertebrates, though not sampled for this ERA, and aquatic plant life are considered the foundation of the aquatic food chain. Benthic invertebrates are consumed by bottom-feeding fish, which in turn are consumed by piscivorous predators. These piscivorous predators can be subdivided into three main groups: piscivorous fish, represented by the northern pike and larger yellow perch; piscivorous mammals, represented by the mink; and piscivorous birds, represented by the great blue heron and osprey. Both the muskrat and red-winged blackbird are modeled as being herbivorous; with the omnivorous amphibians and reptiles represented by the bullfrog and painted turtle.

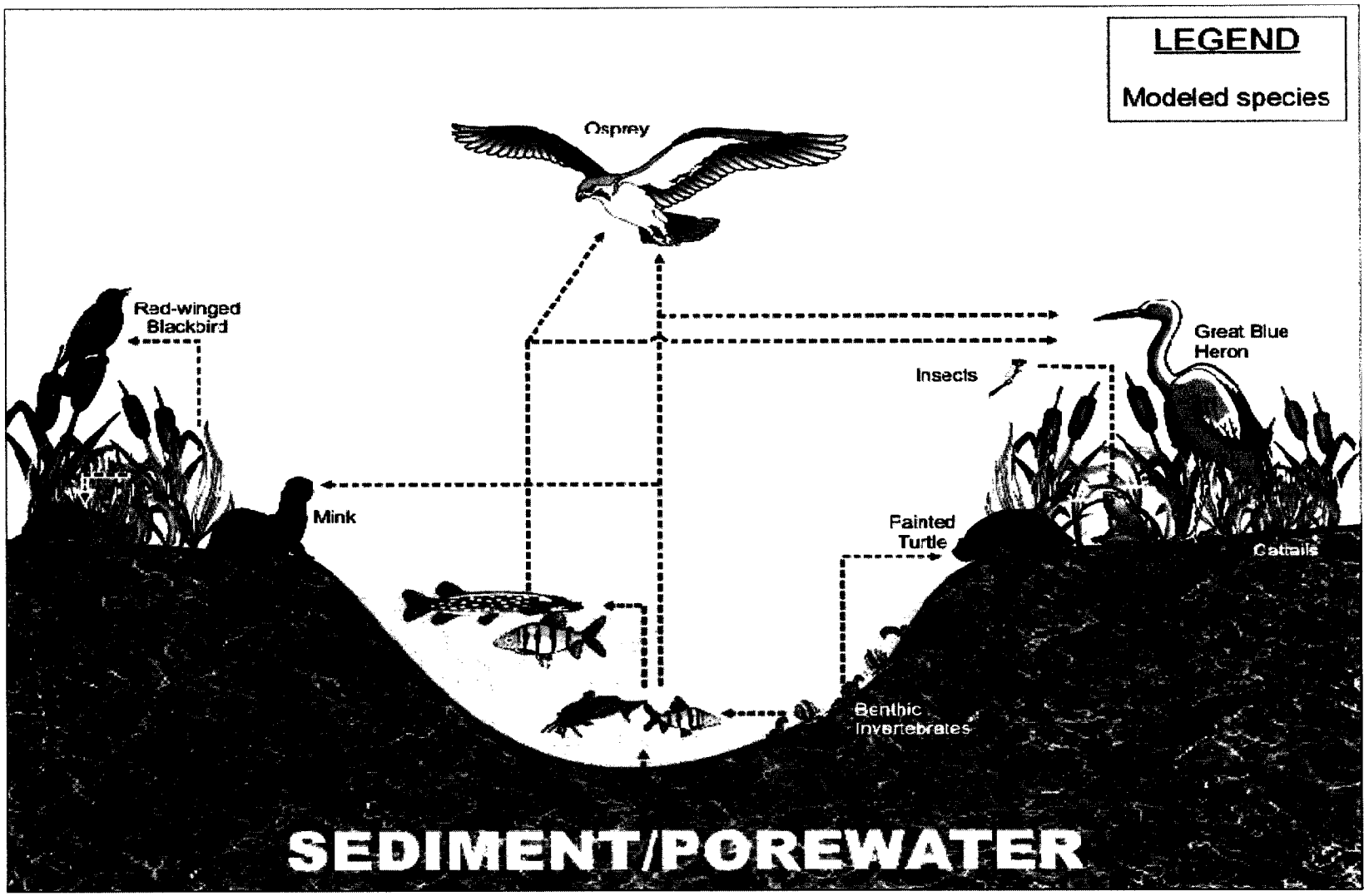

Figure 3.1: Conceptual Model of the Impacted Area of the Kingston Inner Harbour

3.2.13 Assessment and Measurement Endpoints

Assessment endpoints state the environmental objectives to be achieved and must be ecologically relevant, explicitly defined, and capable of being assessed (CCME, 1996). Assessment endpoints are seldom based on ecosystem-level endpoints as they are difficult to predict or define; instead, they are usually defined at the population level and sometimes at the community level (CCME, 1996).

Based on the VECs and conceptual model that have been adopted in this ERA, the following assessment endpoints have been selected for assessment: the survival, fecundity, and growth of (1) herbivorous mammals, (2) piscivorous mammals, (3) non-piscivorous birds, and (4) piscivorous birds.

Because they are generally not measureable in a practical or numerical sense, assessment endpoints must be expressed in terms of measurement endpoints. Measurement endpoints are quantifiable ecological characteristics associated with the assessment endpoint, and are usually expressed at the individual or population level (CCME, 1996). More than one measurement endpoint may be expressed for a single assessment endpoint (CCME, 1996).

The measurement endpoint for fish is to compare estimated whole-body CoPC concentrations with conservative fish tissue toxicity thresholds to assure protection of the most sensitive of the attributes of survival, fecundity, and growth.

The measurement endpoint for herbivorous mammals and non-piscivorous birds is to compare the estimated dietary intake of CoPCs of representative species (muskrat and red-winged blackbird, respectively) with conservative NOAEL values (through the calculation of HQs) to assure protection of the most sensitive of the attributes of survival, fecundity, and growth.

The measurement endpoints for piscivorous mammals and piscivorous birds are: (1) to compare estimated dietary intake of CoPCs of representative species (mink, and great blue heron osprey, respectively) with conservative NOAEL values (through the calculation of HQs) to assure protection of the most sensitive of the attributes of survival, fecundity, and growth; and (2) comparison of estimated whole-body fish concentrations for Hg and PCB with objectives stated in (i) the Canadian Tissue Residue Guidelines for

the Protection of Wildlife Consumers of Aquatic Biota, and (ii) the Great Lakes Water Quality Agreement, which seeks to protect piscivorous wildlife.

3.3 Exposure Assessment

3.3.1 Contaminants of Potential Concern

An exposure assessment must identify contaminants, exposure media, and exposure pathways, as well as major data gaps or uncertainties (CCME, 1996). As previously detailed, laboratory analysis of surface water has shown negligible levels of contamination present in these samples compared with the Canadian Water Quality Guidelines for the Protection Aquatic Life. Because these guidelines are very conservative, surface water can be effectively ruled out as an exposure pathway. However, in sediment samples taken within the impacted area, several contaminants are found to exceed the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Because they are the dominant and most widespread contaminants within the Kingston Inner Harbour, the seven CoPCs that will be evaluated for their risk to receptors in this ERA are As, Cr, Cu, Pb, MeHg, Zn, and PCBs (see Chapter 2). Chemical and toxicological background information for the CoPCs is presented in CCME (1999a) and ESG (2009b). With specific regard to Cr, this substance is assumed to be entirely in the Cr(III) state. Analysis of soils from the former Davis Tannery property (Conestoga-Rovers and Associates, 2006; Stokes, 1977), as well as sediments and pore water from within the impacted area of the Kingston Inner Harbour (see Chapter 4), has determined that negligible concentrations of Cr(VI) are present. All Hg is assumed to be in the more toxic MeHg form as the results of Bloom (1992) have found that more than 95 percent of the Hg present in fish is in the MeHg form. No (Me)Hg data was generated for food items other than fish.

3.3.2 Determining Average Daily Dose of CoPCs for Receptors

Average daily dose (ADD) is the average amount of a given chemical that a receptor is exposed to on a "mg per kg of body mass per day" basis. Normalized to the receptor's body mass, the ADD is then compared with a TRV of identical units to assess risk. Wildlife may be exposed to contaminants through various exposure pathways and a

number of exposure media, including biota tissue, soil, sediment, water, vapor, and gas. Exposure pathways include oral, dermal, and inhalation. However, ERAs regularly consider dermal and inhalation exposure pathways to be negligible compared with the oral exposure pathway (Suter, 2006).

Oral exposure to a contaminant in an aquatic ecosystem can occur through consumption of contaminated food, water, and/or sediment, as well as direct consumption of the contaminant itself (Suter, 2006). As previously mentioned in this chapter, testing of the water overlying the impacted sediments has shown that contaminant concentrations in the water are well below applicable guidelines. Additionally, no contaminant is present within the impacted area in a form that can be directly consumed by a receptor. Consequently, for this ERA, the sole pathway of exposure is oral, and the two environmental media that will be considered as potentially consumable are contaminated food and sediment.

To determine the ADD of a specific contaminant for a particular receptor, the exposure assessment requires consideration of a number of exposure factors. Equation 3.1 is the formula typically used in ecological risk assessments to determine a receptor's ADD:

$$ADD = \left\{\left[\sum_{i=1}^{n}(EPC_{fi} \times F_i)\right] + (EPC_{sed} \times F_{sed})\right\} \times \frac{FIR \times F_{site} \times ED}{BW} \qquad \mathbf{(3.1)}$$

where:

i. $\underline{EPC_{fi}}$: is the exposure point concentration of the receptor's *i*th dietary food item, defined as the average concentration of contaminant present in the food item and having units of ($mg \cdot kg^{-1}$ (wet weight (ww));

ii. $\underline{F_i}$: is the fraction of the receptor's diet that the *i*th food item comprises; this is a dimensionless quantity;

iii. EPC_{sed}: is the exposure point concentration of sediment within the impacted area, defined as the average concentration of contaminant present in the sediment and having units of ($mg \cdot kg^{-1}$ (ww));

iv. F_{sed}: is the fraction of the receptor's diet that sediment comprises; this is a dimensionless quantity;

v. FIR: is the food ingestion rate, defined as the total mass of dietary intake receptor consumes on a daily basis and having units of ($kg \cdot day^{-1}$ (ww)). In this aquatic ERA, the dietary intake of a receptor can be comprised of both food and incidental sediment intake;

vi. F_{site}: is the fraction of the receptor's diet that is harvested from the impacted site; this is a dimensionless quantity;

vii. ED: is the exposure duration, defined as the fraction of the year that the receptor feeds at that site. This quantity is important for migratory animals and is dimensionless; and

viii. BW: is the body weight of the receptor, and is expressed in (kg).

The EPC is an estimate of the average concentration of a CoPC for a particular environmental media within the impacted area. Because of the practical difficulty in estimating the actual average concentration for a site, the USEPA (1992b) recommends the use of the 95-percent upper confidence limit of the mean (UCL95) for sample sizes of a minimum of 10. However, when there are fewer than 10 data samples of environmental media, maximum figures can be used. The variables found in Equation 3.1 must be determined to calculate the ADD of each receptor in the conceptual model. These variables are discussed below for each individual receptor, and the data are summarized in Table 3.1.

3.3.3 Muskrat

There is little difference in the body weight of male and female muskrats. A study of muskrats in New York State resulted in the average winter weight being 1.480 kg for males and 1.350 kg for females (USEPA, 1993). In a study of muskrat in Idaho, the average adult spring weight was 0.909 kg for males and 0.837 for females. To make a year-round approximation, the average of these four weights (1.14 kg) will be used in this risk assessment. When feeding exclusively on green plants, muskrats are reported to consume an *annual average* of 34 percent (ww) of their body mass per day (USEPA, 1993). Because it is a preferred food item for the muskrat, and data are readily available, this ERA assumes that the entire diet of the muskrat is made up of cattail roots. Muskrats have a very limited home range, with USEPA (1993) not reporting a value greater than 0.17 ha for any of the studies included. Proulx and Gilbert (1983; cited in Erb and Perry, 2003) found that muskrats predominantly stayed within a 17 to 30 m range of their den. Because of this small home range, it is assumed that any muskrat inhabiting the impacted area will harvest all its food from this location. Muskrats do not hibernate and are still active in the winter; it is therefore assumed that they inhabit the impacted site throughout the year.

Although sediment ingestion is rarely considered for most receptors, this exposure pathway can be important for semi-aquatic wildlife, especially for non-bioaccumulative chemicals (Beyer *et al.,* 1997; Suter, 2006). No data could be found regarding the sediment ingestion rate of muskrats; however, owing to the nature of the submerged roots, and guided by results observed in Beyer *et al.* (1994) for mammals that feed on roots and tubers, it is conservatively estimated that muskrats ingest sediment at a rate that is 3 percent of their food intake rate.

3.3.4 Mink

The body weight of mink is highly variable (USEPA, 1993); however, Sample *et al.* (1996) suggest using 1.04 kg. In Appendix C the mink's FIR was calculated to be 0.23 $kg \cdot d^{-1}$ (ww); the sediment ingestion of the mink is negligible (Sample and Suter, 1999). Mink are active the entire year and their home ranges are highly variable, with riverine home ranges being linear and those in marsh habitats having a circular home range

(USEPA, 1993). The extent of a mink's home range is primarily based on availability of food, but additionally on the age and sex of the mink, as well as the season (USEPA, 1993). Based on radio-tracking techniques, Gerell (1970) found that the home range of adult males along a Swedish stream was 2.6 km (range of 1.8 to 5.0 km) and the average for adult females was 1.9 km (range of 1.0 to 2.8 km). As the length of shore line within the impacted area is a minimum of 2.0 km, and based on Gerell (1970), the average of the mean home ranges for male and female mink is 2.25 km. It is conservatively estimated that mink inhabiting this area will harvest 100 percent of their diet from the impacted area.

3.3.5 Red-Winged Blackbird

Sample *et al.* (1996) reported a toxicological study by Stickel *et al.* (1983) in which the average weight of red-winged blackbirds was 0.064 kg. Using the allometric equation from Nagy (1987), Sample *et al.* (1996) estimated the FIR of this species to be approximately 0.014 kg/d (ww). In the spring their diet consists mainly of seeds, with insects becoming most of their food intake in summer, with their diet in fall once again consisting mainly of seeds. In a study of red-winged blackbird diet in southwestern Ontario, McNicol *et al.* (1982) found that in non-agricultural areas, almost 40 percent of their diet was seeds, while the remainder consisted mainly of insects. As no data are available for insects, it is assumed that the entire diet of the red-winged blackbird consists of cattail seeds. Based on Weir (2008) and the study of McNicol *et al.* (1982), it is assumed that red-winged blackbirds inhabit the impacted area from the beginning of March until the end of October. Red-winged blackbirds spend most of the breeding season within their nesting territories, to defend breeding space (Orians, 1985). As a result, it has been conservatively assumed that 100 percent of their feeding takes place within the impacted area.

3.3.6 Great Blue Heron

Sample *et al.* (1996) lists the body weight of the great blue heron to be 2.4 kg. In Appendix C the great blue heron FIR was calculated to be 0.53 kg/day (ww). Sample and Suter (1999) consider the sediment ingestion rate of the great blue heron to be negligible.

The home range of the great blue heron is variable, and is greatly influenced by the local availability of food (USEPA, 1993). A study of great blue herons in Minnesota found that they travel 0 to 4.2 km, and average 1.8 km, between heronries and foraging areas (USEPA, 1993). The linear distance of the impacted area, from the marsh to the middle of the Great Cataraqui River, is a minimum of 0.80 km. Based on an average foraging radius of 1.8 km, as well as the abundance of small fish within the impacted area, it is assumed that approximately 50 percent of the great blue herons prey is captured inside the impacted area. Great blue herons are migratory birds, and based on figures in USEPA (1993) and Weir (2008), it is assumed that they inhabit the Kingston Inner Harbour from mid-March to mid-November.

3.3.7 Osprey

Sample *et al.* (1996) lists the average body weight of the osprey as 1.5 kg. In Appendix C, the FIR was calculated to be 0.39 kg/d (ww). Sample and Suter (1999) consider the sediment ingestion of osprey to be negligible. The home range of osprey is highly variable, and is primarily dependent on the abundance of local fish (USEPA, 1993). The foraging radius of osprey on a Minnesota lake was only 1.7 km, whereas a study in coastal Nova Scotia found the foraging radius to be 10 km (USEPA, 1993). However, because of the relatively shallow conditions in the impacted area which favors the capture of fish, as well as the high population of fish in the impacted area, a foraging radius of 1.7 km will be assumed. Again, as the minimum linear distance across the impacted area is approximately 0.80 km, it is assumed that the osprey obtains approximately 50 percent of its prey in the impacted area. Ospreys are migratory, and based on figures in USEPA (1993) and Weir (2008); it is assumed that they inhabit the Kingston Inner Harbour from the beginning of April to the end of October. As ospreys are known to have very high nest site fidelity, it is expected that the same nesting ospreys return to the nest each year (USEPA, 1993), and perhaps even successive generations (Kristensen, 2010).

Table 3.1: Receptor Characteristics and Exposure Factors Used in ERA

Receptor	Food Item	F_i[1]	F_{sed}[1]	FIR ($kg \cdot day^{-1}$)	F_{site}[1]	ED[1]	BW (kg)
Muskrat	Cattail root	0.97	0.030	0.39	1.0	1.00	1.14
Mink	Fish	1.0	0	0.23	1.0	1.00	1.04
Red-winged blackbird	Cattail Inflorescence	1.0	0	0.014	1.0	0.67	0.064
Great blue heron	Fish	1.0	0	0.53	0.50	0.67	2.40
Osprey	Fish	1.0	0	0.39	0.50	0.59	1.50

[1] Value is dimensionless

3.3.8 Exposure Point Concentrations for Cattail Root Consumption

The muskrat diet is modeled on cattail root consumption with incidental sediment ingestion. Cattails were sampled both within the marsh and on the south shore of Belle Park. To determine the most conservative estimate of risk to the muskrat, the EPC_f and EPC_{sed} for each respective CoPC were taken from the location with the highest concentration. Five cattail samples were obtained from the marsh and their roots (Table B1) were analyzed for all CoPCs except Hg and PCBs. In addition, sediment samples were taken at all five cattail locations (Table B2). From the south shore of Belle Island, two cattails were obtained and their roots analyzed for metals and PCBs (Table B3). Sediment samples were also collected at these locations (Table B4). To convert the cattail root dry-weight laboratory concentrations into wet-weight data, a conservative estimate (70 percent) of the percent moisture in the cattail roots was made. This estimate was based on the results of Vetayasuporn (2007), who reported that cattail samples had 74.9 percent moisture content. Also analyzed on a dry-weight basis, percent moisture data were not available for the sediment samples.

Tinney (2006) and Asquini *et al.* (2007) found that sediments within the Kingston Inner Harbour were generally about 90 percent water. To convert the sediment dry-weight laboratory concentrations to a wet-weight concentration, an assumption of 80 percent moisture was assumed. In instances where dry-weight sample laboratory results were under the detection limit, for conservatism the full detection limit was assumed when converting this dry-weight concentration to a wet-weight concentration. The

limited size of the data set for both cattail root and sediment samples taken from both the marsh and the south shore of Belle Park did not permit calculation of a reliable UCL95; instead, maximum figures are used for all EPC_f and EPC_{sed}. The data used for cattail root and sediment concentrations are summarized in Table 3.2; note that CoPC concentrations are in ppm except for PCB concentrations, which are quoted in ppb. Hg data were not available for these samples.

Table 3.2: EPC Values for Sediment and Cattail Roots within the Impacted Area

Value	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	Hg (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)	PCB (ppb, ww)
EPC_f	1.2	55	2.7	N/A[1]	4.4	24	12
EPC_{sed}	2.5	8100	21	N/A[1]	85	86	37

[1] Not available

3.3.9 Exposure Point Concentrations for Cattail Seed Consumption

The red-winged blackbird diet is modeled based on a cattail seed diet, which is based on CoPC concentrations in the cattail inflorescence. Because it has been assumed that all foraging by this receptor is conducted within the marsh, CoPC concentrations were obtained from the inflorescence of the five marsh cattails described in the previous paragraph (Table B5). Again, as the percent moisture content was not analytically determined for the cattail samples, based on the value Vetayasuporn (2007) reported for percent moisture in cattails, a conservative moisture content of the cattail roots is assumed to be 70 percent. In instances in which dry-weight sample laboratory results were under the detection limit, the full detection limit was assumed when converting this dry-weight concentration to a wet-weight concentration. The CoPC concentrations that were used for cattail seeds are summarized in Table 3.3. Hg and PCB data was not available for these samples.

Table 3.3: EPC Values for Cattail Seed Consumption within the Impacted Area

Value	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	Hg (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)	PCB (ppb, ww)
EPC_f	0.30	0.60	2.0	N/A[1]	0.60	6.3	N/A*

[1] Not available

3.3.10 Exposure Point Concentrations for Fish Consumption

In autumn of 2009, brown bullhead, yellow perch, and northern pike were collected from the impacted site and a reference site (located approximately 2 km upriver, adjacent to the Great Cataraqui Marsh). These were subsequently analyzed for CoPC concentrations (not including MeHg). Detailed analytical results for the fish are presented in Tables B6-B8.

For brown bullhead, whole-fish samples were analyzed while whole-body-minus-one-fillet samples were analyzed for yellow perch and northern pike. In determining metal EPC_f's for piscivorous wildlife, only brown bullhead and yellow perch samples were taken into consideration as the northern pike is rarely consumed by either great blue herons (USEPA, 1993) or ospreys (USEPA, 1993; EC, 2005). This is especially true of the northern pike samples obtained in fall 2009, as most exceeded the maximum size that is typically consumed by the great blue heron and the osprey. Although incomplete whole-body samples were analyzed for yellow perch (or northern pike), this creates conservatism in the data (*i.e.* overestimation of non-bioaccumulative metal concentrations including As, Cr, Cu, Pb, and Zn) because these CoPCs generally do not accumulate in the muscle tissue of the missing fillet. The UCL95 for each of these CoPCs was calculated and these results are presented in Table 3.4. In instances where dry-weight sample laboratory results were under the detection limit, the full detection limit was assumed when converting this dry-weight concentration to a wet-weight concentration. For these samples, the percent moisture values for each individual fish were determined by laboratory analysis.

Historical data for the impacted site and a reference site (located above Kingston Mills, in Colonel By Lake) were obtained from Scheider (2009) for MeHg and PCB concentrations, and are presented in Tables B9-B10. Impacted site data for brown

bullhead, yellow perch, and northern pike were available from this data set. However, from the reference site, only yellow perch samples were in sufficient number for comparison, with only two brown bullheads and no northern pike reported for this location. Additionally, all data from Scheider (2009) were analyzed as fillet samples. To convert this data to whole-body concentrations, relations must be obtained from the literature.

The method used for converting fillet concentrations to whole-body concentrations for mercury was performed according to the formula determined by Peterson *et al.* (2005). To generate the whole-body concentrations for PCBs, USEPA (2006) data analysis for Lake Michigan samples suggests that yellow perch fillet concentrations should be multiplied by 5.5 to convert to whole-body PCB concentrations. The brown bullhead data from Table B8 (that were already whole-body concentrations) were used for PCB concentrations as these values were available for this species in this data set, and USEPA (2006) did not have a conversion factor for brown bullhead. As the sample sizes for the individual data sets were large enough, the UCL95 of the mean was calculated for MeHg and PCBs using ProUCL 4.00.04, and the results are also included in Table 3.4.

Table 3.4: EPC Values for Fish Consumption within the Impacted Area. Values derived from collected and historical data.

CoPC	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	MeHg (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)	Total PCB (ppm, ww)
EPC_f	0.30	0.86	1.1	0.044	0.47	26	0.65

3.3.11 Calculation of Receptor Average Daily Doses

Using Equation 1.1, the data presented in Tables 3.1 to 3.4 were used to calculate the receptor ADD for each CoPC. These ADDs are presented in Table 3.5.

Table 3.5: Calculated ADDs for ERA Receptors. All units in ($mg \cdot kg^{-1} \cdot day^{-1}$).

Receptor	As	Cr(III)	Cu	MeHg	Pb	Zn	Total PCB
Muskrat	0.43	100	1.1	N/A	2.3	8.8	0.0042
Mink	0.065	0.19	0.24	0.0096	0.10	5.6	0.14
Red-winged blackbird	0.044	0.088	0.29	N/A[1]	0.088	0.93	N/A[1]
Great blue heron	0.022	0.064	0.081	0.0033	0.035	1.9	0.050
Osprey	0.023	0.064	0.082	0.0033	0.035	1.9	0.050

[1] Not available

3.4 Hazard Assessment

3.4.1 Identification of Receptor Toxicological Reference Values

To determine if a receptor's ADD for a particular CoPC might result in risk, it is compared with a TRV. The TRVs that will be used in this ERA are found in Table 3.6. The TRVs used for As, Cr(III), Cu, Pb, and Zn have been taken from those derived in the USEPA's Eco-SSL program. In producing each respective TRV, the USEPA used the following general four-step process: (1) it conducted an extensive literature search of all available toxicological data on that CoPC, (2) completed a review of the literature and extracted applicable data, (3) evaluated and scored data, and (4) derived the TRV (USEPA, 2003). For CoPCs in which there was no derived Eco-SSL TRV *(i.e.* Hg and PCBs), data were selected from the literature. Note that the TRV for PCBs is based on Aroclor 1254, the more toxic of the two PCB mixtures (also Aroclor 1260) that dominate the impacted area, and will therefore add conservatism to the associated HQ.

Toxicological research is usually conducted on very few species, such as mice, rats, chickens, and quail (Knopper *et al.,* 2009). Allometric scaling is utilized when applying toxicological data from one species to another, as it has been observed that, between species, a relationship exists between metabolic rate (reflected in the TRV) and body mass (Knopper *et al.,* 2009). Applicable to both mammalian and avian species, this relationship (Equation 3.2) can be used to estimate a receptor's TRV for a given chemical based on a test species' TRV (NOAEL) that has been determined in toxicological research (Sample *et al.,* 1996; Knopper *et al.,* 2009):

$$TRV_{receptor\ species} = TRV_{test\ species}\left(\frac{BW_{test\ species}}{BW_{receptor\ species}}\right)^{1/4} \quad (3.2)$$

The form of Equation 3.2 suggests that larger animals will have smaller TRVs than smaller animals. As an amalgamation of many different studies on many different types of receptors, the Eco-SSL TRVs (*i.e.* used for As, Cr(III), Cu, Pb, and Zn) are inappropriate for body mass scaling. However, the individual species toxicological data upon which the MeHg and PCB TRVs are based makes these values appropriate for body mass scaling.

Table 3.6: TRVs for Receptors Modeled in ERA. All units in ($mg \cdot kg^{-1} \cdot day^{-1}$).

Receptor	As	Cr(III)	Cu	MeHg	Pb	Zn	Total PCB
Muskrat	1.04[a]	2.40[b]	5.60[c]	--	4.70[f]	75.4[g]	0.051[(based on h)]
Mink	1.04[a]	2.40[b]	5.60[c]	0.015[d]	4.70[f]	75.4[g]	0.053[h]
Red-winged blackbird	2.24[a]	2.66[b]	4.05[c]	--	1.63[f]	66.1[g]	0.358[i]
Great blue heron	2.24[a]	2.66[b]	4.05[c]	0.0051[e]	1.63[f]	66.1[g]	0.145[i]
Osprey	2.24[a]	2.66[b]	4.05[c]	0.0058[e]	1.63[f]	66.1[g]	0.163[i]

[a] USEPA (2005a)
[b] USEPA (2005b)
[c] USEPA (2005c)
[d] Taken from Sample *et al.* (1996) and based on Wobeser *et al.* (1976)
[e] Values derived using Equation 2 and mallard duck weight of 1.0 kg, using NOAEL from Sample *et al.* (1996) and based on Heinz (1979)
[f] USEPA (2005d)
[g] USEPA, (2005e)
[h] Brunström *et al.* (2001)
[i] Values derived using Equation 2 and pheasant weight of 1.0 kg, using NOAEL from Sample *et al.* (1996) and based on Dahlgren *et al.* (1972)

3.4.2 Toxicity Thresholds for Whole-Body Fish Tissue

Toxicity thresholds for fish, whole-body concentrations at which CoPCs are likely to become hazardous to fish populations, were obtained from the literature. Table 3.7 contains fish toxicity thresholds for non-bioaccumulative CoPCs (Cr figure is based on a wildlife toxicity threshold), and Table 3.8 contains toxicity thresholds for bioaccumulative CoPCs.

Table 3.7: Toxicity Thresholds for Whole-body Fish Tissue for Metals[1]

CoPC	Toxicity threshold ($mg \cdot kg^{-1}$ ww)	Reference
As	2.0	McGeachy and Dixon (1992)
Cr(total)	N/L[2]	---
Cu	11.1 – 42.0	Stouthart *et al.* (1996)
Pb	0.4 – 8.8	Holcombe *et al.* (1976)
Zn	40 - 60	Spehar (1976)

[1] Taken from Hinck *et al.* (2009)
[2] Not located. Hinck *et al.* (2009) did not indicate a Cr fish toxicity threshold. A subsequent literature search was also not successful.

Table 3.8: Toxicity Thresholds for Whole-body Fish Tissue for MeHg and PCBs

CoPC	Toxicity threshold ($mg \cdot kg^{-1}$ ww)	Reference
MeHg	0.21	Beckvar *et al.* (2005)[1]
Total PCBs	4.2	Hansen *et al.* (1974)

[1] Taken from ENVIRON (2007)

3.4.3 Canadian Tissue Residue Guidelines for the Protection of Wildlife Consumers of Aquatic Biota

To protect wildlife whose primary pathway of exposure to harmful chemicals is via aquatic prey items, the Canadian Tissue Residue Guidelines (CTRGs) for the Protection of Wildlife Consumers of Aquatic Biota were introduced to address CoPCs that tend to biomagnify in the aquatic food chain (CCME, 1999b; see Chapter 1 of this report). The guidelines were derived using a similar risk assessment approach to that outlined in the above sections. However, because the guidelines are intended for application across a wide variety of aquatic environments and species, large uncertainty factors were incorporated into the risk assessment equations (CCME, 1999c). This means that the tissue residue guidelines are highly conservative when compared with a species and site-specific ecological risk assessment.

The guideline for MeHg is 33.0 ppb (ww) for all receptors (CCME, 2000). Application of the CRTGs for PCBs is more complex, and the reader is referred to CCME (2001) for a background on PCBs and Aroclors. As every mixture has unique

toxicological properties, each Aroclor is assigned a toxic equivalency factor (TEF) "based on their ability to induce a response in the cytochrome enzyme system relative to the most potent inducer, 2,3,7,8-TCCD" (CCME, 2001). For a given sample, individual Aroclor concentrations in whole-fish samples are multiplied by their associated TEF, and the results for all Aroclors in the sample are summed to give a value expressed in toxic equivalency units (TEQs). These sums are then compared against guideline values, which are 0.79 ng TEQ·kg^{-1} (ww) for mammalian receptors and 2.4 ng TEQ·kg^{-1} (ww) for avian receptors (CCME, 2001). The mammalian and avian TEFs for the three Aroclors known to be present in the Kingston Inner Harbour are presented in Table 3.9.

Table 3.9: TEFs for Aroclors Present within the Impacted Area[1]

Mixture	Mammalian TEFs (ng TEQ·mg^{-1})	Avian TEFs (ng TEQ·mg^{-1})
Aroclor 1242	5.1	234.6
Aroclor 1254	30.1	44.5
Aroclor 1260	11.3	25.5

[1] CCME (2001)

3.4.4 Considerations from the Great Lakes Water Quality Agreement (1978)

As detailed in Chapter 2, the GLWQA seeks to restore and protect the chemical, physical, and biological integrity of the Great Lakes Basin Ecosystem, and includes a number of targets and guidelines to achieve these objectives (EC, 2009). Under the GLWQA, both nations have agreed to specific objectives for the Great Lakes System. Pursuant to the specific objectives, and created for the protection of birds and animals that consume fish, the total concentration in fish tissues (whole-fish, ww) should not exceed 0.1 ppm for PCBs, and should not exceed 0.5 ppm for mercury (IJC, 1987). IJC documents specifically detailing the methods by which these values were derived could not be located.

In addition to identifying criteria for certain contaminants in fish, another agreement contained within IJC (1987) was to identify hot spots or areas of concern (AOCs) across the Great Lakes, which can include rivers, harbors, and connecting channels (Hartig and Thomas, 1988). Specifically, IJC (1987) defined AOCs as

"geographic areas that fail to meet the general or specific objectives of the agreement where such failure has caused or is likely to cause impairment of beneficial use or the area's ability to support aquatic life" (IJC, 1987). Under the agreement, the IJC lists 14 discrete impairments of beneficial use, including fish tumors and other deformities. While the Kingston Inner Harbour is not formally recognized as an AOC by the IJC, it does exhibit characteristics that have qualified other areas within the Great Lakes as such.

3.5 Ecological Risk Characterization

3.5.1 Calculation of Hazard Quotients

Based on the exposure scenarios generated for this ERA, Table 3.10 contains the calculated HQs of each CoPC for each respective receptor. There is negligible risk to all receptors due to As, Cu, Pb, and Zn. For the muskrat, risk is negligible due to PCBs (MeHg was not assessed); however, risk is high due to Cr(III) (HQ = 42) in ingested sediment and cattails. Because of the high Cr(III) concentrations found in the sediments of the impacted area, sediment ingestion for the muskrat appears to be a highly significant contributor to risk for this receptor. For Cr(III), the muskrat's HQ = 42, with food ingestion contributing only 7.6 to this value while sediment ingestion contributes 35. The muskrat is the only receptor that was assessed to have non-negligible risk due to Cr(III).

Table 3.10: Calculated HQs for ERA Receptors. All values are dimensionless.

Receptor	As	Cr(III)	Cu	MeHg	Pb	Zn	Total PCB
Muskrat	0.42	**42**	0.20	N/A	0.50	0.12	0.082
Mink	0.062	0.077	0.042	0.64	0.021	0.074	**2.6**
Red-winged blackbird	0.020	0.033	0.072	N/A	0.054	0.014	N/A
Great blue heron	0.010	0.024	0.020	0.65	0.021	0.029	0.33
Osprey	0.010	0.024	0.020	0.57	0.021	0.029	0.30

The red-winged blackbird has negligible risk from all CoPCs. The mink is at negligible risk due to MeHg; however, the mink HQ for PCBs is 2.6, indicating that risk

is intermediate due to this CoPC. For the great blue heron and the osprey, HQs for MeHg and PCBs are less than 0.70 in all cases. However, it is evident from the magnitude of the HQs for the great blue heron and the osprey that the assumption regarding the amount of their prey obtained from the impacted site, denoted in Equation 1.1 by F_{site}, can have a significant effect on the results of the ERA. The HQs in Table 3.10 were calculated for the great blue heron and the osprey assuming $F_{site} = 0.50$ (*i.e.* half their prey is obtained in the impacted area). Sensitivity of the results to this assumption is explored in Table 3.11, which shows the calculation of HQs for MeHg and PCB assuming $F_{site}=1.0$.

Table 3.11: HQs for MeHg and PCBs for Selected Receptors Assuming $F_{site} = 1.0$.
All values are dimensionless.

Receptor	MeHg	Total PCB
Great blue heron	1.3	0.67
Osprey	1.2	0.60

The results presented in Table 3.11 indicate that for the great blue heron and the osprey, when $F_{site} = 1.0$ is assumed, HQs greater than 1.0 for MeHg result, all other factors remaining constant, resulting in intermediate risk to this CoPC.

3.5.2 Comparison of Estimated Whole-Body Fish Tissue Concentrations to Fish Toxicity Thresholds

In making comparisons of fish tissue residue concentrations to the fish toxicity thresholds presented in Table 3.7 and Table 3.8, all fish species (including northern pike) and all locations for which data was available (including reference areas) were screened. When a value range for fish toxicity thresholds was present for the CoPCs in Table 7 (*i.e.* Cu and Pb), the minimum value was assumed. As displayed in Table 3.7, no comparison for Cr could be made as no fish toxicity threshold could be found in the literature.

When compared with the fish sample data in Table B7 for As, Cu, Pb, and Zn, almost all of these samples are noted to be far below the fish toxicity thresholds. The only sample that exceeded one of these thresholds was a single impacted site brown bullhead for Pb. Except in the case of Cr, there was no discernable difference between the

concentrations of these CoPCs in impacted site fish samples and those in reference site samples.

Comparison of the fish tissue concentrations of MeHg, as presented in Table B9 and B10, against the associated toxicity threshold in Table 3.8, revealed that the MeHg concentrations in most of these samples are for below 50 percent of the toxicity threshold. While the highest concentration among brown bullhead and yellow perch was 0.10 ppm, two impacted site northern pike samples (0.24 ppm and 0.29 ppm) exceeded the MeHg toxicity threshold, though these were both notably large and therefore much older fish. For MeHg, there was no discernable difference between concentrations found in impacted site brown bullhead and yellow perch compared with reference site samples. No data were available for northern pike at the reference site.

Comparison of the fish tissue concentrations of PCBs, as presented in Table B9, with the associated toxicity threshold in Table 3.8, revealed that no species sampled at any location exceeded the toxicity threshold. However, because the reference site tissue concentrations for PCBs presented in B10 were all below the detection limit, it is noted that the PCB tissue residue concentrations in the impacted site fish were much greater than at the reference site.

3.5.3 Comparison of Fish Tissue Concentrations to CRTGs

When concentrations of MeHg in fish samples in Table B9 are compared with the CTRG for MeHg, it is found that only 1 of 21 (5.0 percent) of brown bullhead exceed the 0.033 ppm guideline; however, 12 of 13 (92 percent) yellow perch and 15 of 15 (100 percent) northern pike are above the guideline. Looking specifically at yellow perch, it is acknowledged that 12 of 12 (100 percent) of the fish from the reference site at Colonel By Lake are also above the guideline. However, the MeHg UCL95 for Colonel By Lake site is 0.060, while the UCL95 for the impacted site is 0.069. The impacted site UCL95 is 15 percent above the reference site UCL95.

With regard to PCBs, calculation of the TEQ requires knowledge of the concentrations of specific Aroclor mixtures. The PCB data used in this ERA when modeling piscivorous wildlife were the impacted site brown bullhead data in Table B8 and the yellow perch data from Table B9. The brown bullhead PCB data in Table B8

contain concentrations of the specific Aroclors found at the site. However, the yellow perch data in Table B9 does not contain Aroclor concentrations; instead the yellow perch PCB concentrations are expressed only in terms of total PCBs.

The Aroclor concentrations for brown bullhead in Table B8 reveal that Aroclor 1254 and Aroclor 1260 are the most dominant mixtures, with all concentrations of Aroclor 1242 below the detection limit. To assess the sensitivity of the TEQ to an assumed concentration of Aroclor 1242, TEQs were first generated for impacted site samples assuming the concentration of Aroclor 1242 was the full detection limit, and then assuming the concentration of Aroclor 1242 was zero. The results for both methods are presented in Table B8. Even assuming the concentration of Aroclor 1242 was zero for the five impacted site brown bullhead samples in Table B8, the average TEQs of both mammalian (20 ng TEQ·kg^{-1} ww) and avian (43 ng TEQ·kg^{-1} ww) receptors exceeded their associated guideline by 26 and 18 times, respectively. Any additional Aroclor 1242 in these samples would further increase the TEQ further above the tissue residue guidelines.

Calculating the TEQs for the impacted site yellow perch data as presented in Table B9 was not directly possible, since individual Aroclor concentrations were not reported. However, as it is known that Aroclor 1254 and Aroclor 1260 are the dominant mixtures in the Kingston Inner Harbour, for the purposes of determining the *minimum* TEQs for the yellow perch samples in Table B9, it was assumed that the total PCB concentration was entirely due to Aroclor 1260 as it had a *lower* TEF than Aroclor 1254 (see Table 3.9). Based on the 13 yellow perch from the impacted site, the results of this calculation are also presented in Table B9. The UCL95 of the mammalian TEQ is 8.2, and the UCL95 of the avian TEQ is 19, exceeding the CTRGs by 10 times and 7.7 times, respectively. To generate more accurate TEQs for the impacted site, the results of PCB analysis in fish samples from the impacted site (Table B8) were used to determine the average Aroclor ratio for PCB concentrations in the Kingston Inner Harbour; this ratio is approximately 78 percent Aroclor 1260, 19 percent Aroclor 1254, and 3.0 percent Aroclor 1242. Using this ratio, the UCL95 of the mammalian TEQ is 11, and the UCL95 of the avian TEQ is 27, exceeding the CTRGs by 14 times and 11 times, respectively. A

similar calculation for yellow perch samples at Colonel By Lake (Table B10) was not possible as all samples were found to be below the PCB detection limit.

Based on these results, fish tissue residue concentrations of PCBs indicate that fish from the impacted site are accumulating much higher levels of PCBs, and these levels greatly exceed guidelines created for the protection of piscivorous wildlife. The inconsistency in risk estimation for comparisons of fish tissue residue concentrations for MeHg and PCBs to the CTRGs, and the results of HQ calculations can be explained by the highly conservative nature of the CTRGs. As outlined in previous sections, the risk assessment equations for the guideline derivation use multiple uncertainty factors to employ a large degree of conservatism (CCME, 1999c). For example, the guidelines ensure the protective applicability of toxicological values to other piscivorous wildlife species though an interspecies uncertainty factor, which is consistently more than 100-fold (CCME, 1999c). This leads to an evaluation of greater apparent risk when applying the CRTGs in comparison with a site-specific ERA.

3.5.4 Comparison of Estimated Whole-body Fish Tissue Concentrations to GLWQA Criteria

As previously discussed, created for the protection of birds and animals that consume fish, the GLWQA guidelines state that the total concentration in fish tissues (whole fish, ww) should not exceed 0.5 ppm for mercury, and should not exceed 0.1 ppm for PCBs.

This ERA has based the UCL95 for MeHg on the brown bullhead and yellow perch data from Table B9. The UCL95 for this data set is 0.044, with only 1 of 34 fish being above 0.5 ppm.

This ERA has based the UCL95 for PCBs in fish on the brown bullhead data from Appendix B8, as well as yellow perch data from Table B9. The UCL95 for this data set is 0.65 ppm, exceeding the GLWQA criteria by 6.5 times, and there is not a single fish sample from the impacted site that was found to be below the criteria of 0.1 ppm.

Indications of large risk to piscivorous wildlife from these GLWQA criteria, while not as great as comparisons based on CTRGs would suggest, still exceed the risk that is estimated from the calculation of the site-specific risk assessment HQs. As

previously explained, no IJC documents could be located that detailed the derivation procedure for the GLWQA criteria; however, it is likely that the GLWQA criteria also incorporated a large degree of conservatism during guideline derivation.

3.5.5 Field Observations of Fish Morphological Abnormalities

As previously stated, the brown bullhead is highly regarded as a sentinel species because of its very limited home range, along with its intimate relationship to the sediment through diet and cold weather dormancy. During the autumn 2009 fish sampling program conducted in the Kingston Inner Harbour 14 brown bullhead were caught in the impacted area, and 19 at the reference site. Using Rafferty and Grazio (2006) as a guide, all fish were visually inspected for skin discoloration or black pigmentation, lesions and ulcers of the lip or body, fin and tail erosion, and missing, deformed, or shortened barbels. These anomalies may be attributed to a variety of causes, from chemical exposure to infectious disease. No internal organ inspection was made, although obvious signs of physical abnormalities were noted. Of the 14 brown bullhead caught in the impacted area, 11 (79 percent) suffered from one or more of the above anomalies. However, of the 19 fish obtained from the reference site, only 2 (11 percent) exhibited any type of anomaly. Furthermore, reference site brown bullhead anomalies were much less severe than those at the impacted site.

As the populations of brown bullhead from the impacted site and the reference site are from the same river system and separated by less than 2 km, the only discernable difference between the two sites is the elevated concentrations of CoPCs at the impacted site. The contaminated sediments at the impacted site may therefore be the cause of the observed anomalies in brown bullhead from that location. Figure 3.2 displays a typical epidermal ulcer found on brown bullhead from the impacted area.

The much higher frequency and magnitude of the external body anomalies of the brown bullhead at the impacted site, compared with the relative absence of these effects at the reference site, is the most direct and compelling evidence of the ecological impacts of the contaminated sediments. Under the GLWQA, the impacted site is exhibiting the impairment of "beneficial use of fish tumors and other deformities". Specifically, this impairment of beneficial use has been identified in 14 of 31 AOCs located within or

partially within the United States (Rafferty and Grazio, 2006). Within these 14 AOCs, fish tumors and other deformities are most often found on the brown bullhead, leading Rafferty and Grazio (2006) to state that "the ability to accurately and consistently identify tumors or other deformities in brown bullhead is critical for proper assessment and monitoring of the status of this [impairment of beneficial use]". Information on the prevalence of this same beneficial use impairment at Canadian AOCs was not available.

Figure 3.2: Brown Bullhead from the Impacted Area with Epidermal Ulcer

3.5.6 Comparison of Field Observations with Risk Assessment Outcomes for Fish

The widespread evidence for physical abnormalities of the brown bullhead in the impacted area is contradictory to risk assessment outcomes indicating that most CoPC tissue residue concentrations are below the published toxicity thresholds for fish. There may be several reasons might explain this paradox. First, the generalized toxicity thresholds used for assessing risk do not appear to be applicable to brown bullheads. All toxicity thresholds in both Table 3.7 and Table 3.8 are based on toxicological data for species other than brown bullheads; there are currently no TRVs that are specific to brown bullheads. Furthermore, the published TRVs are for fish species with different

habitats from the brown bullhead and they do not share the same degree of exposure to sediments. Toxicity thresholds may need to be uniquely determined for this species; particularly for PCBs, as brown bullheads are known to be especially sensitive to this CoPC.

Second, sediments within the impacted site contain a mixture of contaminants, while toxicity thresholds are derived from studies assessing exposure to a single contaminant. It is known that in the presence of another chemical, the toxicokinetics and toxicodynamics of a chemical can be significantly altered (Bhat and Ahangar, 2007). The interaction of chemical mixtures can result in three general outcomes: the toxic effect resulting from the simultaneous presence of two or more chemicals can be equal (addition), less than (antagonism), or greater than (synergism) the sum of the toxic effects produced when each chemical is only individually present (Beck *et al.*, 2008). The complex mixture of chemicals present within the impacted portion of the KIH may be producing additive or synergistic effects in fish, which may explain the frequency and magnitude of the observed morphological anomalies for the brown bullhead. TRVs do not take into account these possible additive or synergistic effects and therefore may underestimate risk in areas where mixtures of contaminants are present.

3.6 Sources of Uncertainty

Sources of uncertainty that have been identified and considered relevant for this ERA are summarized below.

3.6.1 Receptor Characteristics

The receptor characteristics used in the calculation of ADDs in this ERA were obtained from a variety of sources. Although many of these are considered benchmarks for these data, reported values may not reflect the characteristics that receptors actually exhibit in the Kingston Inner Harbour. Accordingly, conservative values for these characteristics (*e.g.* home range) were used in this ERA to provide a worst-case scenario.

3.6.2 Lack of Insect Data for Use in Red-Winged Blackbird Diet

Risk assessments usually require the generalization of at least one receptor's diet as data are often not readily available for all biota that receptors might ingest. Nevertheless, except for the red-winged blackbird, all diets of the receptors in this ERA are based on measured concentrations in the food item that comprises the vast majority of their diet and therefore the effect of the generalized diet is minimal. However, although the red-winged blackbird's diet is composed of almost 40 percent seeds with the remainder being mostly insects, because of the lack of data regarding CoPC concentrations in insect biota, the diet of this receptor was based solely on cattail seeds. This limitation may cause an underrepresentation of CoPC exposure to the red-winged blackbird, as many of the insects this receptor will feed on in the marsh, including burrowing mayfly, emerge from the sediments of the marsh and may therefore be expected to potentially have a large body burden of CoPCs.

3.6.3 Small Cattail Data Sets

The cattail data used in this ERA were limited, as the number of samples for cattail inflorescence (5), roots from the Orchard Street Marsh (5), and cattail roots from the south shore of Belle Island (2) was small. This limitation raises the possibility that the actual exposure of the receptors that ingest this biota is underestimated. However, some of these cattail samples were taken from areas known to have the highest sediment concentrations of the various CoPCs. In addition, maxima for the various CoPCs detected in these samples were used as the EPCs, and the full detection limit was used for those in which concentrations were not detected. These compensating measures add conservatism to this ERA to counterbalance possible underestimation related to small sample sizes.

3.6.4 Missing CoPC Data for Cattail Inflorescence and Root

The lack of data for PCB concentrations in cattail inflorescences did not permit calculation of the associated ADD for the red-winged blackbird. This lack of data is assumed to have limited impact on the result of this ERA as the roots of the cattails showed only limited uptake of PCBs, making it unlikely that a significant concentration would be found in the inflorescence.

There was also a lack of Hg data for both the cattail root and inflorescence, which is considered to be a data limitation of this ERA.

3.6.5 Conversion of Fillet to Whole-Body Concentrations for MeHg and PCB

The equation for converting fillet MeHg concentrations to whole-body MeHg concentrations taken from Peterson *et al.* (2005), as well as the conversion factors taken from USEPA (2006) for PCBs, may not be predictive of whole-body concentrations in the Kingston Inner Harbour. As the two studies on which these conversions were based were conducted in water bodies other than the Great Cataraqui River, differences in the qualities of the water bodies may create asymmetries in the proportions in which these chemicals partition between the fillet and the remainder of the body. The data of Peterson *et al.* (2005), however, are based on a large amount of data from 12 of the western United States; therefore their MeHg equation is more likely to be generally applicable to other sites. Conversely, the USEPA (2006) data on which the conversion factors for PCBs were based was solely taken from Lake Michigan. Depending on the degree of differences between Lake Michigan and the Great Cataraqui River (*e.g.* pH), there may be greater variance between the theoretical and actual values calculated in the conversions used for this ERA. The optimal way to eliminate the uncertainty regarding true whole-body fish concentrations for MeHg and PCBs is to analyze homogenized whole-body fish samples.

3.6.6 Fish Concentrations for As, Cr(III), Cu, Pb, and Zn in Yellow Perch and Northern Pike Not Taken From Whole-Body Samples

The fish sample data for As, Cr(III), Cu, Pb, and Zn that was used in modeling piscivorous wildlife were based on homogenized fish samples that were missing one fillet. This fillet was extracted to provide fillet samples for human health risk assessment purposes. Although rendering the whole-body concentrations inaccurate, it is assumed that the procedure used in this ERA will in fact overestimate the concentration of these CoPCs because the portion of the fish that was analyzed accumulates most of the contamination. Jezierska and Witeska (2006) indicate that most metals accumulating in fish are found in the liver, kidneys, gills, and digestive tract. In addition, gonads, bones, and brain can also have high metal concentrations, while muscle shows low relative

concentrations. Jezierska and Witeska (2006) state that Cu shows a distinct accumulation in the liver; Pb deposits primarily in the liver, kidneys, and spleen, but is also found in the digestive tract and gills; and Zn is found in the highest concentrations in the gills, but is also found in the digestive tract, liver, and kidneys. Culioli *et al.* (2009) reports that As accumulates most in the operculum and liver, followed by the gills and axial skeleton.

3.6.7 Fish Tissue Residue Toxicity Thresholds

The fish tissue residue toxicity thresholds presented in Table 3.7 and Table 3.8 serve as a useful guideline against which to compare fish tissue residue concentrations from the impacted site as well as the reference site. However, as these values were not developed in the same species as have been sampled for this ERA, nor were they necessarily developed in water bodies with similar chemical characteristics (*i.e.* pH, alkalinity, etc.), it is unlikely that these toxicity thresholds exactly reflect those that would be expected for the species in this ERA that have been extracted from the Great Cataraqui River. Nevertheless, in the absence of more accurate data and consistent with common ERA practice, it was deemed to be acceptable to apply these toxicity thresholds as a benchmark for assessing fish tissue concentrations.

3.7 Conclusions

Based on the exposure scenarios developed in this semi-quantitative screening level ERA for the Orchard Street Marsh and southwest portion of the Kingston Inner Harbour, muskrats are identified as a species that is at high risk due to Cr(III) ingestion, and mink are at intermediate risk due to PCBs. Depending on their actual feeding characteristics within the impacted area, great blue herons and osprey may be at intermediate risk due to MeHg.

Comparisons of fish-tissue CoPC concentrations with published fish toxicity thresholds suggest that the fish community in the impacted area is not at risk. The results of fish tissue analysis indicate that MeHg levels in yellow perch and northern pike at the impacted site exceed the CRTGs, but only a modest degree above that found at the reference site. However, all sampled species greatly exceed the PCB CRTGs developed for both the protection of mammalian (26 times) and avian consumers (18 times) of

PCBs. Fish samples also greatly exceed the GLWQA specific objective for PCBs in whole-fish, with the UCL95 being approximately 6.5 times higher that the criteria of 0.1 ppm set by the IJC protocol. Of the fish samples collected by ESG in fall 2009, as well as the data obtained from Scheider (2009), not a single fish tissue sample was found to be below the IJC-mandated PCB criteria of 0.1 ppm. However, the CRTGs are highly conservative in comparison with a site-specific risk assessment.

Field observations of the brown bullhead indicate a substantial frequency of morphological abnormalities for fish in the impacted area that appear rare at the reference site. In contrast to those obtained at the reference site, and with the only difference between the two sites being the elevated concentrations of CoPCs in the sediments of the impacted site, most brown bullhead caught within the impacted site suffer from the GLWQA-defined beneficial use impairment of fish tumors and other deformities. Comparison of whole-body tissue residue concentrations of CoPCs for this species to published fish toxicity thresholds has not indicated the likely presence of risk. However, the available fish toxicity thresholds are not specific to brown bullheads, which may be particularly sensitive to sediment contamination. In addition, toxicity thresholds do not account for possible additive or synergistic effects from the complex mixture of contaminants in the impacted portion of the KIH, and therefore the assessed risk may be underestimated. The frequency of observed morphological abnormalities for brown bullhead at the impacted site suggests that contaminated sediments pose an ecological risk for this species. Further ecotoxicological studies could be useful in confirming these results.

In addition to assessments of ecological effects due to contaminated sediments from the impacted area (bioaccumulation of contaminants, sediment toxicity tests, and analyses of benthic community structure (ESG, 2010a)), and results of a human health risk assessment (ESG, 2010b), the results of this ERA provide another line of evidence that biological effects are occurring at this site. Therefore, a remediation strategy options and feasibility analysis is warranted.

CHAPTER 4: REMEDIATION STRATEGY OPTIONS AND FEASIBILITY ANALYSIS

4.1 Assessing the Potential Sediment Remediation Options for the Impacted Area

Three generic active responses exist for the management of contaminated sediment: MNR, capping, and dredging (Chapter 2). Due to the nature, widespread distribution, and abundance of contaminants within the sediments of the Kingston Inner Harbour, MNR is unlikely to be an appropriate primary remedy. Metals are completely nondegradable to nontoxic forms and will persist indefinitely (Baird and Cann, 2008), and PCBs are highly resistant to degradation by biological or chemical means and will persist for very long periods of time (Baird and Cann, 2008). For example, the protracted period required for PCBs to naturally degrade was a significant factor in the USEPA's decision to dredge PCB-contaminated sediments from within the Hudson River (USEPA, 2002). Additionally, the existence of relatively shallow depths within the impacted area, combined with sediment re-suspension factors such as nautical recreation and wind-induced wave action, appears to contribute to continuous redistribution sediments (ESG, 2009a). These factors hinder the covering of contaminated sediments with clean sediments from natural sedimentation processes (ESG, 2009a). The COA framework cautions that when conditions exist for buried sediments to become re-suspended, environmental risks can be present (EC and OMoE, 2008).

In appropriate situation, *in-situ* capping is an attractive remediation alternative because it is an acceptable compromise between cost, logistics, regulatory approval, and environmental risk (Zeller and Cushing, 2006). However, *in-situ* capping can be inappropriate when water depth is inadequate to accommodate the cap with present and forecasted uses (*e.g.* navigation, recreation), typical or occasional hydrodynamic conditions may compromise the cap (*e.g.* regular river current velocity, occasional periods of high flow), or the sediments to be sequestered are of inadequate strength to support the cap (*e.g.* low-density, high water content) (Förstner and Apitz, 2007). The impacted area of the Kingston Inner Harbour possesses features that likely make *in-situ* capping an unsuitable alternative:

i. frequented by motor boaters and other water sport enthusiasts, the average depth of the river is only 1.2 m, with this level typically falling below 1.0 m in late summer when water traffic is still high. Propeller wash emanating from boat motors, even during periods of higher water levels, is sufficient to churn and re-suspend underlying sediments in many areas. Remediation of the impacted area should seek to facilitate unrestricted use of the entire water body by the local population and tourists, not create mobility restrictions that may be needed if a cap was present.

ii. as detailed in Section 2.6.3, soft, fine-grained, water-rich sediments are ubiquitous throughout the impacted area and may not be sufficient to support the capping material.

The Hamilton Harbour contains most of the contaminants found within the Kingston Inner Harbour, and a 35 cm cap was employed in a portion of Hamilton Harbour during its remediation. However, in contrast with the Kingston Inner Harbour, the capped area within Hamilton Harbour had an average depth of 15 m (Azcue *et al.,* 1998). At the PCB-contaminated Hudson River Superfund Site, although *in-situ* capping was judged to have the potential to achieve substantial cost savings from reduced transportation and disposal costs, dredging was selected as the best suited remediation alternative (USEPA, 2002). For this latter project, many capping options were evaluated and rejected for this project due to potential future problems with aquatic re-vegetation and root penetrations, and because of concerns about the reliability and long-term stability of the cap (TAMS Consultants Inc., 2000; 2002) associated with navigational and recreational uses (USEPA, 2002).

Ex-situ capping is a potential remediation alternative for the impacted site; however, adopting this approach would necessitate the contamination of another aquatic site that is sufficiently large to hold all dredged sediments from the Kingston Inner Harbour. As this practice is not in agreement with the fundamental tenets of sustainability or long-term environmental stewardship, this alternative is not considered to be a likely selection.

If remediation is required for the Kingston Inner Harbour, dredging is considered to be the option most likely to achieve short-term and long-term human health and ecological risk reduction. However, given the possibility for the impacted area to contain historically significant remnants of vessels (see Section 2.3), a thorough archeological survey of the site is first recommended. Throughout most of the summer, there is sufficient depth to allow dredging to occur. Although post-remediation environmental monitoring must occur after dredging operations are complete, this monitoring would not necessitate the magnitude of detail required for monitoring the integrity of a cap, nor would it have the associated long-term maintenance issues that capping requires. Although dredging is likely the most expensive remediation alternative, dredging would not place mobility restrictions on water vessels that capping may require, and there would be no concerns about the ramifications of Kingston Inner Harbour characteristics that can affect the integrity of a cap, such as the damaging effects of propeller wash or the presence of soft, water-rich sediments. Finally, as dredging is the only option that physically removes the contamination from the impacted area, it enjoys a greater acceptance with regulatory agencies and the public than either MNR or capping (Zeller and Cushing, 2006).

An evaluation of the potential impacts of a dredging operation is necessary to determine dredging feasibility through an assessment of potential adverse effects on the environment that may include release of toxic chemicals (Vellinga, 1997). Although Cr(VI) has not been detected in surface water within the impacted area (ESG 2009a; 2009b), no research to date has determined if this highly soluble and toxic contaminant is present within the underlying sediment pore water. If present, dredging could release this contaminant into the water column. The remainder of this chapter outlines the details of a study that was conducted to determine if Cr(VI) was present within the pore water of the impacted area. This research uses peepers to sample contaminated sediment pore water. The Canadian Water Quality Guideline for the Protection of Aquatic Life for chromium in freshwater is 8.9 ppb for Cr(III) and 1.0 ppb for Cr(VI) (CCME, 2006)

4.2 Introduction to Pore Water Sampling Using Peepers

First developed by Hesslein (1976), equilibrium dialysis cells, or peepers, can be placed in sediments and function on the principal of equilibrating an initially pure sample of water with the surrounding pore water via a semi-permeable dialysis membrane. After sufficient time for equilibration to occur, the peepers are removed from the sediments and the water is analyzed in a laboratory. To conserve speciation of chemicals, samples must be preserved under an inert atmosphere (Bufflap and Allen, 1995a). Analytical results of the peepers provide a depth profile of pore water concentrations for dissolved analytes of interest. The following design requirements must be considered: cell volume (V) must be adequate to allow laboratory analysis; the surface area (A) of the semi-permeable portion of the cell must be adequate to minimize effects of sediment heterogeneity; the interval between cells must be small enough to produce a sufficient level of resolution; the peeper apparatus must be constructed such that insertion into sediment results in minimal alteration of conditions; and the time required to achieve full equilibration must be acceptable (Teasdale *et al.,* 1995).

Ex-situ methods of pore water extraction have been developed; however, artifacts are inevitable because sediment samples must be removed from their natural environment to collect the pore water (Beck *et al.,* 2007; Bufflap and Allen, 1995b). Peepers are attractive because of their simplicity, and they require less equipment than other *in-situ* methods (Carignan, 1984). A disadvantage of peeper use is the possibility of the dialysis membrane damage, and care must be taken to choose a suitable material that resists microbial breakdown (Teasdale *et al.,* 1995). In addition, the relatively long time required for peepers to equilibrate with surrounding waters is a disadvantage (Van Oploo *et al.,* 2008).

The time required to achieve full equilibration within each cell depends on the design factor (F), which is calculated by dividing V/A (Brand and Hasselmann, 1991), but can also depend on sediment porosity, temperature, diffusion coefficients of contaminants, strength of adsorption to sediment particles, and dissolution of the sediment particles (Carignan *et al.,* 1985). The smaller the value of F, the less time required for equilibration.

Using plastic peepers has the advantages of cost minimization and ease of creating the window for the membrane. However, a significant drawback to the use of plastic is its oxygen content (Teasdale *et al.,* 1995), as one of the primary sources of error in pore water analysis is the oxidation of anoxic water (Bufflap and Allen, 1995b). Therefore, plastic peepers must be thoroughly deoxygenated (Teasdale *et al.,* 1995). Carignan *et al.,* (1994) suggested that before use in sampling, peeper materials should be exposed to an anoxic environment for at least 30 days before construction, and exposure to O_2 should be minimized during and between uses.

4.3 Materials and Methods

4.3.1 Peeper Design

Peeper cell design for the purposes of this research is based on that used by Serbst *et al.* (2003). All nitrogen used throughout the experiment was ultrahigh purity (UHP) quality, obtained from Air Liquide Canada Inc. in Kingston. Peeper cells (Figure 4.1) were constructed from 5.0 mL Nalgene® linear low-density polyethylene (LLDPE) vials obtained from Thermo Fisher Scientific Inc. in Rochester, New York. A hole of approximately 19 mm was created in the vial lid using a custom-made metal punch-and-die. After 34 days of peeper cells being deoxygenated under nitrogen protection, and the day before being deployed to the field, deionized water was de-oxygenated for 120 min using nitrogen purging. Still under nitrogen protection, peeper cells were constructed by filling the vial using an adjustable pipette, the disposable plastic cap of which had been deoxygenated for 48 hours. Once filled, the peeper opening was covered with a 1.0 μm Nucleopore® polycarbonate filter and the cap was closed to secure the membrane in place. Peeper cells were then placed into the peeper housings and remained under nitrogen protection until deployment to the field.

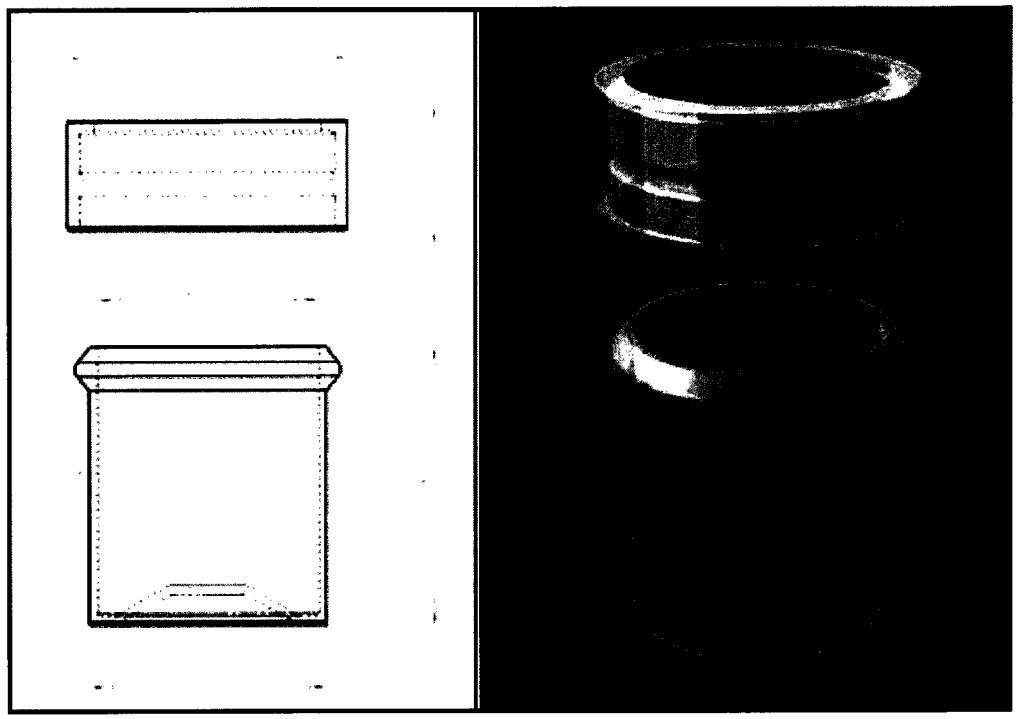

Figure 4.1: Peeper Cell Design (all dimensions in mm). Dimensions and construction of 5.0 mL LLDPE peeper cells are shown. The approximate 19 mm hole in the vial lid was made using a custom-made punch-and-die, and a 1.0 μm Nucleopore® polycarbonate filter is placed between the lid and main body before closure.

A peeper housing is shown in Figure 4.2. These were constructed from a high-density polyethylene (HDPE) sheet obtained from Piedmont Plastics Inc. in Scarborough, ON. A total of five peeper housings were constructed, each capable of holding 20 cells, with side-by-side pairs descending 10 cells deep. This construction was selected to provide field duplicates that would verify the accuracy of the peeper method. The small-diameter holes in the peeper housing were machined using a vertical milling machine to allow insertion of the peeper cell, but hold it securely in place by friction. The caps of the cells have slightly larger diameters than the bottoms. The large-diameter holes in the peeper housing were machined to allow the caps of the cells to recess into the holes, and for sediments to completely surround the top of the peeper cells. When inserted into the cell holes in the housing, the peeper cells were pushed in to be slightly below flush with the face of the housing (~0.5 cm), to protect the membrane during insertion into the sediments. The centers of each peeper cell holder are 4.5 cm apart, vertically. If the sediment-surface water interface is at the top of the recess for the first peeper cell, the

depth to which the bottom cell will measure is approximately 42.5 cm. A single hole through the top of the peeper was made to allow marker tape to be tied to the peeper and aid recovery, and a wedge-shaped bottom was machined to aid insertion into sediments. Before being deployed to the field, peeper housings were deoxygenated for 30 days.

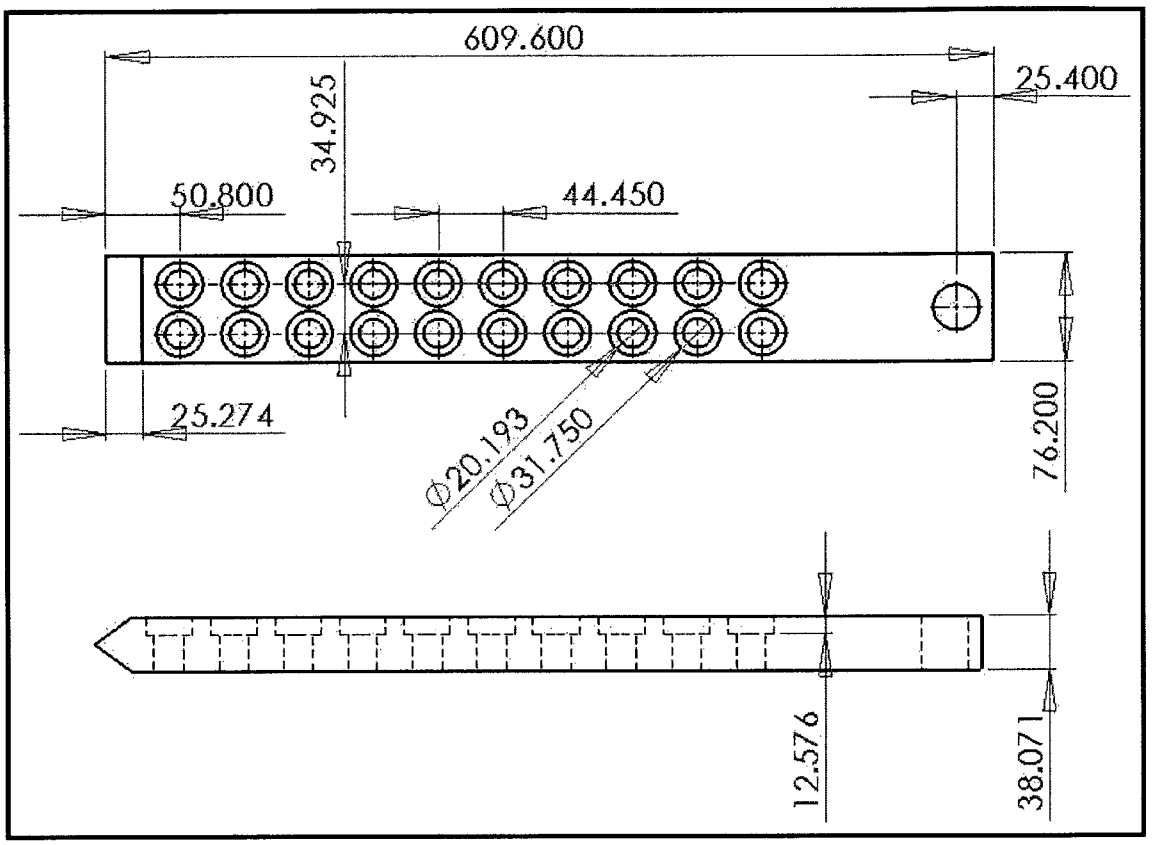

Figure 4.2: Peeper Housing Design (all measurements in mm). Each peeper housing was made of HDPE and the holes were made using a vertical milling machine. If the top peeper cell is inserted just below the surface water-sediment interface, the maximum depth of pore water that can be sampled is approximately 42.5 cm.

4.3.2 Peeper deployment

Five peeper housings and a total of 90 peeper cells (9 rows x 2 per column = 18 per peeper housing) were deployed to the field, each capable of reaching a depth of 38 cm. Van Oploo *et al.* (2008) reported that most commonly encountered dissolved species equilibrate in approximately 10 days when sampled with peepers having F = 10 mm;

Carignan *et al.* (1994) observed that 15 days was a frequently used equilibration time for peepers; and Carignan *et al.* (1984) stated that equilibration times can take from three to 20 days. In this experiment, peeper dimensions resulted in F = 18 mm and were deployed into sediments adjacent to the former tannery in August, 2009, for a period of 20 days. Locations of peepers deployed to the impacted site (Figure 4.3) were selected based on proximity to the area where the effluent-contaminated marsh discharged into the Great Cataraqui River, and where groundwater flow suspected to emanate from below the former tannery discharged into the river. In particular, peeper 1 was deployed to a location in the river, at the confluence of the marsh and the river, where a core sample contained the greatest concentration of chromium yet measured in the Kingston Inner Harbour sediments (83,000 ppm at 25-30 cm depth). The reference site was located approximately 1.2 km upriver, in a similar marshy environment. The day the peepers were deployed to the field, they were quickly taken from their nitrogen environment and placed into large heavy-duty Ziploc® bags. The bags were then purged with nitrogen for 10 seconds, and the inflated bags were sealed. The bags were immediately taken by motor boat to their deployment locations and were placed in position by scuba diver. Because the sediments are extremely soft at the research site, and the water was shallow, emplacement did not exceed the two-minute window used by Van Oploo *et al.* (2008). When they were retrieved, the peepers were extracted from the sediment by scuba diver, taken immediately to the surface, and placed in a large heavy-duty Ziploc® bag. The bag was purged for 10 sec with nitrogen, inflated and then sealed. This process did not take longer than two minutes. When the peepers were redeployed to the laboratory, they were placed back in their original nitrogen environment and washed of any surface sediment using deoxygenated, deionized water.

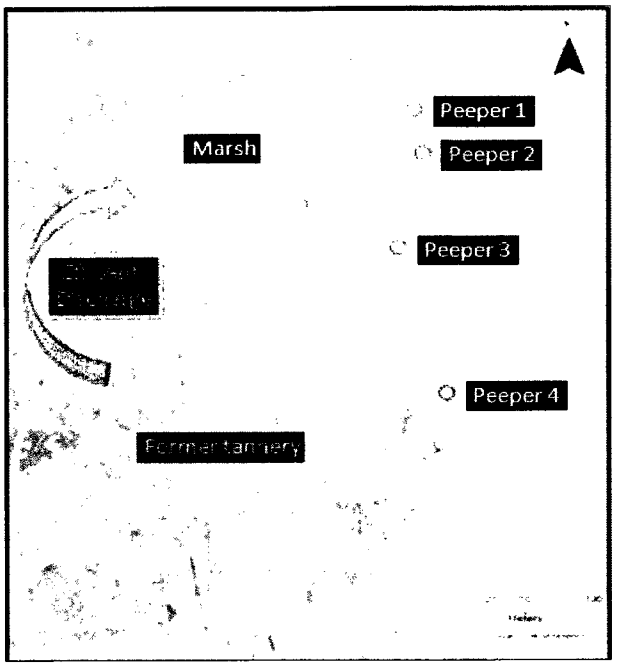

Figure 4.3: Locations of Peeper Deployment to Impacted Site. Peeper locations were selected based on proximity to the highest concentrations of chromium in river sediment, and locations where groundwater is suspected to flow from beneath the tannery surface. The flow path of historic discharged effluent from the tannery is shown in red; the reference site is located 1.2 km north (upriver), on the west side of river.

4.3.3 Speciation Analysis Procedures

Total chromium values were measured to determine the concentration of chromium in sediment pore waters, taking into consideration all species. In addition, speciation analysis was conducted to determine the concentration of Cr(III) and Cr(VI) in sediment pore waters, to compare the concentrations of these individual species to CCME guidelines and determine the likelihood of adverse ecological impacts being present. A second speciation analysis was conducted, identical to the previously mentioned analysis, with the added step that ethylenediaminetetraacetic acid (EDTA) was added to each sample. This process is similar to that used by Gürleyuk and Wallschläger (2001) and was performed to provide a comparison between different speciation analysis methods. EDTA chelates and stabilizes Cr(III), therefore potentially allowing greater detection of dissolved Cr(III). Each peeper cell had three subsamples prepared from it. Two chromium speciation analysis subsamples, one with 0.12 g of EDTA stock solution added

and the other without, were prepared and analyzed using high performance liquid chromatography (HPLC) coupled to an inductively coupled plasma – mass spectrometer (ICP-MS). A third subsample, prepared for determining total chromium, was analyzed using ICP-MS. For each subsample, 1.0 mL of peeper cell sample was placed into an HPLC vial. After the addition of EDTA, those samples were heated at 70°C for one hour to speed the chealating and stabilization of Cr(III). Spiked samples were prepared by adding 0.050 g of stock solution containing Cr(III) and Cr(VI) to the 1.0 g samples.

4.4 Quality Assurance and Quality Control

4.4.1 General

Quality control (QC) tests were incorporated into the analysis; these consisted of a field duplicate for each sample and an analytical duplicate and a spiked sample (known concentration of Cr(III) and Cr(VI) added to a sample) added to every batch of 10 samples (10 percent frequency rate). Analytical duplicates were analyzed to determine reproducibility of results for both chromium speciation and chromium totals analysis. Measured values between the limit of detection (LOD) and the limit of quantification (LOQ) were annotated as "trace". Calibration curve and spike solutions were prepared with $CrCl_3(H_2O)_6$ as a source of Cr(III) and K_2CrO_4 as a source of Cr(VI). QC calibration check samples were prepared with Cr(III) (Inorganic, CGCR (3)10-1, Cr(III)) and the same K_2CrO_4 to have 54.3 ppb Cr(III) and 50.7 ppb Cr(VI) in water. QC percent difference was calculated, where a positive result indicates the measured value is above the theoretical value, and a negative value indicates the measured value is below the theoretical value. The range of values of QC percent differences is presented in this manner, but the average value of QC percent difference is calculated by averaging the *absolute value* of individual QC sample percent differences, to avoid overestimating the degree to which the measured and theoretical values agreed. The relative percent difference (RPD) of field duplicates were calculated only when both samples were above LOD, and the concentration value for that location and depth was reported as the average between the field duplicates. For this research, the acceptable average RPD values are defined as being less than 20 percent. Spiked samples were prepared to increase the concentration of a sample by 93 ppb Cr(III) and 100 ppb Cr(VI); the acceptable spike

percent recovery is defined as being greater than 80 percent. Appendix D contains all data generated in this study. Table 4.1 reports the analytical conditions for speciation analysis.

Table 4.1: Analytical Conditions for Speciation Analysis

Parameter	Specific Conditions
Inductively coupled plasma – mass spectrometer	Thermo Instruments X Series
Forward radio-frequency power	1400 W
Reflected radio-frequency power	< 2 W
Nebulizer gas flow rate	0.99 L/min
Auxiliary gas flow rate	0.90 L/min
Coolant gas flow rate	13.0 L/min
Nebulizer type	Concentric
Spray chamber temperature	3°C
Peripump rate	17 rpm
Analysis mode	CCT (Collision cell, H_2 flow rate: 3.35)
Analysis pressure	6.7×10^{-7} mbar
Expansion pressure	1.8 mbar
HPLC [b]	Thermo Spectra System (P4000 quaternary HPLC pump, SCM100 vacuum degasser, AS300 autosampler)
Curve points	0.10, 1.0, 10, 100, 1000 (ppb)
QC checks	High QC: 750 ppb Low QC: 50 ppb
Internal standards	Sc, Y, Rh, In, Tb, Ho, Bi
Injection volume	100 µl
Anion-exchange column	Dionex IonPak AS7, 4x250 mm
Anion-exchange mobile phase	60mM NH_4NO_3 pH =8.0
Flow rate	1.0 mL/min

[a] Thermo Instruments, Mississauga, ON, Canada
[b] HPLC = high-performance liquid chromatography

4.4.2 Total Chromium Analysis

Average percent difference between the absolute value of theoretical and measured values of 13 QC calibration check standards was 11 percent (range of -17 percent to 20 percent). Of 15 blanks, one blank measured a trace of chromium (greater than 0.82 ppb and less than 2.7 ppb, see Table 4.2 for detection limits). The duplicate results are summarized in Table 4.2: of the 45 field duplicate pairs measuring above

LOD, the average RPD was 15 percent (range of 0.42 percent to 48 percent). Of eight analytical duplicate pairs above LOD, average RPD was 4.2 percent (range of 0.14 percent to 18 percent). Spiked sample results are reported in Table 4.3 and will be discussed in Section 4.5.2.

Table 4.2: Summary of Data for Total Chromium Samples. All samples for total chromium analysis measured above LOD, and 57 percent of samples measured above LOQ. Acceptable average RPD is defined as being less than 20 percent; average RPD of both field duplicates and analytical duplicates were well within this figure.

Measurement	Value
LOD	0.82 ppb
LOQ	2.73 ppb
Total Samples	90
Field Duplicates	
Total field duplicates above LOD	90
Total field duplicates between LOD and LOQ	39
Total field duplicate *pairs* above LOD	45
Average RPD	15%
Standard deviation	12%
Range	0.42% to 48%
Analytical Duplicates	
Analytical duplicate pairs above LOD	8
Analytical duplicates below LOQ	8
Average RPD of analytical duplicate pairs	4.2%
Standard Deviation	5.9%
Range	0.14% to 18%

Table 4.3: Summary of Spike Sample Recovery for Total Chromium. Spike recovery for total chromium samples are shown above. Acceptable recovery is defined to be greater than 80 percent recovery. Samples from nearest the marsh (peepers 1-3) demonstrated weak recovery, while the reference peeper and the peeper farthest from the marsh demonstrated acceptable recovery. The relevance of these results will be discussed in Section 4.2.

Spike Sample Number	Peeper location	% Recovery
SPK 1	Reference	86
SPK 2	Reference	90
SPK 3	1	59
SPK 4	1	42
SPK 5	2	47
SPK 6	2	33
SPK 7	3	61
SPK 8	3	54
SPK 9	4	89

4.4.3 Speciation Analysis without EDTA

Average percent difference between theoretical and measured values for 12 QC samples was 12 percent (range of -23 percent to 14 percent) for Cr(III) and 11 percent (range of -25 percent to 9.8 percent) for Cr(VI). Of 20 blanks, one blank measured a trace of Cr(III) and four blanks measured a trace of Cr(VI).

The few concentrations of either field or analytical duplicates above LOD make statistical assessment of the peeper method difficult to perform for these samples and this analysis. Average RPD for the two field duplicate pairs measuring a Cr(III) concentration above LOD was 16 percent; there were no Cr(VI) field duplicate pairs for which RPD could be calculated. For the 45 field duplicate pairs for Cr(III), all but two pairs were in agreement with respect to the value being below detection limit or containing trace amounts. No analytical duplicates had a Cr(III) concentration above LOQ. For Cr(VI), 40 of 45 field duplicate pairs (89 percent) were in agreement with respect to the sample concentration being below LOD or containing trace amounts. Table 4.4 contains a summary of the results from field and analytical duplicates. Table 4.5 contains a summary of spike recovery data, and the significance of this data is discussed in Section 4.5.3.

Table 4.4: Summary of Sample Data for Speciation Analysis without EDTA. Few samples for speciation analysis without EDTA measured above LOD, and none measured above LOQ. RPD for field duplicates for both Cr(III) are within acceptable range; no field duplicate RPD could be calculated. No analytical duplicates of either Cr(III) or Cr(VI) were above LOD.

Measurement	Cr(III)	Cr(VI)
LOD	0.23 ppb	0.14 ppb
LOQ	0.76 ppb	0.45 ppb
Total Samples	90	90
Field Duplicates		
Total field duplicates above LOD	6	5
Total field duplicates between LOD and LOQ	6	5
Total field duplicate *pairs* above LOD	2	0
Average RPD	16%	N/A
Standard deviation	N/A	N/A
Range	-25% to 7.6%	N/A
Analytical Duplicates		
Total analytical duplicates above LOD	0	0
Average RPD	N/A	N/A
Standard Deviation	N/A	N/A
Range	N/A	N/A

Table 4.5: Summary of Spike Sample Recovery for Speciation Analysis without EDTA. Zero (or virtually zero) percent Cr(VI) spike recovery was measured at the three peepers closest to the marsh (peepers 1-3), and was believed to have been reduced to Cr(III). This would account for percent recoveries for Cr(III) in many cases being greater than 100 percent. This result, as well as lowered recovery at peeper 4, is discussed in Section 4.5.3.

Spike sample number	Peeper location	Cr(III) % recovery (%)	Cr(VI) % recovery (%)
SKP 1	Reference	110	90
SKP 2	Reference	120	76
SKP 3	1	140	0.0
SKP 4	1	130	0.0
SKP 5	2	130	0.0
SKP 6	2	76	0.0
SKP 7	3	93	0.0
SKP 8	3	94	0.0
SKP 9	4	100	62

4.4.4 Speciation Analysis with EDTA

Average percent difference between theoretical and measured values for 13 QC samples was 9.2 percent (range of 1.0 percent to 21 percent) for Cr(III) and 5.7 percent (range of -3.2 percent to 18 percent) for Cr(VI). Of 16 blanks, one blank measured a trace of Cr(III) and four blanks measured a trace of Cr(VI). For Cr(III), average RPD of 44 field duplicates pairs measuring above LOD was 18 percent (range of 0.50 percent to 49 percent), and the average RPD of nine analytical duplicates measuring above LOD was 31 percent (range of 6.2 percent to 76 percent). For Cr(VI), RPD of the single field duplicate pair measuring above LOD was 5.3 percent. No analytical duplicate was above LOD. Table 4.6 contains a summary of the results from field and analytical duplicates. Table 4.7 contains a summary of spike recovery data, and the significance of this data is discussed in Section 4.5.4.

Table 4.6: Summary of Sample Data for Speciation Analysis with EDTA. Cr(III) concentrations were higher when analyzed with EDTA, as opposed to being analyzed without EDTA. Cr(VI) was only detected in four samples, all of which came from the reference site. Average RPD of field duplicates was within the acceptable range. Average RPD of analytical duplicates was higher than 20 percent, but all samples were under LOQ.

Measurement	Cr(III)	Cr(VI)
LOD	0.10 ppb	0.11 ppb
LOQ	0.33 ppb	0.36 ppb
Total Samples	89	89
Field Duplicates		
Total field duplicates above LOD	89	5
Total field duplicates between LOD and LOQ	34	5
Total field duplicate *pairs* above LOD	55	1
Average RPD	18%	5.3%
Standard deviation	12%	N/A
Range	0.50% to 49%	N/A
Analytical Duplicates		
Analytical duplicate pairs above LOD	9	0
Analytical duplicates below LOQ	9	0
Average RPD of analytical duplicate pairs	31%	N/A
Standard Deviation	22%	N/A
Range	6.2 to 76%	N/A

Table 4.7: Summary of Spike Sample Recovery for Speciation Analysis with EDTA. Cr(VI) is completely absent in all spiked solutions and believed to have been reduced to Cr(III). As a result, total chromium percent spike recovery was calculated. The cause and significance of these figures are discussed in Section 4.4.

Spike sample number	Peeper location	Cr(III) % recovery (%)	Cr(VI) % recovery (%)
SKP 1	Reference	170	0.0
SKP 2	Reference	180	0.0
SKP 3	1	150	0.0
SKP 4	1	160	0.0
SKP 5	2	130	3.2
SKP 6	2	170	0.0
SKP 7	3	2.2	0.0
SKP 8	3	1.3	0.0
SKP 9	4	150	7.4

4.5 Results and Discussion

4.5.1 General

Total chromium pore water concentrations in the peepers reached a maximum concentration of approximately 6.4 ppb at both peepers 1 and 2. These two peepers were the closest in proximity to the maximum chromium sediment concentrations at the confluence of the marsh and the river. In virtually all samples, Cr(VI) concentrations were below the detection limit (0.14 ppb for speciation analysis without EDTA and 0.11 ppb for speciation analysis with EDTA). This suggests that impacted area sediments adjacent to the former tannery may be a reducing environment for Cr(VI), or at least do not allow the oxidation of Cr(III) to Cr(VI). Some possible causes of this are discussed in the subsequent sections. The results may also suggest that the deoxygenation procedure used before peeper deployment was sufficient and oxygen emissions from plastics were negligible, as oxygen contamination would promote oxidation of Cr(III), producing elevated Cr(VI) concentrations. The possibility of indigenous Cr(VI) being reduced to Cr(III) throughout the experimental procedure will be discussed in the following sections.

4.5.2 Total Chromium Analysis

Figure 4.4 depicts the total chromium concentrations at each peeper location. These represent the total chromium that passed through the 1.0 μm membrane into the peeper containers and was injected into the plasma, and includes chromium in forms (possibly particulate and colloidal) that are not traditionally or conventionally thought of as "dissolved" (typically operationally defined as that passing through a 0.45 μm filter). Figure 4.4 clearly shows the general trend that total chromium pore water concentrations generally increase northward, as the peeper locations become closer to the marsh's confluence with the river. Note that the profile for peeper 4, the most distant peeper from the highest sediment concentrations of chromium, is very similar to the reference location peeper located approximately 1.2 km upriver from the tannery site. It appears from the concentration profiles in Figure 4.4 that peepers 1-3 reach their maximum chromium pore water concentrations at approximately 29 cm, 20 cm and 20 cm, respectively. The depth of maximum total chromium pore water concentration for peeper 1 corresponds with the depth at which the core sample reached its maximum sediment chromium concentration at 83,000 ppm at 25-30 cm. It is likely that the peepers did not reach the maximum depth of dissolved Cr(III), since the profiles did not show lower concentrations at the greatest depth. It is not clear why peeper 4's total chromium concentrations continued to increase past 40 cm, but this may be the result of all samples for this peeper being less than LOQ.

The percent spike recovery for the reference peeper (86 percent, 90 percent) and peeper 4 (89 percent) show acceptable recovery. However, percent spike recovery for peepers 1-3 are much lower (ranging from 33 percent to 61 percent). This discrepancy is not believed to be due to instrument error, since QC measurement of both Cr(III) and Cr(VI) in calibration check solutions (in distilled deionized water) was at acceptable levels throughout the experiment. Therefore, the discrepancy is likely a characteristic of the pore water in the samples used for the spiked samples for peeper locations 1-3. For example, sediments highest in chromium concentrations might have, within the pore water, a chemical presence that interferes with the detection of chromium by ICP-MS. Because the spike sample for peeper 4 was the most distant from the highest chromium concentrations, it is possible that its pore water closely resembles the reference site in which this matrix effect is not seen. It is likely that this pore water matrix effect is

attributable to a yet undetermined Cr(VI) reducer in the impacted area sediments, and this possibility is explored in more detail in Section 4.5.3 when results for speciation analysis without EDTA are discussed.

Alternatively, it is possible that the locations of peepers 1-3 have higher concentrations of fine sediments able to bypass the dialysis membrane and infiltrate the peeper cells. In this scenario, the Cr(III) spike added to the samples of peepers 1-3, and any reduced Cr(VI), may have adsorbed to these fine sediments and settled to the bottom of the HPLC vial, never making it into the ICP-MS for analysis. Regardless of the reason for the lower spike recoveries at peepers 1-3, the low spike recovery in the region of the maximum chromium concentrations for peeper 1 and 2 suggests that a scaling factor of 2.5-3 could be applied at these points. If all chromium is in the Cr(III) form, this would cause the concentrations of the maximums for peeper 1 and 2 to exceed the CCME guideline of 8.9 ppb (for Cr(III)) and some ecological impacts may potentially result.

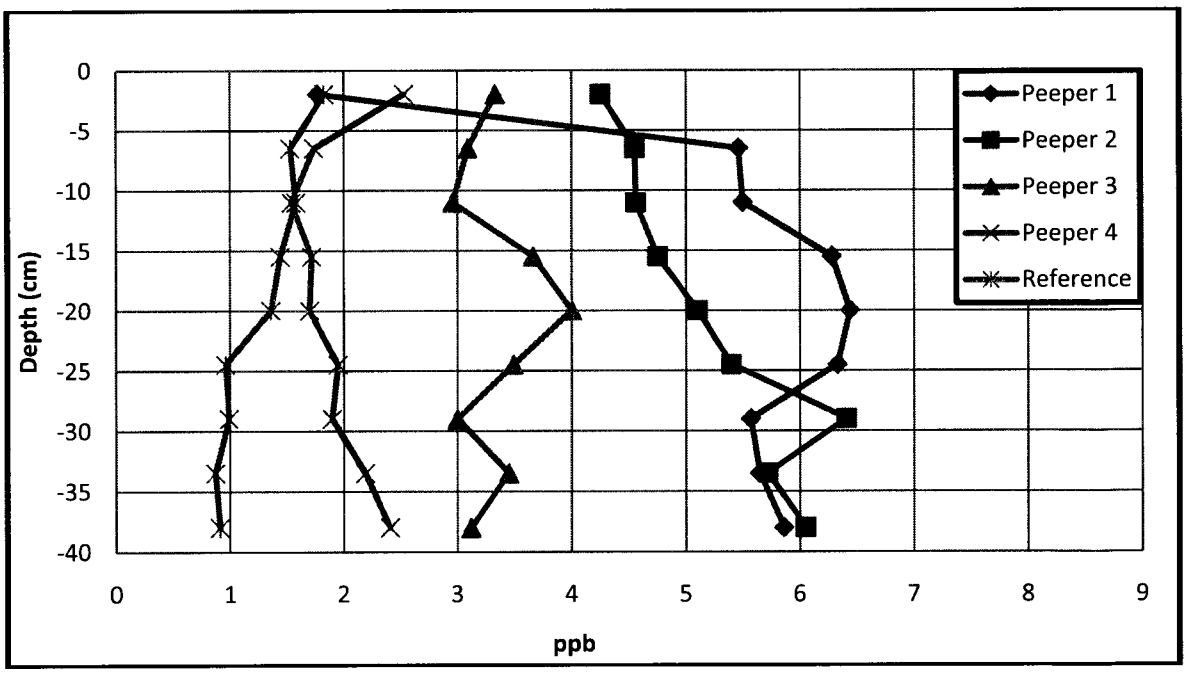

Figure 4.4: Total Chromium Concentrations for Peeper Locations. Peeper 1 is closest to the area of highest sediment chromium concentration; peeper 4 is most distant. The reference peeper is located 1.2 km upstream. Peepers 1-3 have maximum Cr(III) pore water concentrations at 29 cm, 20 cm, and 20 cm depth, respectively. All reference peeper values and peeper 4 values lie below LOQ.

4.5.3 Speciation Analysis without EDTA

The spiked sample Cr(VI) concentrations show acceptable recovery for the reference site, lower recovery for peeper 4, and zero percent recovery for peepers 1-3. These are very important results, since they indicate the presence of a substance in the impacted site sediments that reduces Cr(VI), but is not present at all sites (*e.g.*, reference site). This type of matrix in the pore water means that Cr(VI) persistence in the pore water system adjacent to the tannery is not very likely, as it is quickly being reduced to Cr(III). Potential matrix components that might have this effect are humic chemicals and plant exudates, as well as AVS. With respect to AVS, tannery effluent is known to be high in sulfides, and all effluents were known to be discharged directly to marsh from 1912 to 1967. In this scenario, the sediments adjacent to the former tannery could be particularly rich in sulfides. It is hypothesized that sulfides emanating from tannery effluents precipitated in the river, eventually forming Cr(VI)-reducing AVS in the sediments. Sampling to determine the AVS concentration in the vicinity of the former tannery is needed to validate this theory.

The spiked samples show high Cr(III) percent recovery, in that they tended to measure above 100 percent in samples where Cr(VI) recovery was lowered, which likely reflects the additional Cr(III) created from the reduced Cr(VI).

Cr(III) and Cr(VI) were below LOD in most samples, and values of detectable Cr(III) were substantially lower than the total chromium concentrations presented in Section 4.5.2. These results suggest negative bias in the speciation analysis measurement technique that is likely specific to HPLC, which is not employed in total chromium analysis. This effect is possibly due to the presence of fine sediment and colloidal material present in the peepers that passed through the dialysis membrane during their 20 day placement in the sediments, or contamination of the HPLC vials during preparation of the samples for analysis. Indeed, as was determined by Asquini *et al.* (2005) and Tinney (2006), 95 percent of sediments are in the grain size fraction of less than 63 μm. Such particulates would provide adsorption sites to Cr(III) and these Cr(III)-rich particulates would be incapable of moving down the HPLC column. Consequently, lower Cr(III) concentrations upon ICP-MS analysis would result.

4.5.4 Speciation Analysis with EDTA

Figure 4.5 depicts Cr(III) concentrations at each peeper location when conducting speciation analysis using EDTA. Only five samples had a Cr(VI) concentration above LOD, all of which came from the reference site. In contrast to total chromium results, concentrations for peepers 1 and 2 generally increase with depth, all the way to the maximum peeper depth of 38 cm. The reason for this trend is not known, but may be a result of lower depths having larger grain sizes, as Cr(III) adsorbs more strongly to finer-grained particulates.

All spiked samples analyzed for the speciation analysis with EDTA method had zero (or virtually zero) percent recovery of Cr(VI), including reference site and peeper 4 spike samples. As proposed earlier, AVS may be a contributing factor but does not explain the absence of Cr(VI) in all of these samples, as Cr(VI) recovery was present in the reference site and peeper 4 for speciation analysis samples not treated with EDTA (calibration check solutions had good recoveries of Cr(VI) using this speciation analysis method). An additional potential factor in these samples is the heat treatment (70°C for one hour) used to promote complexation of Cr(III) with EDTA. This may have facilitated unforeseen reactions in the pore water of the reference site, and all tannery peepers, with pore water matrix components not present in water-based calibration check standards. These reactions may have reduced Cr(VI) to Cr(III), but this may not take place under normal temperatures. Because of the complete absence of Cr(VI) recovery in the spiked samples, percent spike recovery was calculated assuming all chromium present in the spike sample was in the Cr(III) form. Nevertheless, as is shown in Table 4.7, and similar to speciation analysis without EDTA, only modest recovery figures were measured. A possible factor for this, as was suggested for speciation analysis without EDTA, was that Cr(III) may have adsorbed onto particulates that had no mobile capability in an HPLC column. Results for peeper 2, comparing analytical results for total chromium and speciation analysis with EDTA, is given in Figure 4.6.

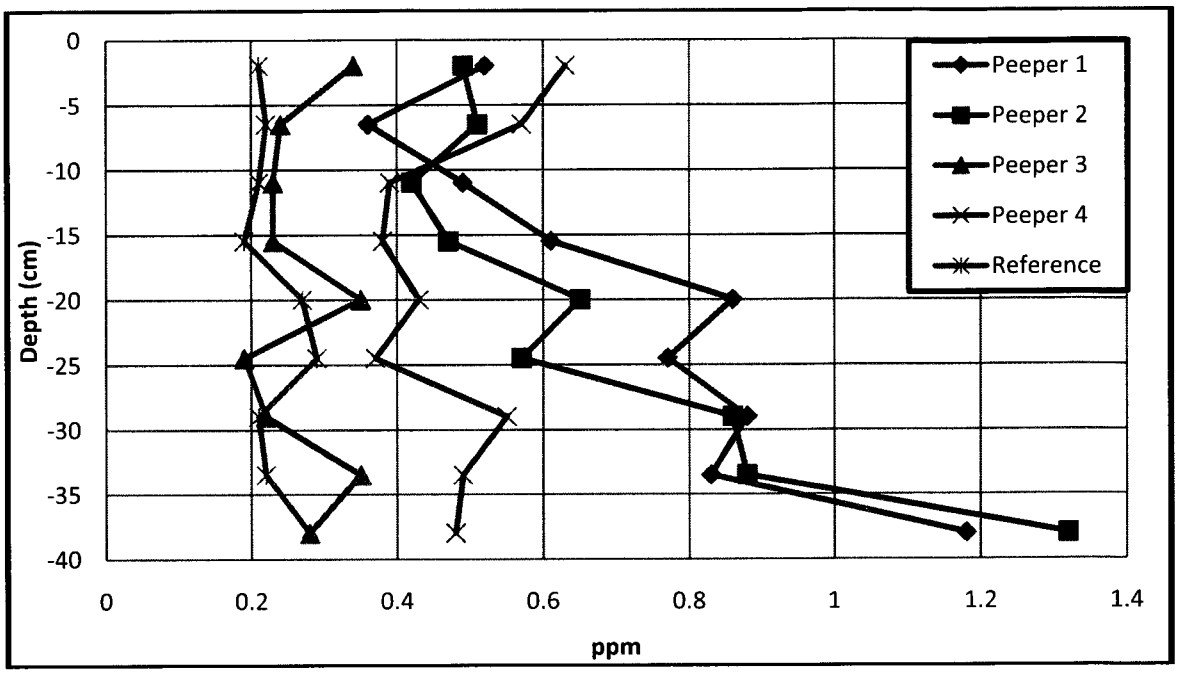

Figure 4.5: Cr(III) Concentrations for Peeper Locations using Speciation Analysis with EDTA. Cr(VI) was not detected in peepers 1-4, and assumed to be non-existent or reduced to Cr(III). Spike recovery data for Cr(VI) showed complete reduction of all Cr(VI), but also that Cr(III) is lost in the analytical process. It is believed this Cr(III) loss is due to the immobility of Cr(III) in the HPLC column, therefore being unmeasured in the ICP-MS. Chromium values in Figure 4.5 are lower than those of total chromium values presented in Figure 4.4, when HPLC was not used.

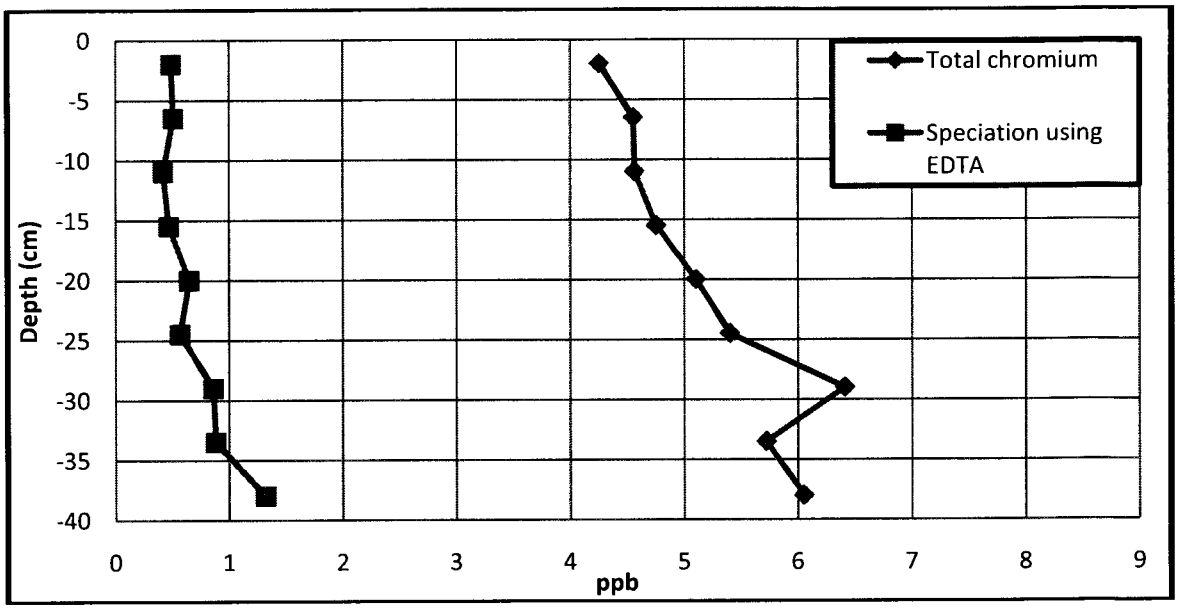

Figure 4.6: Comparison of Results for Peeper 2 for Total Chromium Analysis and Speciation Analysis with EDTA. All chromium in speciation analysis with EDTA is assumed to be Cr(III), based on the results of Cr(VI) percent spike recovery for those samples and that no Cr(VI) was measured above detection limit. Measured Cr(III) (and therefore total chromium) values are believed to be lower than total chromium analysis values due to the presence of fine sediments and colloids in the samples, as these particulates are immobile in an HPLC column. Speciation analysis with EDTA employs HPLC, but total chromium analysis does not, therefore this effect is not seen in the latter.

4.5.5 The Case for Cr(III) in Kingston Inner Harbour Pore Waters

As stated at the beginning of this section, no Cr(VI) was detectable in any pore water samples, an observation resulting from the use of two speciation analysis methods. The spike recoveries in samples showed that for some samples (a) matrix component(s) was rapidly reducing Cr(VI) (introduced prior to analysis) to Cr(III), but this was not systematic since some spiked samples prepared at the same time demonstrated high Cr(VI) recovery. Therefore, the Cr(VI) reduction was likely not attributable to a systematic experimental factor. The rapidity with which the Cr(VI) was reduced to Cr(III) (< 36 hrs) suggests that any indigenous Cr(VI), if it ever had been present in the pore water, would have been rapidly (on an environmental scale) reduced to Cr(III). However, the spiking experiment was a static system, and the environmental conditions in the pore water are dynamic, so these results do not exclude the possibility that Cr(VI) may survive for very short time periods that are nevertheless long enough to affect

biological life in the sediments. Future experiments should be carried out to model this scenario (*e.g.* spiked samples prepared immediately before analysis, and time trials or kinetic studies of Cr(VI) reduction in these particular pore waters).

These results provide strong evidence for the absence of Cr(VI) in Kingston Inner Harbour pore waters and sediments; thus all the chromium present in the pore water (total chromium in Figure 4.4 is assumed to be Cr(III)). Moreover, most of the Cr(III) is likely in the form of particulates and colloidal materials and is not "dissolved," so its availability to living organisms may be limited. If groundwater from beneath the former tannery is discharging into the river, it does not appear to contain a measurable amount of Cr(VI) at the locations sampled by the peepers. If this groundwater does exist, this result may be a consequence of Cr(VI) having already been reduced in surface or subsurface soils, the humic nature of the peat and gyttja river sediments, the presence of root exudates, or the presence of AVS in the sediments. Studies of groundwater beneath the Davis Tannery property by Milley (2010) were not found to have Cr(VI).

4.6 Summary of Chromium Speciation Analysis Results

Conditions in the Kingston Inner Harbour have favored the reduction of Cr(VI) to Cr(III) in the sediments that were measured. This result may be because of the presence of humic compounds and root exudates from plants in the wetland, or AVS levels in the sediment, all of which reduce Cr(VI). Measurements of AVS and organic carbon in the river sediments and pore waters adjacent to the former tannery should be measured to test the latter hypothesis. The total chromium analysis results also indicate that if groundwater is discharging into the river from below the tannery, at least at the locations measured by the peepers, all chromium is in the Cr(III) form.

While speciation analysis results demonstrated strong reducing conditions for affected site sediments, total chromium results are the most reliable for chromium measurements. The total chromium results suggest that the maximum concentration of dissolved Cr(III) was within the measurement range of the peepers, although the peepers used in this study likely did not reach the bottom of the chromium sediment contamination. However, as this research has shown that no significant or consistent Cr(VI) concentration above LOD was found at any depth at the affected site, it suggests

an overwhelming reducing environment in the sediments. It is likely that the strength of the reducing environment will only increase with depth; therefore it is probable that greater depths will only contain Cr(III) in the pore water. The presence of AVS in the sediments adjacent to the former tannery, if it could be confirmed, would strengthen this argument. Another pore water study could be undertaken to verify the pore water chromium speciation of these deeper sediments. A peeper sampling depth of at least 75 cm is recommended to accomplish this.

The peeper method of pore water sampling has modest reliability in delivering consistent results, as shown by good field and analytical duplicate reproducibility. Peepers are relatively inexpensive to construct and simple to deploy, but diligence must be exercised in their preparation, deployment, and recovery to avoid altering redox conditions of sampled pore water. It is important that dialysis membrane pore size be small enough to eliminate most fine sediments, especially if liquid chromatographic methods are employed in speciation analysis, since they are only capable of analyzing dissolved species. Dialysis membranes should have a pore size no greater than 0.45 μm.

The analytical methods used in this experiment proved to be complementary. Speciation analysis with and without EDTA showed an absence of detectable Cr(VI) in impacted site pore waters, therefore implying that only Cr(III) is present. In comparison, though, Cr(III) detection for speciation analysis with EDTA was much stronger than speciation analysis without EDTA. However, because particulates were probably present, Cr(III) (and thus total chromium) had low measurements for these two methods, though reliability will increase if smaller pore size dialysis membranes are used on the peeper cells. As a result, total chromium measurements, which did not employ the use of HPLC, became important. Scaling of these latter measurements, based on percent spike recovery, results in some Cr(III) pore water concentrations above CCME guidelines for the protection of aquatic life, and may therefore indicate the possibility for some potential risk to ecological receptors.

4.7 Conclusions of Remediation Options and Feasibility Analysis

The result of this remediation options and feasibility analysis has established that dredging is the most appropriate remediation strategy for the impacted sediments. The water depth of the impacted area is of sufficient depth to permit dredging operations to be conducted, and dredging is feasible because there exists no toxic Cr(VI) in sediment pore water.

MNR has been assessed to be an inappropriate remediation strategy for the impacted area because of the concentrations and nondegradable nature of the contaminants present at the site, the widespread distribution of this contamination, and the tendency of contaminated sediments to become resuspended and redistributed.

In-situ capping is assessed to be an unsuitable remediation strategy for the impacted area because characteristics of the Kingston Inner Harbour (water depth, presence of fine-grained sediments), as well as present and future recreational uses, make cap construction, maintenance, and long-term integrity difficult or impossible. *Ex-situ* capping is unfavorable because the nature of the strategy is not in agreement with the fundamental tenets of sustainability or long-term environmental stewardship.

CHAPTER 5: LIFE CYCLE ASSESSMENT OF TWO POTENTIAL SEDIMENT DEWATERING AND DISPOSAL ALTERNATIVES

5.1 Introduction

Section 2.11 provides a description of the LCA framework, as well as the impact assessment method that will be used in this LCA. For the purpose of this chapter, the "impacted area" is the area of contaminated sediments within the Great Cataraqui River south of Belle Park and east of the former Davis Tannery property (see Chapter 2). Remediation alternatives for the contaminated sediments of the Orchard Street Marsh are different from those for the river sediments, and have not been explored in this LCA.

Previous studies (ESG 2010a; 2010b; 2009a) and Chapter 3 of this thesis have established that biological effects are occurring as a result of contaminated sediments within the impacted area. Chapter 4 has established that dredging is the most appropriate sediment remediation strategy, given the natural characteristics of the impacted area, and that Cr(VI) was not found within the pore water of these sediments. However, subsequent to being dredged, sediments from the impacted area must be dewatered before disposal or reuse. Grain size analysis has determined that 95 percent of grain sizes within the impacted area are in the fraction less than 63 μm (Tinney, 2006; Asquini *et al.*, 2007). These sediments are predominantly soft, high-organic, water-rich mud that is at least 80 percent water (wet weight) (Asquini *et al.*, 2007). Preliminary leachate tests conducted on samples of impacted area sediment have determined that they can be disposed of in a non-hazardous waste landfill (MacMillan and Presley, 2010).

The presence of contaminated sediments within the impacted area has increased the difficulty of redeveloping an adjacent brownfield property at the former site of the Davis Tannery. This 15-ha brownfield is being considered for remediation, in preparation for redevelopment into residential property. However, the redevelopment of this brownfield will likely not proceed unless the sediments within the impacted area have been successfully remediated. The necessity to remediate this aquatic site is augmented by the fact that the river is part of a UNESCO World Heritage Site (UNESCO, 2009). For the purpose of this LCA, the former tannery brownfield will be referred to as the "brownfield site."

5.2 Goal and Scope Definition

5.2.1 Goal

The goal of this LCA is to explore the utility of LCA methodology as a tool for assessing the environmental impacts of aquatic remediation alternatives, specifically for the dewatering and disposal of dredged sediments. Within this LCA, two alternatives for the dewatering and disposal of contaminated sediments that are dredged from the impacted area will be compared. As the City of Kingston has declared its intention to become the most sustainable city in Canada (Foster, 2010), a potential application for this LCA is to inform remediation decision-making for contaminated sediments in the impacted area.

5.2.2 Scope

The two sediment dewatering and disposal alternatives that will be compared for dredged contaminated sediments from the impacted area are: (1) mechanical processing, and (2) natural dewatering. The details of each alternative have been explained in Section 2.10. The function of each of these alternatives is to dewater and dispose of contaminated sediments that are having adverse biological effects within the impacted area, and must be removed by dredging. The functional unit chosen for this LCA is the dewatering and disposal of 200,000 m^3 of dredged sediment volume.

This LCA will use the LCIA method of Impact 2002+ and has focused on the midpoint categories of global warming, non-renewable energy, respiratory inorganics, and terrestrial ecotoxicity, as they are high-leverage impact categories for the types of systems explored. This LCA was performed using the ecoinvent database within the SimaPro 7.1.8 software package. Hotspot analysis has been conducted to identify processes that contribute most significantly to midpoint and damage categories. In addition, characterization has been performed to identify relative contributions of inputs from the various processes, and normalization has been performed to identify the high-leverage impact categories. The methodological framework of this LCA was conducted in accordance with the requirements and guidelines published in ISO 14040 and ISO 14044 (ISO, 2006a; 2006b).

5.2.3 General Assumptions

The system boundaries of both the mechanical processing system and the natural dewatering system have been chosen such that processes that are required in both systems are not included, as they are assumed to offset. These offsetting processes are outlined below, as are additional general assumptions that impact both systems:

i. Dredging operations. These operations include sediment dredging, loading of dredged sediment onto a barge, and subsequent sediment transport by barge to the shore. It is assumed that these actions will have an identical impact in both the mechanical processing system and the natural dewatering system.

ii. Uses of dredged sediment. Only sediment that is having adverse biological effects will be dredged from the impacted site. Therefore, it is assumed that unless cleaner grain size fractions are separated from more contaminated grain sizes by the MSWP, sediments are unfit for reuse and must be landfilled. This LCA will not consider the alternative of using the contaminated sediments in an immobilized form, in products such as concrete, unless decision-makers indicate such an intention in the future.

iii. Dewatering of sediments during dredging. Dewatering of sediments will occur as a consequence of the dredging process itself, aside from that which occurs within the two dewatering and disposal systems that will be examined. For example, after sediments are dredged and placed in a barge for transport to the shore, decanting of water takes place in the barge (Inspect-Sol, 2003). For the purpose of this LCA, a volume of wet sediment, as it sits in the river, will be referred to as a "dredged sediment volume," as this is a volume that has been extracted from the river by dredging. The volume of wet sediment that reaches the shore by barge and has been subject to this initial dewatering, will be referred to as the "input sediment volume," as this volume of wet sediments will be the

input into each respective dewatering and disposal system. This initial dewatering is estimated to result in a 50-percent volume reduction due to water loss (Inspect-Sol, 2003). Therefore, a dredged sediment volume of 200,000 m^3 (the functional unit) will result in an input sediment volume of 100,000 m^3. Sediments that have been processed in either the mechanical processing system or the natural dewatering system will be referred to as "processed sediments".

iv. Dredged sediment offloading point. Since there is no information regarding an appropriate location for the input sediments to be offloaded from the barge onto land, it has been assumed that they will be offloaded at the location of the brownfield site.

v. Movement of sediments after dredging. It has been assumed that the location of the MSWP for the mechanical processing system, and the sediment loading point (for transport of input sediments to the dewatering location) in the natural dewatering system, are both at the brownfield site. It is therefore assumed that the impacts resulting from movement of the input sediments from the barge to either the MSWP, or to the transport bound for the dewatering location, is identical (or of negligible difference) and will offset. Additionally, as site preparation at the brownfield site will be required for the mechanical processing system and the natural dewatering system, the impacts of this preparation is assumed to be identical and offset.

vi. Sediment qualities. The impacted area sediment is known to be 95 percent fine-grained sediments (less than 63 μm) and 5 percent fine sand (Tinney, 2006; Asquini *et al.*, 2007). As determined by Inspect-Sol (2003), the specific gravity of sediments within the lower Kingston Inner Harbour is 2.1. Based on this figure, it is assumed that the density of dry sediments is 2,100 $kg \cdot m^{-3}$.

vii. Location of landfill. Based on information from the City of Kingston (MacLatchy, 2010) at the time of writing, the final destination for contaminated processed sediments is assumed to be the Moose Creek landfill. This landfill is operated by Lafleche Environmental Inc. at 17125 Lafleche Road, Moose Creek, ON (southeast of Ottawa).

viii. Acquisition of heavy equipment. It is assumed that the terrestrial heavy equipment that is needed to excavate and transport sediments within the various unit processes of each system, such as dump trucks and excavators, are all available locally in Kingston. Therefore, the impacts resulting from the transport of this heavy equipment to the locations where they will be used is assumed to be negligible and will not be considered.

5.2.4 Mechanical Processing System Boundaries

There are different possibilities for locations from which the MSWP could be brought to Kingston, and different possible locations it could be sent to upon completion of the Kingston project. Bringing the MSWP to Kingston from another location will be referred to as an "acquisition scenario," and the transportation of the MSWP from Kingston to a subsequent location will be referred to as a "release scenario." The impacts from an acquisition scenario will always be allocated to the Kingston project. Two general possibilities exist for release scenarios: (1) the MSWP is sent to a subsequent project, after use on the Kingston project, for processing of soils and/or sediments, or (2) it is returned directly to the company that owns the MSWP because no subsequent project was identified. In the event of the former, release scenario transportation impacts will be allocated to the subsequent project and not to the Kingston project; in the event of the latter, release scenario transportation impacts will be allocated to the Kingston project.

The system boundaries for the mechanical processing system are shown in Figure 5.1. Assumptions made about the processes within the system boundaries include:

i. MSWP materials. The exact materials that the MSWP is constructed of are not known. However, a significant portion of the frame would have to be

steel to make it robust enough for international shipping. For the purpose of this LCA, the MSWP was assumed to be constructed entirely of low-alloyed steel.

ii. MSWP production. It has been assumed that the MSWP will operate on a 24-hr work day, with 18 hrs of actual production, at an average wet sediment processing rate of 76 $m^3 \cdot hr^{-1}$ (Mann, 2009). Exact power requirements of the MSWP are not known; therefore the power requirements of a similar process have been used as proxy data (73.6 $MJ \cdot tonne^{-1}$ (t^{-1}) dry mass; Arevalo *et al.*, 2007).

iii. MSWP acquisition scenario. The present location of the MSWP is Stuart, FL (Mann, 2009). However, a project that requires the MSWP will be undertaken and completed in Toronto before its use in Kingston (Tejani, 2010). Therefore, for the purpose of this LCA, it is assumed that the MSWP will be shipped to Kingston from Toronto.

iv. MSWP release scenario. It is not presently known where the MSWP would be shipped after completion of the Kingston project. If no subsequent project for the MSWP is identified, a likely destination would be Green Bay, WI, where the dredging company that owns the MSWP is currently undertaking operations and would likely have available land for its storage (Mann, 2009). However, for the purpose of this LCA, it is assumed that a subsequent project for the MSWP will be identified, and to which the impacts of its transport from Kingston can be allocated.

v. Electricity generation. Data listing the power generation sources for the Province of Ontario were taken from the Ontario Power Authority (OPA, 2005). This report details that the largest power sources for the province include: nuclear (51 percent), hydroelectric (22 percent), coal (19 percent), natural gas (7.0 percent), and wind power (1.0 percent).

vi. Destination for clean sand reuse. The brownfield site is likely to be remediated and redeveloped if contaminated sediments from the impacted area are dredged. Therefore, it is assumed that clean sand separated in the MSWP will remain on the brownfield site for use during its redevelopment. In calculating the benefits from this sand reuse, it has been assumed that sand needed for redevelopment of the brownfield site would have come from a local sand quarry, located 25 km away.

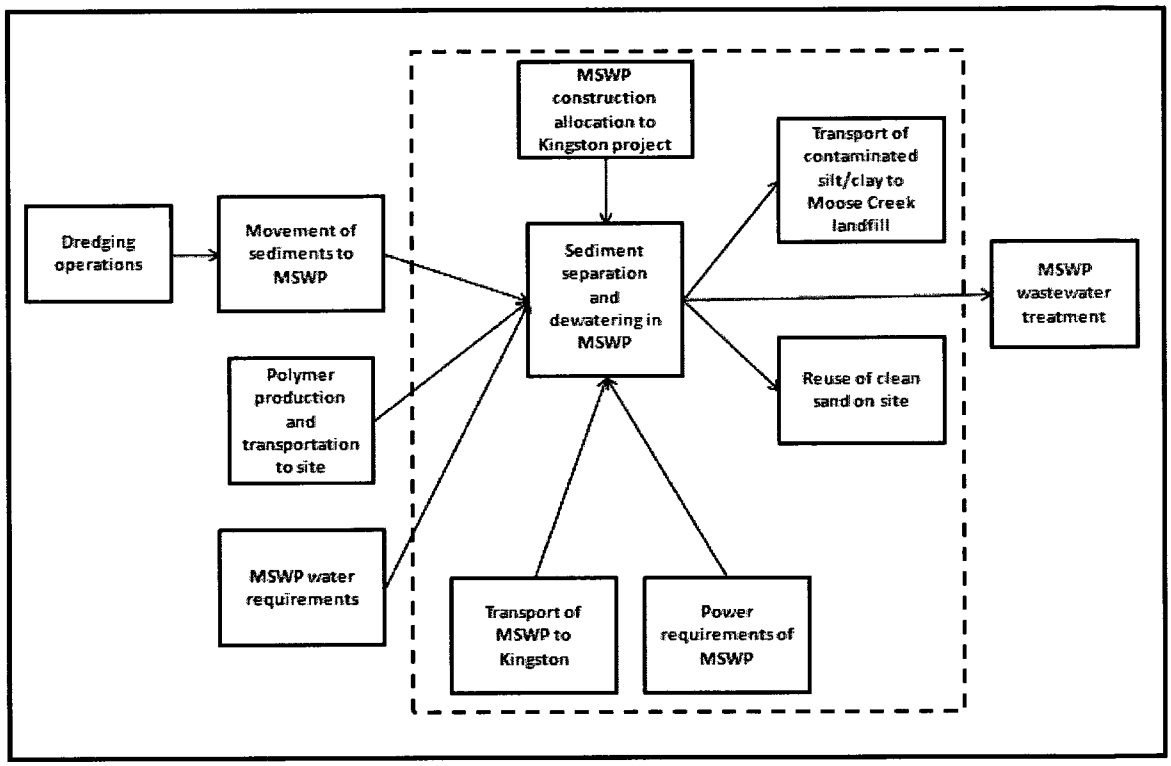

Figure 5.1: System Boundaries for the Mechanical Processing System

The reason for excluding the "movement of sediments to MSWP" process from the mechanical processing system has already been explained. The system boundaries defined in Figure 5.1 imply that the following additional processes were not considered in this LCA:

i. Polymer production and transportation to site. Polymers are added during sediment processing within the MSWP to promote flocculation. These polymers are added at a rate of 1.5 $kg \cdot t^{-1}$ (dry sediment) (Mann, 2009). However, the composition of the polymers that are used depends on site-specific sediment characteristics. It is not known what the composition of the polymers used on the sediments of the impacted area would be; therefore this process has been excluded from the system boundaries.

ii. MSWP water requirements. The mechanical grain size separation method used by the MSWP is water-based; as sediments are put into the MSWP, water must be added to facilitate the separation process. However, it is not known what volumes are required, whether river water can be treated and used in the MSWP, or whether water from the local water system must be obtained. Because there is a lack of information regarding this process it has been excluded from the system.

iii. MSWP wastewater treatment. Wastewater from the MSWP may require treatment, as it contains polymers and may contain dissolved contaminants liberated from sediments during processing. Apart from the lack of data on the volumes of water the MSWP would typically require, it is not known if the MSWP can treat the water and discharge it into the river, or whether it must be diverted to local water treatment facilities. For these reasons, this process has been excluded from the system.

5.2.5 Natural Dewatering System Boundaries

The system boundaries for the natural dewatering system are shown in Figure 5.2. Assumptions made about the processes within the system boundaries include:

i. Location of dewatering site. It has been assumed that a presently existing dewatering site, used for a previous sediment remediation project in Kingston, could also be used for this project. This dewatering location,

known as Knox Farm, was constructed to hold 60,000 m^3 of input sediment volume and is located 10 km (by road) north of the brownfield site, approximately at the corner of Perth Road and McAdoo's Lane.

ii. Expansion of Knox Farm. As the Knox Farm site is presently capable of holding only 60,000 m^3 of input sediment volume; expansion of this site is required for holding larger input sediment volumes. There is a large unused municipal land parcel adjacent to the Knox Farm site; it is assumed that this site can be expanded onto that land to suit the needs of this project. Impacts from producing the original 60,000 m^3 of holding pits at Knox Farm are allocated entirely to the project for which it was constructed. To accomplish the expansion necessary for input sediments from the impacted site, soil excavation and transport processes must be accounted for. During the original construction of the Knox Farm site, excavated soils were not stored on site (R.V. Anderson Associates Ltd., 2003). For the purpose of this LCA, the hauling distance of excavated soil to expand the Knox Farm dewatering location has been assumed to be 5 km from Knox Farm. The impact of expanding Knox Farm does not include other actions that would be necessary to create the site, such as the construction of berms or compaction of the excavated pits. It was not determined how these additional processes could be modeled or what exact actions are required to accomplish these tasks.

iii. Density of soil at Knox Farm. It is not known what the density of the soil is that must be excavated at Knox Farm for dewatering pits expansion. The density of the soil at Knox Farm is assumed to be 1,300 $kg \cdot m^{-3}$, as this value is considered to be an ideal soil density for topsoil (Miller and Tidman, 2001).

iv. Loading onto trucks of dewatered sediments bound for landfill. This action only includes the process of using an excavator to load the trucks. It

was not known if, or how much, bulldozing may be required. As a result, the impacts from this possible process have been excluded from the system until further information can be obtained.

Apart from the excluded processes that have already been discussed, the system boundaries in Figure 5.2 imply that dewatering site maintenance has not been considered in the system. The requirements and methods for this maintenance are not known and will therefore be excluded from consideration.

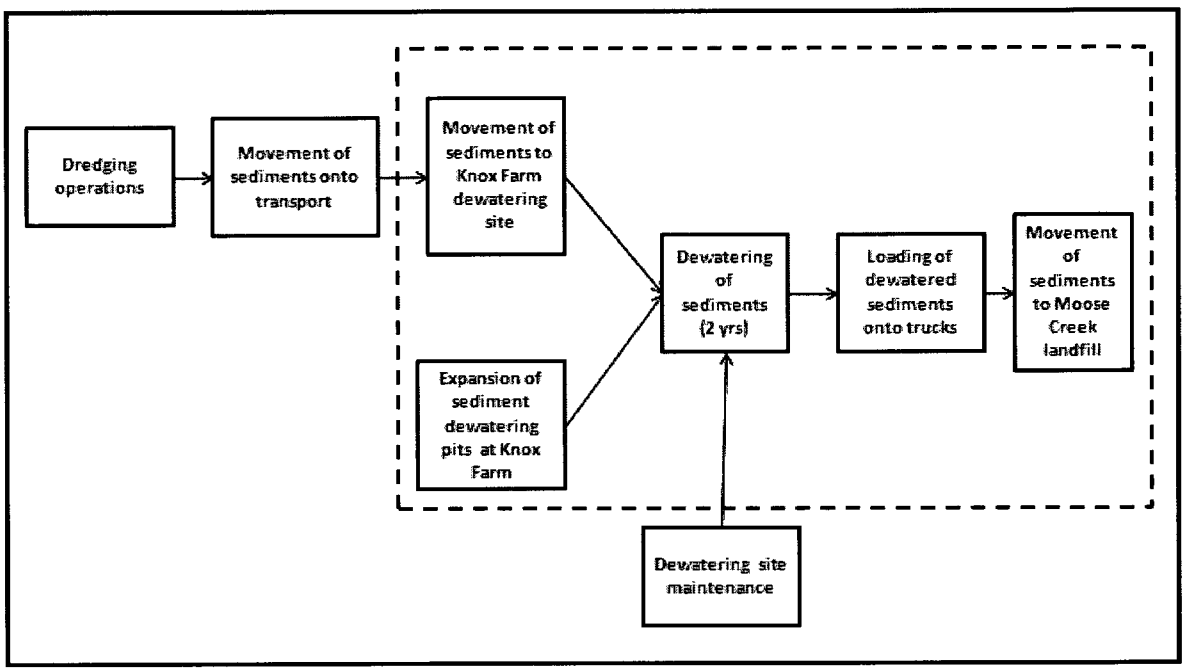

Figure 5.2: System Boundaries for the Natural Dewatering System

5.2.6 Additional Data Limitations

Apart from the data limitations that have already been identified, this LCA has been conducted using European data available in the ecoinvent database. It is understood that these data will likely not identically reflect corresponding North American data values; however, this is acknowledged as an acceptable limitation of this LCA since it will still permit a comparison of the two sediment dewatering and disposal alternatives.

5.3 Life Cycle Inventory Analysis

General data and assumptions that affect both the mechanical processing system and the natural dewatering system have been summarized in Table 5.1, as well as sediment mass calculations that result from a 200,000 m^3 dredged sediment volume (and are based on the aforementioned data and assumptions). Data and assumptions that are specific to the mechanical processing system are summarized in Table 5.2, and a summary of the ecoinvent processes that have been selected to model this system are included in Table 5.3. Data and assumptions specific to the natural dewatering system are summarized in Table 5.4, and a summary of the ecoinvent processes that have been selected to model this system are included in Table 5.5. The processes that are used in this LCA, and are presented in Table 5.3 and Table 5.5, represent the best available data upon which to model the systems being studied. Appendix E.2 contains formulas, derivation of other formulas, and calculation of important values that are used in this LCA.

Table 5.1: Summary of General Data and Assumptions for LCA. Table contains data used to model both the mechanical processing and natural dewatering system.

Item	Value	Comments/reference
Specific gravity of impacted area sediments	2.06	Inspect-Sol (2003)
Density of water	1000 $kg \cdot m^{-3}$	Harris (2007)
Functional unit of dredged sediment volume	200,000 m^3	
Dredged sediment volume reduction due to dewatering during dredging operations	50 percent	Inpect-Sol (2003). Functional unit of 200,000 m^3 of dredged sediment volume results in 100,000 m^3 of input sediment volume
Percent of dredged sediment volume that is water, by mass	80 percent	Asquini *et al.* (2007)
Percent of dredged sediment volume that represents dry sediment, by mass	20 percent	Asquini *et al.* (2007)
Percent of dry sediment that is in grain size fraction of silt/clay (less than 63 μm)	95 percent	Tinney (2006)
Percent of dry sediment that is in grain size fraction of greater than 63 μm (assumed to be fine sand)	5.0 percent	Tinney (2006)
Total wet mass of input sediments (per 200,000 m^3 of dredged sediment volume)	120,000 t	See Appendix E.2.4
Total dry mass of input sediment volume (per 200,000 m^3 of dredged sediment volume)	45,000 t	See Appendix E.2.3

Table 5.2: Summary of Data and Assumptions Used to Model the Mechanical Processing System

Item	Value	Comments/reference
Distance from Toronto, ON to Kingston, ON	260 km	Map Quest (2009)
Distance from Kingston, ON to Green Bay, WI	1,400 km	Map Quest (2009)
Distance from Stuart, FL to Kingston, ON	2,300 km	Map Quest (2009)
Distance from brownfield site to Moose Creek landfill	210 km	Map Quest (2009)
Mass of MSWP	500 t	Mann (2009)
Lifespan of MSWP	20 years	Mann (2009)
Power requirements of MSWP	73.6 $MJ \cdot t^{-1}$ (wet volume)	Figure not specific to MSWP, but based on energy requirements of similar process described in Arevalo *et al.* (2007)
MSWP processing rate, by wet volume of sediment	76 $m^3 \cdot hr^{-1}$	Mann (2009)
Percent water, by mass, of processed sediments coming out of the MSWP	25 percent	Specific to MSWP, from Wevers (2009)
Mass of functional unit volume after separation by MSWP	60,000 t	See Appendix E.2.5
Length of project in Kingston Inner Harbour	110 days	Based on dredging rate equal to MSWP processing rate, 18 hours per day of production; as well as 18 days for MSWP transport from Toronto and setup in Kingston, and 14 days take-down of the MSWP to prepare it for shipping

Table 5.3: Summary of Processes Used to Model the Mechanical Processing System

Process	Process	Database	Comments
Materials for MSWP construction allocated to Kingston project	Steel, low-alloyed, at plant/RER S	ecoinvent	Proxy material as exact materials not known, amount of allocation represents 2.4 percent of lifetime of MSWP (20 years)
Nuclear power electricity for MSWP	Electricity, nuclear, at power plant/UCTE S	ecoinvent	51 percent of Ontario power generated by nuclear power stations (OPA, 2005)
Hydroelectric power for MSWP	Electricity, hydropower, at power plant/GR S	ecoinvent	22 percent of Ontario power generated by hydroelectric power stations (OPA, 2005)
Coal power electricity for MSWP	Electricity, hard coal, at power plant/UCTE S	ecoinvent	19 percent of Ontario power generated by coal power stations (OPA, 2005)
Natural gas electricity for MSWP	Electricity, natural gas, at power plant/UCTE S	ecoinvent	7 percent of Ontario power generated by natural gas power stations (OPA, 2005)
Wind powered electricity for MSWP	Electricity, at wind power plant/RER S	ecoinvent	1 percent of Ontario power generated by wind powered stations (OPA, 2005)
Transport of MSWP	Transport, lorry > 32t, EURO3/RER S	ecoinvent	Transport of MSWP from Toronto, ON to Kingston, ON
Landfilling of processed fine-grained sediments	Transport, lorry > 32t, EURO3/RER S	ecoinvent	Transport of processed contaminated silt/clay sediments to landfill, which have been separated by MSWP
Use of processed clean sand on site	Sand, at mine/CH S	ecoinvent	Environmental benefit of processed clean sand that has been separated by MSWP
	Transport, lorry > 32t, EURO3/RER S	ecoinvent	Environmental benefit of not having to produce and transport sand to former tannery site from local sand quarry (25 km)

Table 5.4: Summary of Data Used to Model the Natural Dewatering System

Item	Value	Comments/reference
Distance from brownfield site to dewatering location	10 km	Map Quest (2009)
Distance from dewatering site to Moose Creek landfill	210 km	Map Quest (2009)
Distance excavated soils are transported during dewatering site expansion	5.0 km	Assumption as soil is not adjacent to Knox Farm
Excavation for expansion of dewatering site	40,000 m^3	Extra dewatering pit volume needed to accommodate input sediment volume resulting from functional unit of dredged sediment volume
Density of soils excavated to expand dewatering site	1300 $kg \cdot m^{-3}$	Assumption based on Miller and Tidman (2001)
Mass of input sediments transported from brownfield site to dewatering site	120,000 t	See Appendix E.2.4
Period of time required for sediment dewatering	2.0 years	Estimate based on dewatering during previous sediment project described in R.V. Anderson Associates Ltd. (2003)
Percent water, by mass, of sediments after sitting at the dewatering location for two years	15 percent	Assumption
Mass of sediments after dewatering period	53,000 t	Assuming 15 percent water content of total mass, see Appendix E.2.6

Table 5.5: Summary of Processes Used to Model the Natural Dewatering System

Process	Process	Database	Comments
Excavation of dewatering pit at Knox Farm	Excavation, hydraulic digger/RER S	ecoinvent	
Movement of soil excavated during Knox Farm expansion	Transport, lorry > 32t, EURO3/RER S	ecoinvent	Movement assumed to be 5 km from Knox Farm
Input sediment transport to Knox Farm	Transport, lorry > 32t, EURO3/RER S	ecoinvent	Transportation of input sediments from brownfield site to Knox Farm
Reloading of processed sediments (after 2 yrs) onto trucks at Knox Farm	Transport, lorry > 32t, EURO3/RER S	ecoinvent	
Transport of processed sediments from Knox Farm to landfill	Transport, lorry > 32t, EURO3/RER S	ecoinvent	Transportation of processed sediments from Knox Farm to Moose Creek landfill

5.4 Life Cycle Impact Assessment

5.4.1 Mechanical Processing System

The system network diagram for the mechanical processing system is displayed in Figure 5.3, with the total impact being 490 Pt. Most of the impacts from this system (76 percent) are the result of the transport required to haul the contaminated fine-grained sediments 210 km from the brownfield site to the Moose Creek landfill. The power requirements for the MSWP account for 20 percent of system impacts. Impacts from transporting the MSWP to Kingston, despite its weight, are relatively small because of the acquisition scenario that it will be available after use in Toronto. The release scenario for the mechanical processing system has also assumed that the MSWP would be used in a project subsequent to Kingston, to which the impacts of moving the MSWP from the Kingston site would be allocated. The sensitivity of the total impact of the mechanical processing system to these assumptions is explored in Section 5.5.2. In comparison to transportation and power requirement impacts, MSWP construction impacts allocated to the Kingston project are small (5.6 Pt, 1.1 percent of the total impact) because of the relatively long life of the MSWP (20 years) in relation to the length of time it will be used for the Kingston project (180 days).

It has been assumed within the mechanical processing system that the MSWP will be operated on the brownfield site. However, as detailed in Section 5.5.3, an alternate venue for the MSWP may be considered, and the sensitivity of the mechanical processing system to the movement of the MSWP to an alternate location is explored.

An environmental benefit is achieved through the reuse of sand during the redevelopment of the former tannery property, which is made possible through the separation procedure of the MSWP. Reuse of sand avoids environmental impacts in two ways: this grain size fraction does not have to be transported to the distant Moose Creek landfill, and it eliminates the need to produce sand at the local quarry and deliver it to the brownfield site (25 km). The grain size distribution of sediments within the impacted area, being comprised of 95 percent silt/clay and 5 percent sand, limits the potential benefits from grain size separation. The low proportion of sand in the impacted area sediments reduces the efficiency of MSWP usage, as the benefits would become greater

had the relative proportion of sand been larger. The sensitivity of the mechanical processing impacts to the ratio of fine-grained sediments and sand is explored in Section 5.5.4.

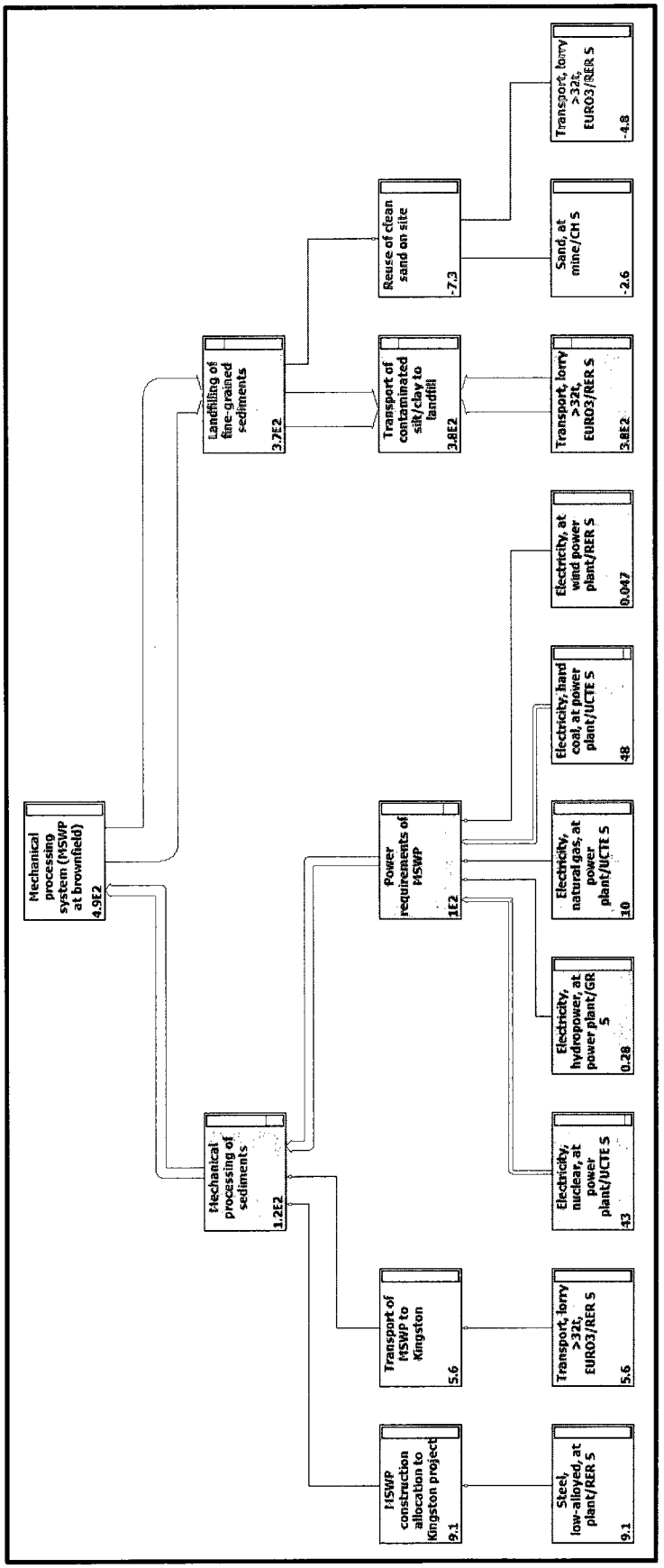

Figure 5.3: Tree Diagram for the Mechanical Processing System. Almost 76 percent of the impacts flow from disposal transport requirements for the fine-grained sediments, which will be landfilled at the Moose Creek landfill, 210 km from the brownfield site. Despite the large mass of the MSWP (500 t), transporting this equipment to Kingston results in a relatively small impact (approximately 1.1 percent of the total) because of the acquisition scenario that it will be available from Toronto, and a subsequent project for the MSWP (to which release scenario impacts will be allocated) will be identified.

Figure 5.4 displays midpoint category characterization of the entire mechanical processing system. All midpoint categories, except ionizing radiation, are dominated by the impacts of transporting contaminated fine-grained sediments from the brownfield site to the Moose Creek landfill. Figure 5.5 displays the normalized midpoint scores for the mechanical processing system, *excluding* waste scenario processes. This assessment reveals that impacts from ionizing radiation are relatively small, and originate almost exclusively from power-generation processes (specifically, from nuclear power generation).

Figure 5.6 displays the normalized midpoint scores for the *entire* mechanical processing system. Within this system, high-leverage midpoint categories are non-renewable energy, respiratory inorganics, and global warming; most of these impacts are related to burning fuel during sediment disposal transport. Terrestrial ecotoxicity has limited leverage on the total impact score, accounting for 5.1 percent of total impacts. The normalized damage scores for the entire mechanical processing system are presented in Figure 5.7. The resources damage category receives the highest proportion of impacts, followed by human health and climate change. A low proportion of impacts to ecosystem quality are present.

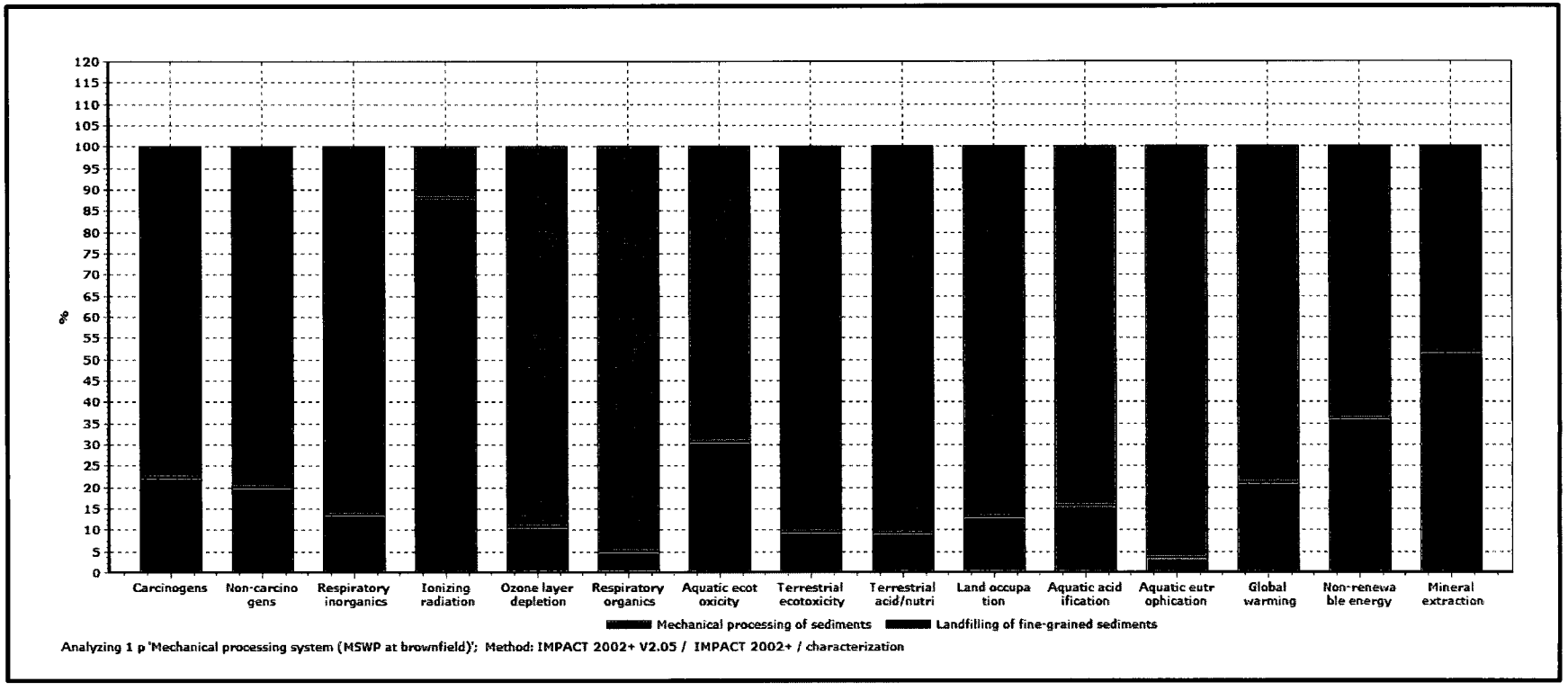

Figure 5.4: Midpoint Category Characterization of the Mechanical Processing System. All categories except ionizing radiation are dominated by impacts originating from contaminated fine-grained sediment disposal, which must be transported 210 km from the brownfield site to Moose Creek landfill.

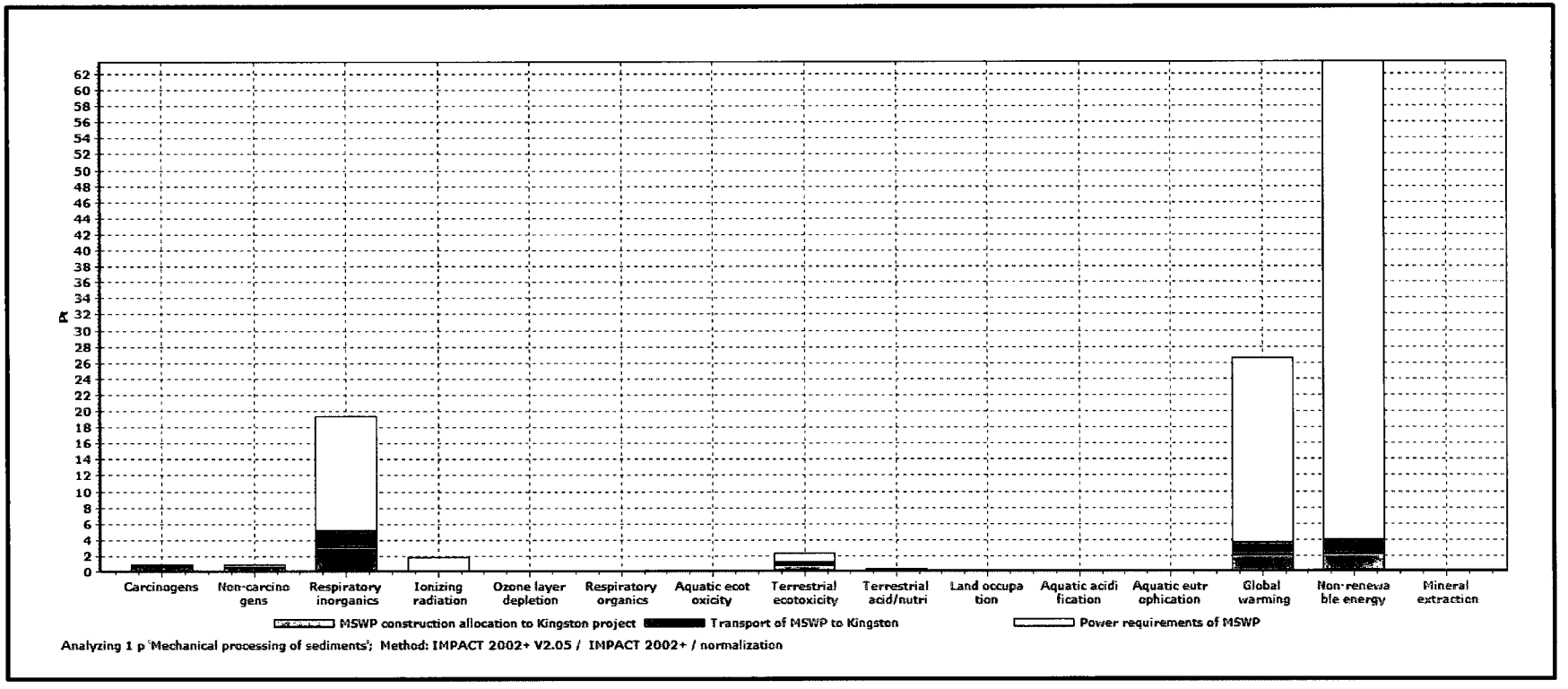

Figure 5.5: Normalized Midpoint Scores for the Mechanical Processing System, Excluding Waste Scenario Processes. Non-renewable energy, global warming, and respiratory inorganics are high-leverage midpoint categories, and are each dominated by impacts originating from power generation for the MSWP. The sole source of ionizing radiation is power generation, and is almost exclusively due specifically to nuclear power generation.

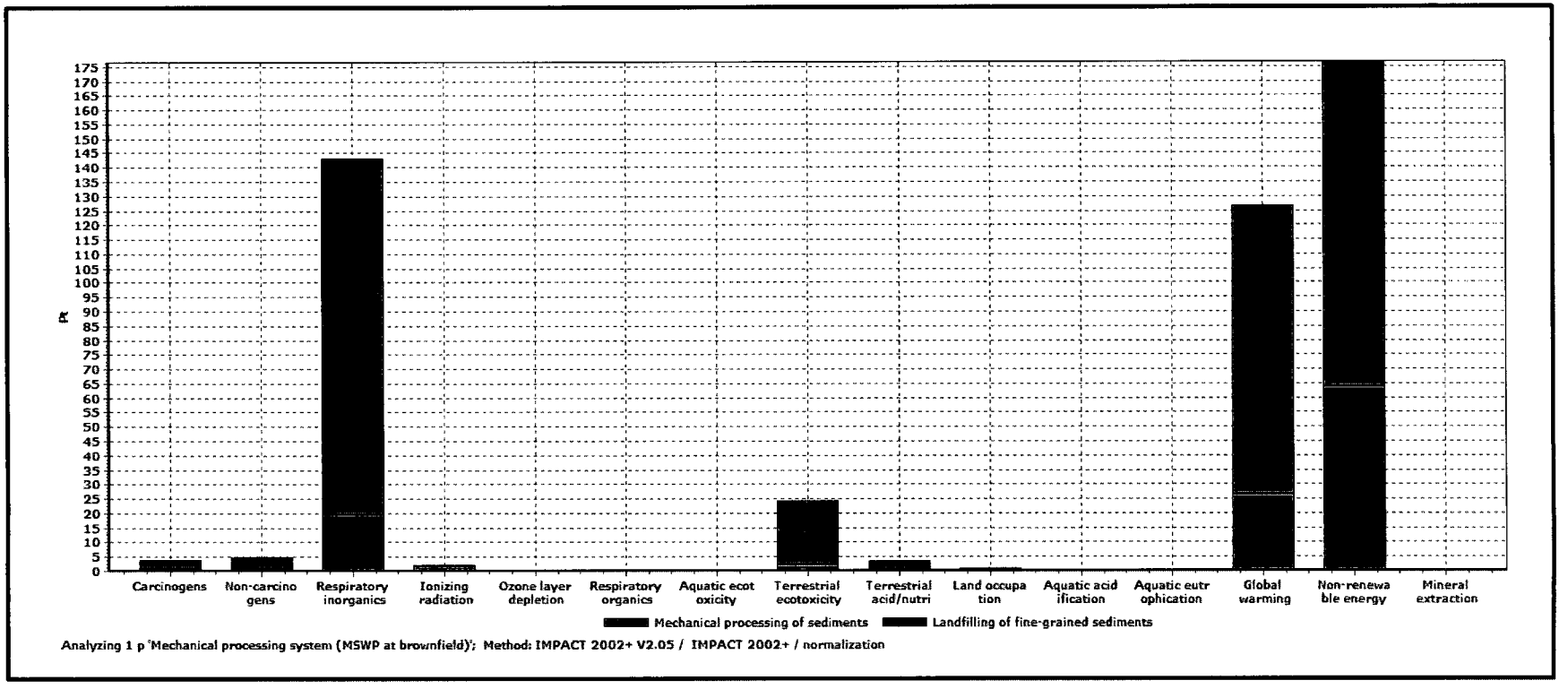

Figure 5.6: Normalized Midpoint Scores for the Entire Mechanical Processing System. Again, the high-leverage midpoint categories are non-renewable energy, respiratory inorganics, and global warming. Across all damage categories the disposal of fine-grained sediments accounts for most impacts, which originate from the burning of fuel during transport processes.

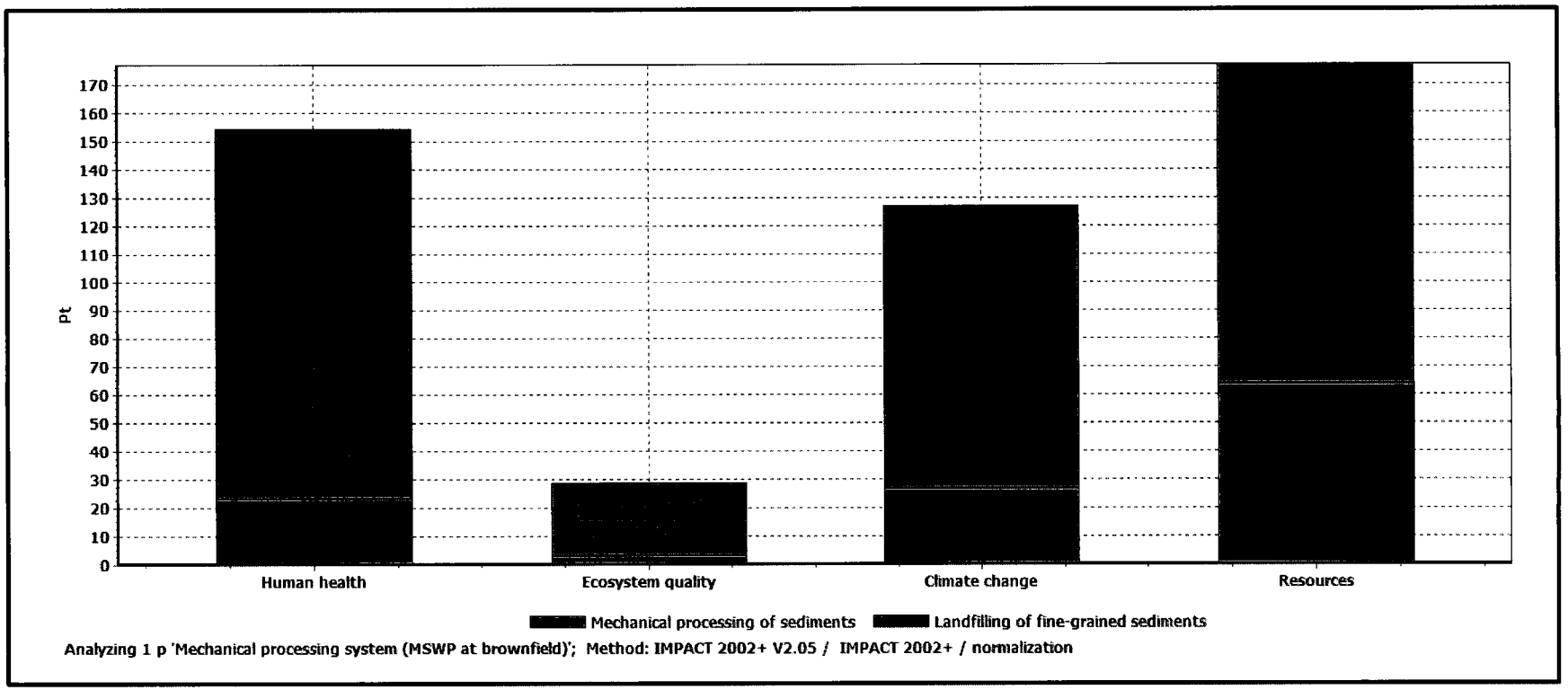

Figure 5.7: Normalized Damage Scores for the Entire Mechanical Processing System. The proportion of impacts of this system is highest to resources, but is also significant to human health and climate change. There are a low proportion of impacts to ecosystem quality.

5.4.2 Natural Dewatering System

The tree diagram for the natural dewatering system is displayed in Figure 5.8, with the total impact being 550 Pt. Similar to the mechanical processing system, and supported by the midpoint category characterization in Figure 5.9, most impacts (97 percent) flow from transport requirements: transportation is required to move excavated soil in the expansion of the dewatering pits (5.0 km), to move the saturated dredged sediments from the brownfield site to Knox Farm (10 km), and then move the dewatered sediments from Knox Farm to the Moose Creek landfill (210 km). The distance that dredged sediments are transported from the brownfield site to Knox Farm is relatively small compared with the distance that dewatered sediments are transported from Knox Farm to the Moose Creek landfill. However, the impacts of the first process are disproportionately large because the dredged sediments that are transported to Knox Farm are saturated, and these will have been substantially dewatered before transport to the Moose Creek landfill.

As previously stated the current dewatering location at Knox Farm can hold 60,000 m^3 of sediments. The process of expanding the sediment dewatering pits (to contain the 100,000 m^3 volume of the functional unit) accounts for the additional 40,000 m^3 of pit volume and has an impact of 21 Pt. Therefore, each additional 100,000 m^3 of dredged sediment that may be dewatered at Knox Farm (beyond the initial 100,000 m^3) will have an impact of 580 Pt, as a full 100,000 m^3 of sediment pit creation will have an impact of approximately 53 Pt. The effect of increasing the sediment pits will be discussed in greater detail in Section 5.5.1.

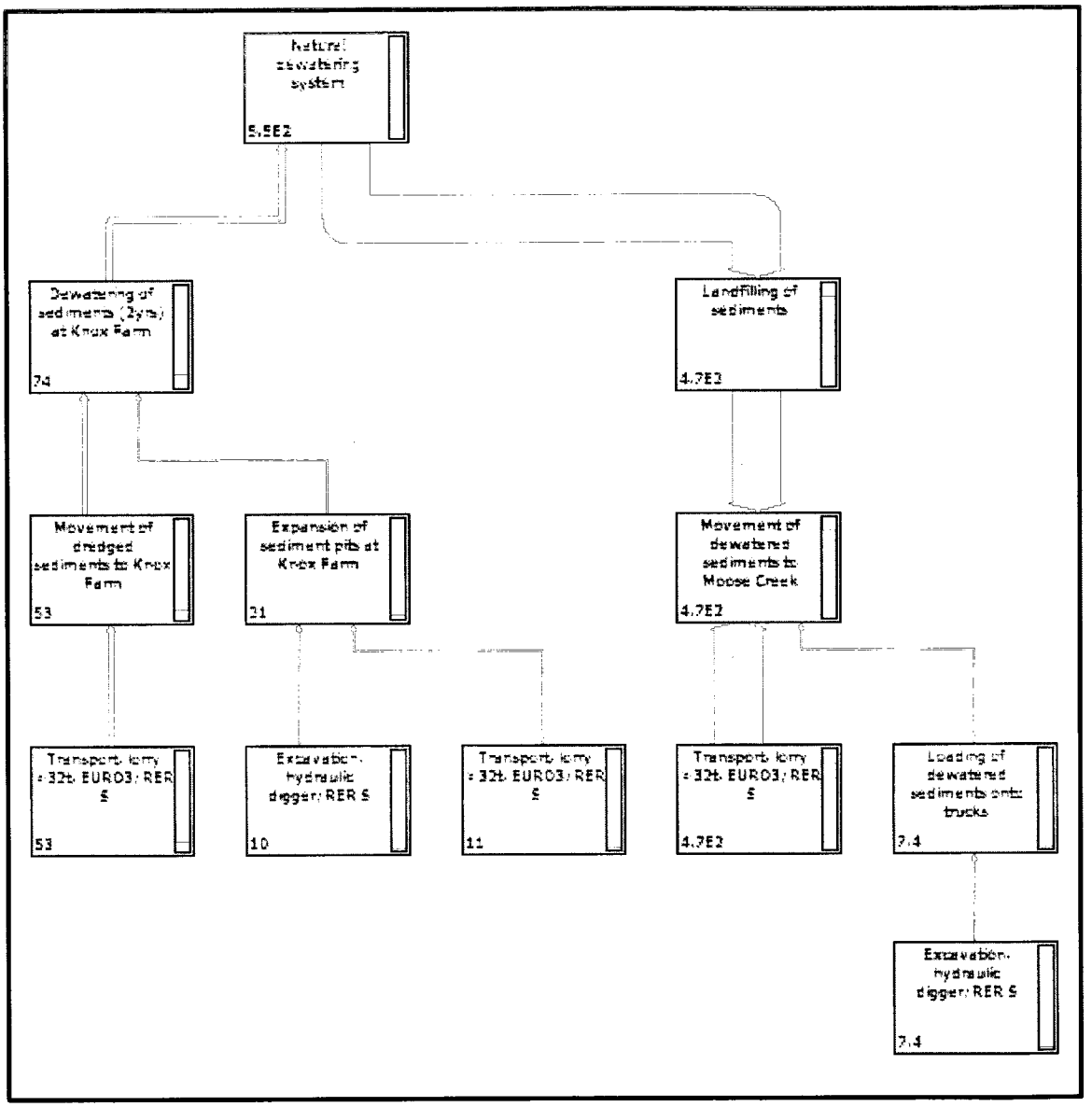

Figure 5.8: Tree Diagram for the Natural Dewatering System. Most impacts in this system (97 percent) flow from transportation requirements: transportation is required to move excavated soil in the expansion of the dewatering pits (5.0 km), to move the saturated dredged sediments from the brownfield site to Knox Farm (10 km), and then move the dewatered sediments from Knox Farm to Moose Creek landfill (210 km).

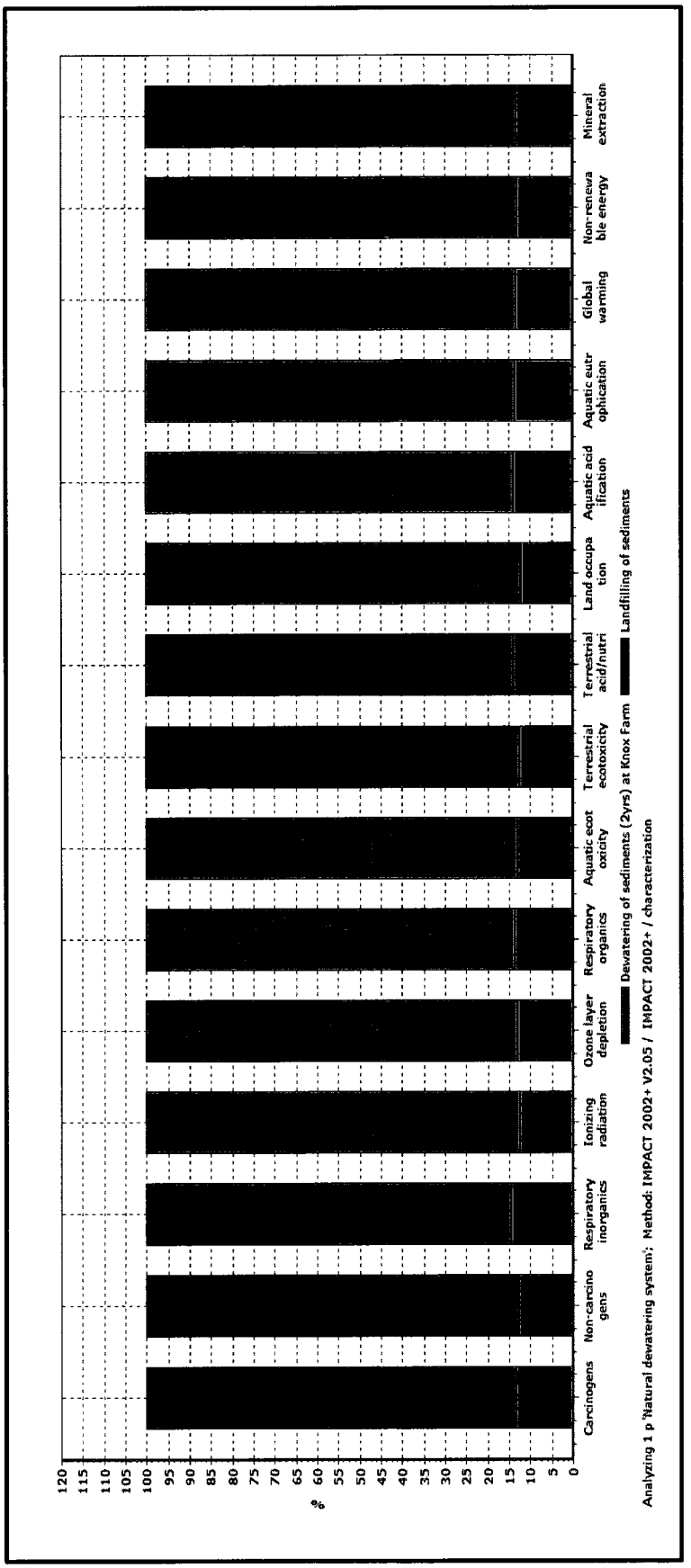

Figure 5.9: Midpoint Category Characterization of the Natural Dewatering System. All midpoint categories are dominated by impacts from transporting dewatered sediments from Knox Farm to Moose Creek landfill, a distance of 210 km.

Figure 5.10 displays the normalized midpoint scores for the natural dewatering system. Within this system, high-leverage midpoint categories are respiratory inorganics, non-renewable energy, and global warming; similar to the mechanical processing system, most of these impacts are the result of burning fuel during transport processes. Figure 5.11 displays the normalized damage scores for the natural dewatering system. The damage category with the highest impacts is human health, followed by resources and then climate change. Similar to the mechanical processing system, there is a low proportion of impacts to ecosystem quality.

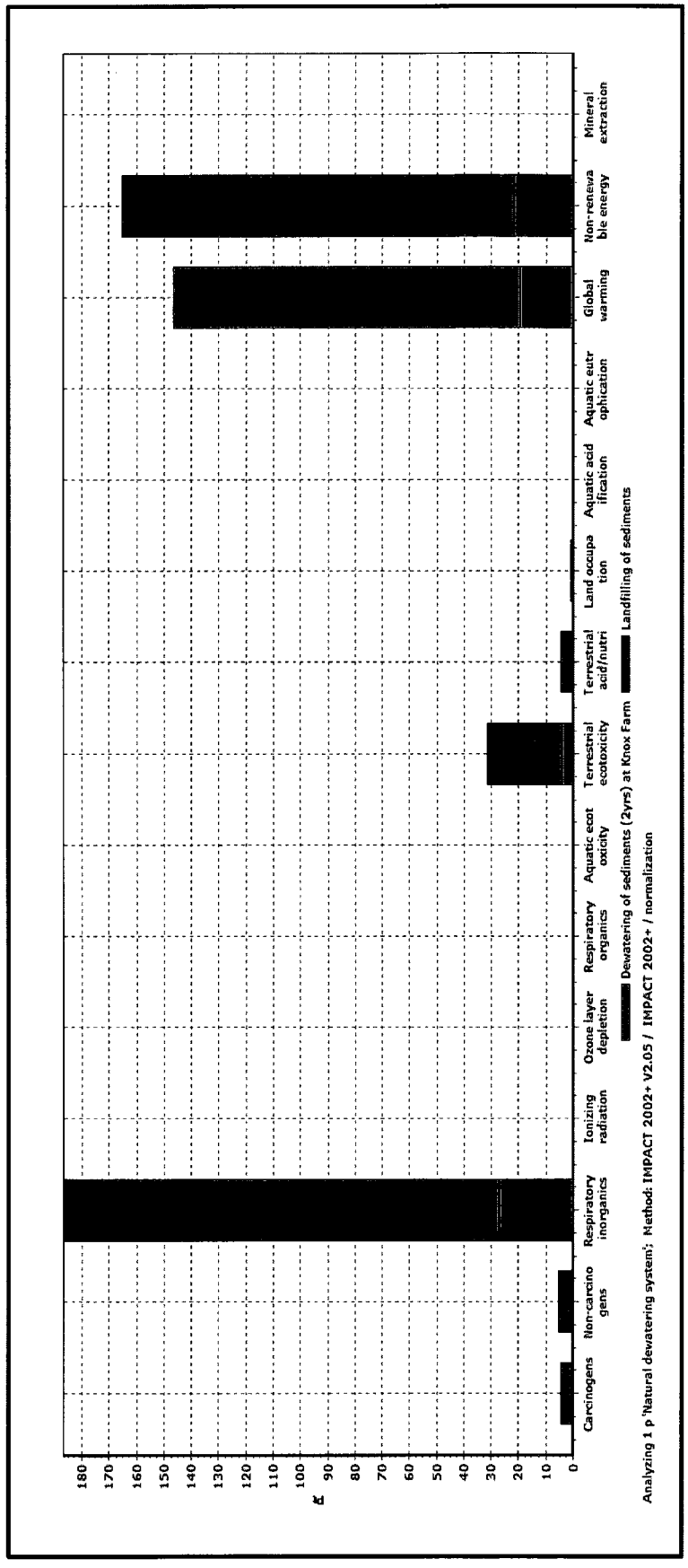

Figure 5.10: Normalized Midpoint Scores for the Natural Dewatering System. The high-leverage midpoint categories for this system are respiratory inorganics, non-renewable energy, and global warming.

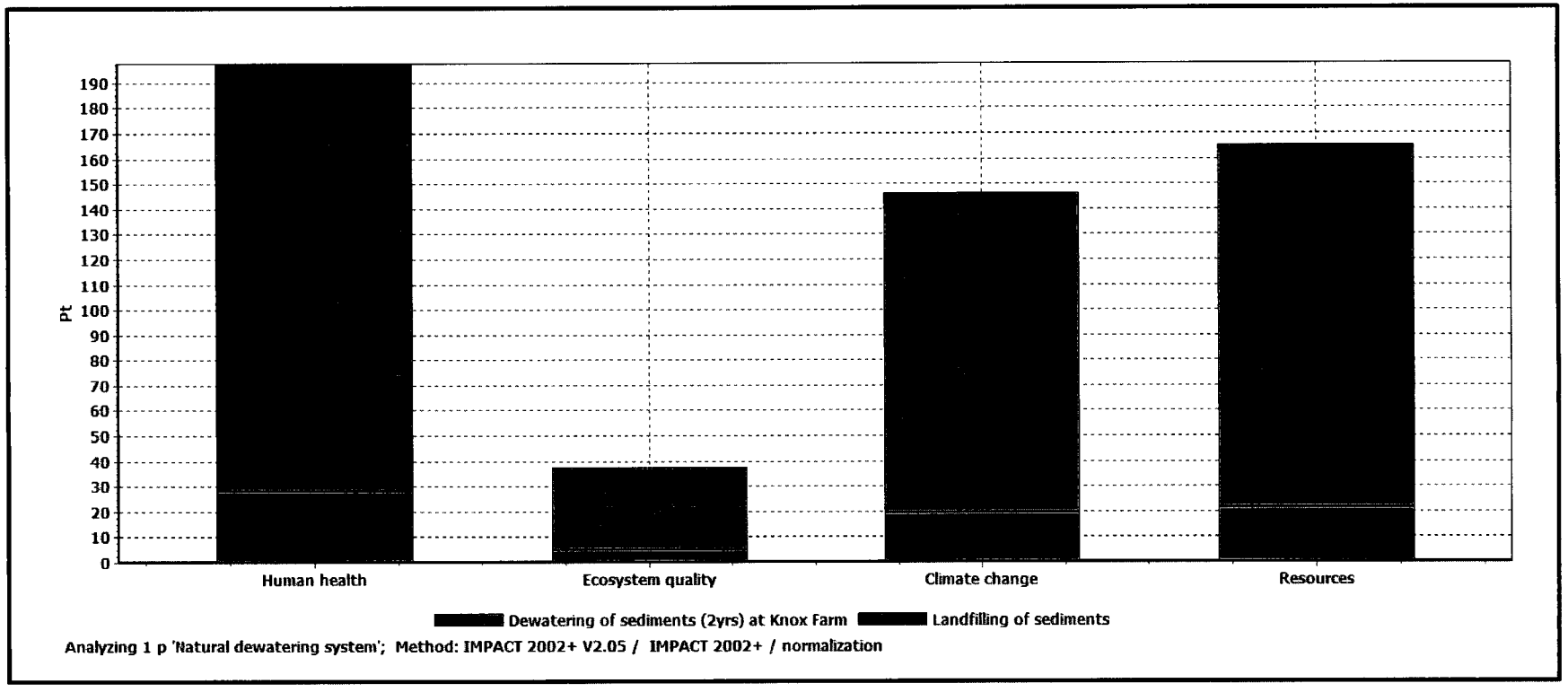

Figure 5.11: Normalized Damage Scores for the Natural Dewatering System. The proportion of impacts of this system is highest to human health, followed by resources and climate change. Similar to the mechanical processing system, there are a low proportion of impacts to ecosystem quality.

5.5 Interpretation

5.5.1 Comparison of Mechanical Processing System to Natural Dewatering System

This LCA is essentially a comparison between the impacts of the fuel requirements that are necessary for each system. In comparing the total impact of each system for the functional unit (the first 100,000 m^3 of dredged sediment), the mechanical processing system (490 Pt) has a slightly lower impact than the natural dewatering system (550 Pt).

In comparing the normalized midpoint scores for the mechanical processing system and the natural dewatering system (Figure 5.12), the impacts in high-leverage midpoint categories from the natural dewatering system are highest in respiratory inorganics and global warming, while the mechanical processing system has higher impacts to non-renewable energy. Figure 5.13 displays a comparison between the normalized damage scores for the two systems: the natural dewatering system is highest in impacts to human health, climate change, and ecosystem quality; the mechanical processing system is highest in impacts to resources. Figure 5.14 displays a comparison of normalized single-score damage results for both systems.

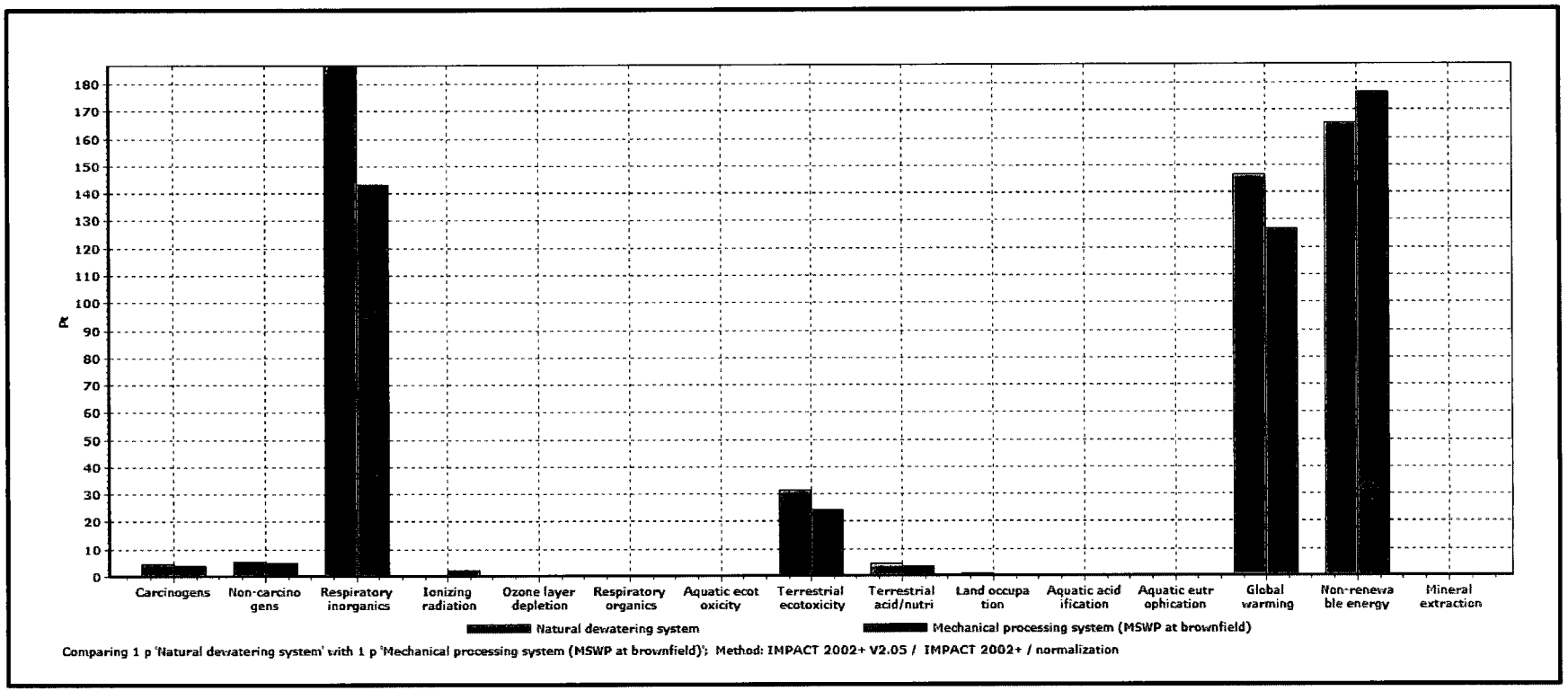

Figure 5.12: Comparison of Normalized Midpoint Scores for Both Systems. Across the high-leverage midpoint categories, the natural dewatering system is highest in impacts for respiratory inorganics and global warming, while the impacts of the mechanical processing system are higher for non-renewable energy.

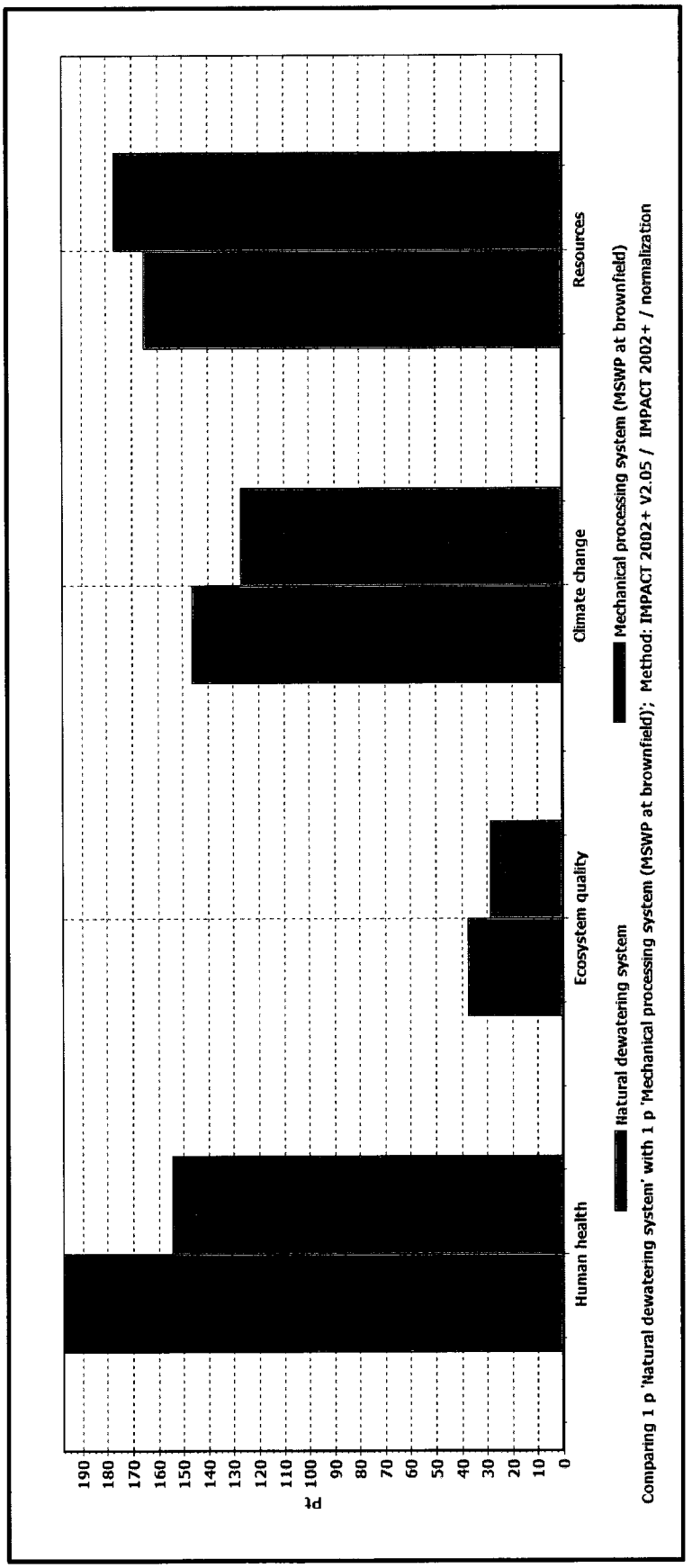

Figure 5.13: Comparison of Normalized Damage Scores for Both Systems. The natural dewatering system is highest in impacts to human health, climate change, and ecosystem quality; the mechanical processing system is highest in impacts to resources.

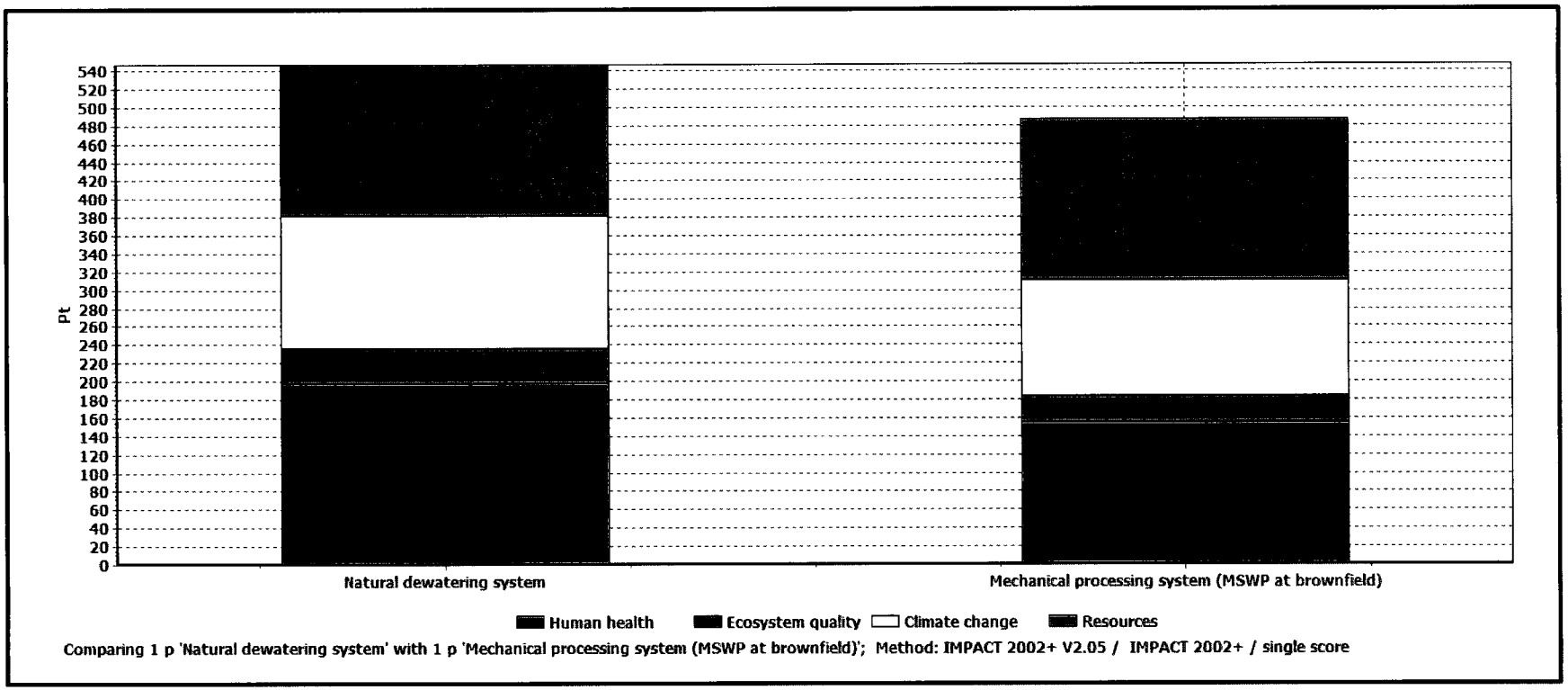

Figure 5.14: Comparison of Single-score Normalized Damage Results for Both Systems. For the functional unit (the first 100,000 m^3 of dredged sediment), the total impact of the mechanical processing system (490 Pt) is slightly lower than the total impact of the natural dewatering system (550 Pt).

As mentioned in Section 5.4.2, the functional unit only accounts for 40,000 m^3 of dewatering pit expansion at Knox Farm, as 60,000 m^3 of volume is already available at the site. Essentially, impacts from expansion of the sediment holding pits at Knox Farm exist for all dewatered volumes above 60,000 m^3; therefore impacts from the natural dewatering system become disproportionately larger as the pit volume required at Knox Farm increases. It is not known what volume of contaminated sediments may potentially be dredged from the impacted area, and it is important to determine the interval of dredged volumes for which each dewatering and disposal alternative is favored.

The impact, in Pt, of the mechanical processing system can be thought of as having two components: a fixed impact and a variable impact. The *fixed* impact is that which is *independent* of the volume of sediment that is dredged from the river, dewatered, and reused or disposed of. The *variable* impact is that which is *proportional* to the amount of sediment that is dredged, dewatered, and reused or disposed of. The fixed impact associated with the mechanical processing system is the sum of two factors: the impact of the transportation of the MSWP to Kingston, and the associated MSWP life span usage during this transport for the steel on which the MSWP construction was modeled. The total fixed impacts for the mechanical processing system is 7.20 Pt, while the remainder of the processes are variable and depend on how much sediment is processed in the MSWP (e.g. electricity for MSWP operation). The variable relationship is assumed to be linear because electrical requirements of the MSWP, disposal transport requirements for the dredged sediments, as well as "impact savings" because of the reuse of sand on site, are all directly proportional to the amount of impacted area sediment processed in the MSWP. When graphed with the x-axis as volume of sediment (s, in thousands of m^3) and the y-axis in Pt, the function describing the impact of the mechanical processing system use is Equation 5.1. Note that the y-intercept is the fixed impact, because it is the impact before any sediment is processed in the MSWP (i.e. when s = 0).

$$(Pt) = 2.40s + 7.20 \qquad \mathbf{(5.1)}$$

The natural dewatering alternative has no fixed impacts; only variable impacts. This system is more complicated than the mechanical processing system because for the first 60,000 m^3 there are no variable impacts due to dewatering location expansion (as 60,000 m^3 of space currently exists), but after 60,000 m^3 there is an additional variable impact due to dewatering location expansion. In this LCA, we have assumed that the dewatering location can be expanded to suit the needs of the project. For the dredged sediment volume interval from zero to 60,000 m^3, the function describing total impacts of the natural dewatering system is Equation 5.2. As the natural dewatering system has no fixed impacts in this interval, the y-intercept equals zero.

$$(Pt) = 2.63s \tag{5.2}$$

In the volume interval of 60,000 m^3 to infinity, which includes the additional variable impacts from the necessity to expand the dewatering pits at Knox Farm, the total impact of the natural dewatering system are described by Equation 5.3. The significance of the y-intercept in this equation is that 33.0 Pt is the excavation and soil transport impacts that are avoided due to the prior existence of 60,000 m^3 of dewatering pits. Notice the greater slope of Equation 5.3 in comparison to Equation 5.2, resulting from the increased variable impact from dewatering pit expansion.

$$(Pt) = 2.90s - 33.0 \tag{5.3}$$

The function describing the mechanical processing system (Equation 5.1) and those describing the natural dewatering system (Equations 5.2 and 5.3) are displayed in Figure 5.15. The function for the natural dewatering system can be seen to increase at 120,000 m^3. The slope of the function describing the mechanical processing system is always lower than that of the natural dewatering system, meaning that the mechanical processing system is less impactful when only considering the actions of dewatering and disposing of contaminated sediments. However, because the mechanical processing system has a fixed impact to overcome, a factor not present within the natural dewatering system, there is a small interval over which the natural dewatering system is the

alternative with the lowest impact. The functions for the mechanical processing system and the natural dewatering system intersect at a dredged volume of 33,000 m^3. At dredged volumes less than 33,000 m^3, the mechanical processing system has a larger total impact than the natural dewatering system. At dredged volumes greater than 33,000 m^3, the mechanical processing system has a lower total impact than the natural dewatering system. However, the divergence in total impact between the two systems is not dramatic; the point at which the total impact of the natural dewatering system begins to exceed a 10 percent increase over the mechanical processing system is at 160,000 m^3.

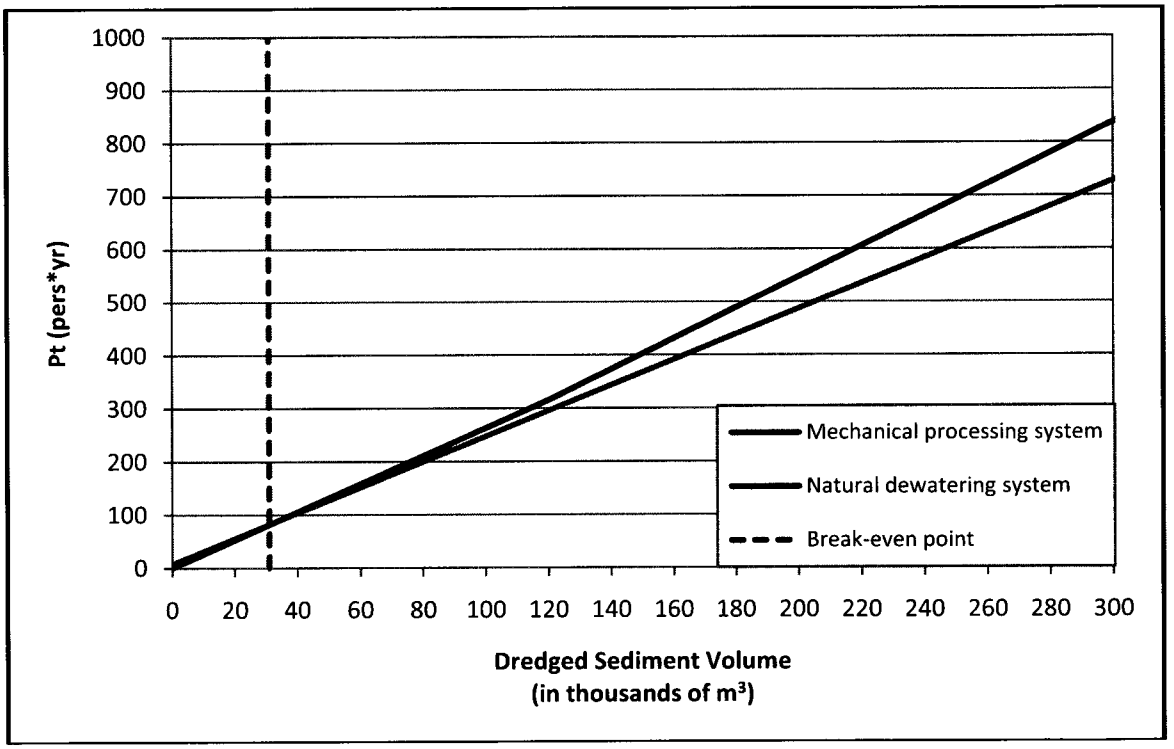

Figure 5.15: Graphical Representation of Impacts for Both Systems. Notice the increase in the slope of the dewatering system function at 120,000 m^3, which is due to the additional impact associated with expanding the current dewatering site at Knox Farm. At dredged volumes above 33,000 m^3, the mechanical processing system has a lower impact than the natural dewatering system. However, the divergence of impacts of the two systems is slight; the total impact of the natural dewatering system is not more than 10 percent greater than the total impact of the mechanical processing system until a dredged volume of 160,000 m^3.

5.5.2 Sensitivity of Results to Acquisition and Release Scenarios for the MSWP

Allocation procedures for MSWP transportation impacts, as well as the MSWP acquisition and release scenarios used in this LCA, have been outlined in Section 5.2.4. Transportation of the MSWP, because of its large weight, can result in significant impacts and the sensitivity of the mechanical processing system to different acquisition and release scenarios will be explored.

Assuming the MSWP acquisition scenario is still Toronto, if the Kingston project is undertaken but no subsequent project is identified, the MSWP release scenario (at the time of writing) is assumed to be Green Bay and transportation impacts of the release will be allocated to the Kingston project. The function describing the total impact of the mechanical processing system, with an acquisition scenario of Toronto and a release scenario of Green Bay, is Equation 5.4.

$$(Pt) = 2.40s + 37.4 \quad \textbf{(5.4)}$$

If the Toronto project for the MSWP had not been identified, the acquisition scenario for the MSWP would have been Stuart, FL. Assuming once again that no MSWP project subsequent to the Kingston project was identified (once again, making the probable release scenario become Green Bay, WI), in this worst-case scenario for MSWP transportation, the function describing the total impact of the mechanical processing system is Equation 5.5.

$$(Pt) = 2.40s + 81.8 \quad \textbf{(5.5)}$$

Figure 5.16 is a graphical comparison between the mechanical processing system (under the three possible MSWP acquisition and release scenarios identified in this LCA) with the natural dewatering system. Notice that the slopes of each of the three mechanical processing systems are identical and their functions are parallel. This characteristic is explained by the fact that MSWP acquisition and release scenarios only affect the fixed

impact (y-intercept) of each respective equation; variable impacts are constant in all scenarios as they are only dependent on how much sediment is processed in the MSWP, which is identical in each case. If the MSWP acquisition scenario is Toronto and the release scenario is Green Bay, the mechanical processing system will only have less impact than the natural dewatering system at dredged volumes above 140,000 m^3. If the MSWP acquisition scenario is Stuart, FL and the release scenario is Green Bay, the mechanical processing system will only have less impact than the natural dewatering system at dredged volumes above 230,000 m^3.

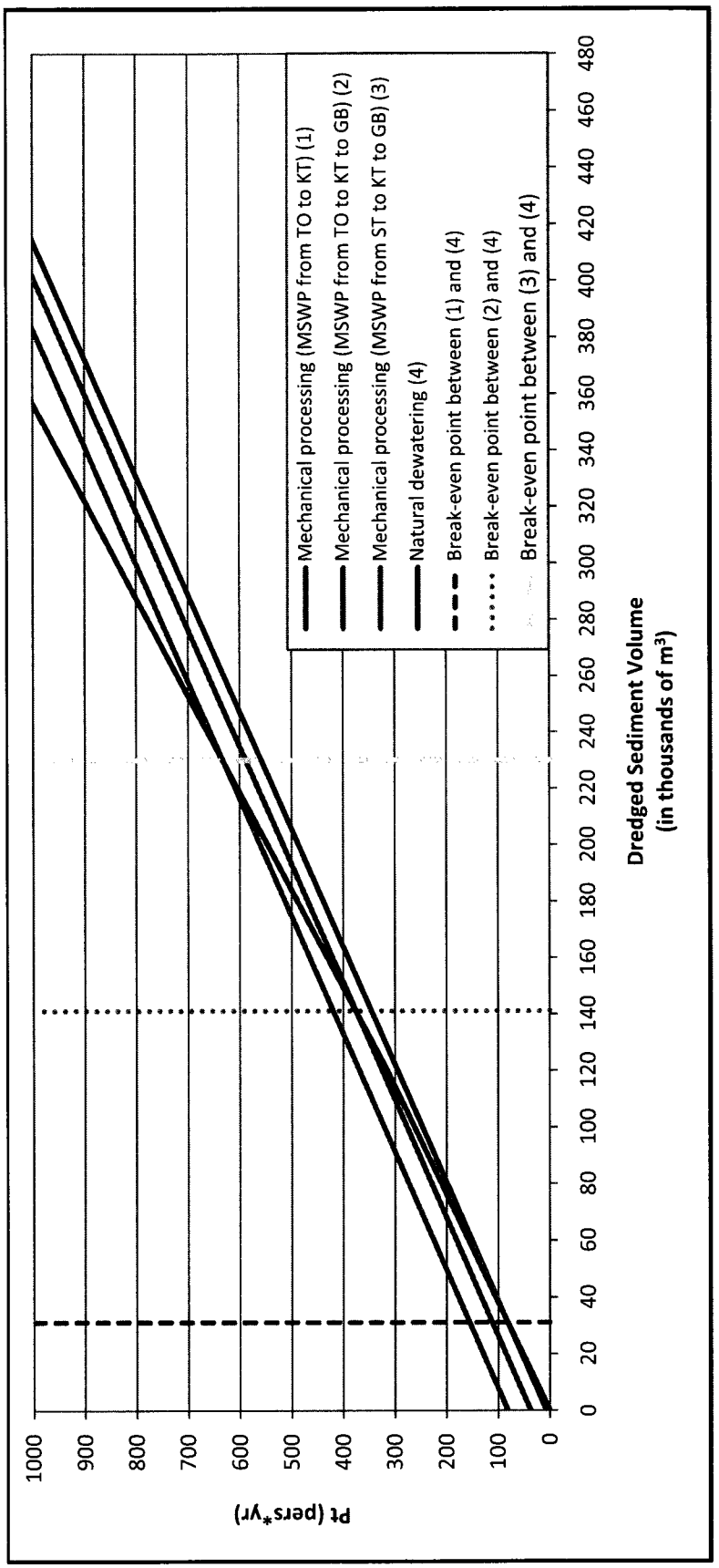

Figure 5.16: Comparison of Acquisition and Release Scenarios for the MSWP of the Mechanical Processing System with the Natural Dewatering System. If the MSWP acquisition scenario is Toronto (TO) and the release scenario is Green Bay (GB), WI, mechanical processing is favored for dredged volumes above 140,000 m^3. If the MSWP acquisition scenario is Stuart (ST), Florida, and the release scenario is Green Bay, mechanical processing is favored for dredged volumes above 230,000 m^3.

5.5.3 Sensitivity of Results to Location of MSWP Operation

This LCA has been modeled based on the MSWP being located at the brownfield site. However, it is possible that remediation managers may explore the option of locating the MSWP at Knox Farm. The MSWP venue may change because having the MSWP at the brownfield site may create too much noise adjacent to a residential area. If options for an alternate venue were to be explored, Knox Farm would be likely as it is relatively close to the brownfield site and there is space to process the sediments near that location. Equation 5.6 describes the impact of transporting the dredged sediments to Knox Farm, processing them with the MSWP at that location, and disposing of the contaminated sediments at Moose Creek landfill. In this alternate MSWP venue scenario, it is assumed that any clean sand would be used at the Knox Farm facility.

$$(Pt) = 2.66s + 7.20 \quad \textbf{(5.6)}$$

Figure 5.17 displays the impact of mechanical processing both at the brownfield site and at Knox Farm, as well as natural dewatering at Knox Farm. Mechanical processing at Knox Farm would not have a lower total impact than the natural dewatering alternative until dredged volumes greater than approximately 170,000 m^3. However, the difference in impacts between the mechanical processing system (at Knox Farm) and the natural dewatering system is relatively small throughout the entire range of potential dredged sediment volumes (likely not greater than 250,000 m^3).

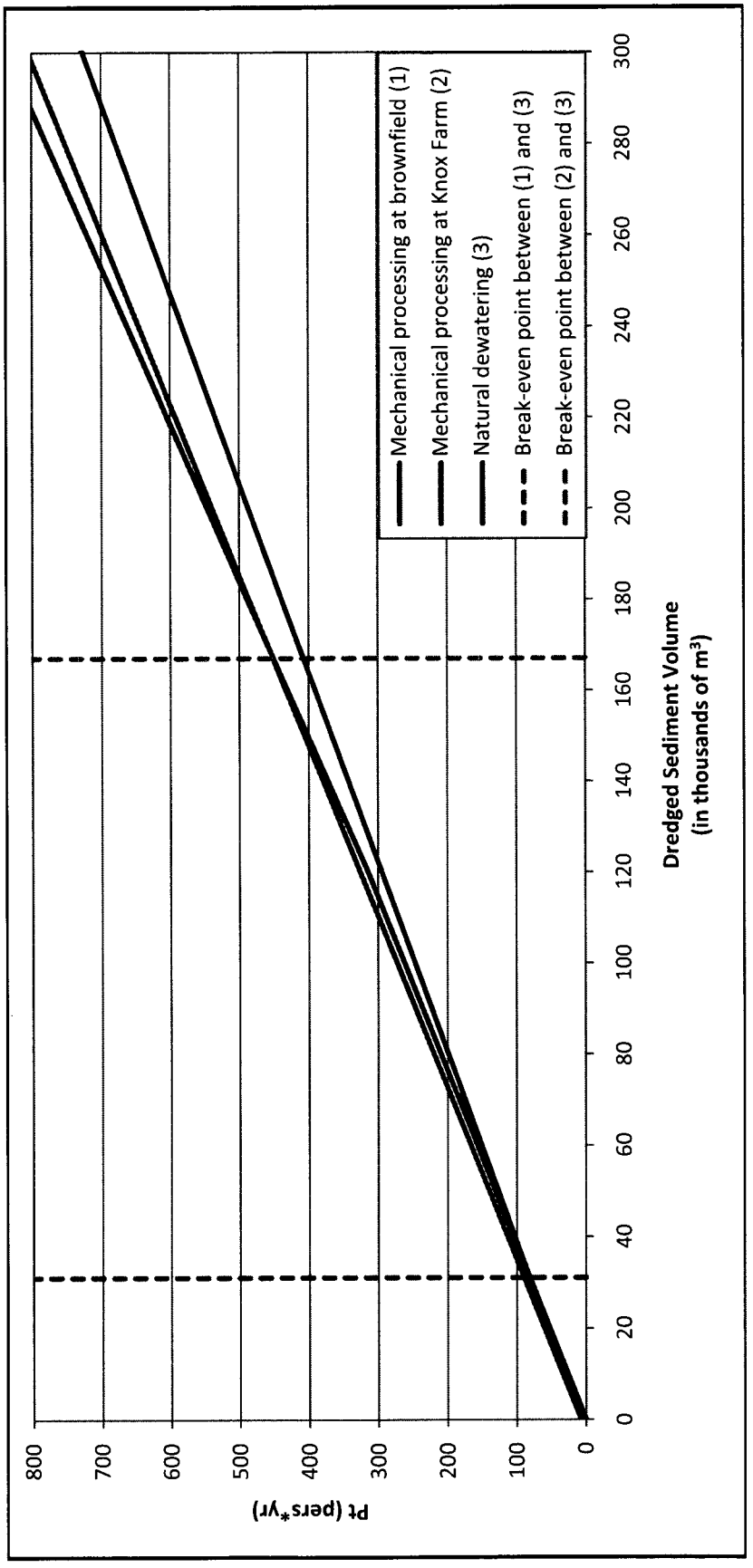

Figure 5.17: Graphical Representation of Impacts of the Mechanical Processing System (at the Brownfield Site and at Knox Farm) and the Natural Dewatering System. If mechanical processing cannot take place at the brownfield site, and the closest alternative location for the MSWP is Knox Farm, natural dewatering is the alternative with the least impacts for all dredged volumes below approximately 170,000 m^3.

5.5.4 Sensitivity of Mechanical Processing System to Fine-Grained Sediment Proportion

Sediments within the impacted area are known to be approximately 95 percent fine-grained sediments and 5 percent sand (Tinney, 2006; Asquini *et al.*, 2007), and this LCA has been modeled accordingly. Because the sand fraction within the sediments of the impacted area is not substantial, the potential benefit from sorting clean sand from contaminated silt/clay is modest. In Figure 5.18, the results for the impacted site have been contrasted with the result that would have occurred had the impacted site possessed a similar sediment grain size composition to the Fox River in Green Bay, WI. Fox River is currently the site of large-scale sediment remediation (due to PCBs), and uses a sediment separation process identical in principal to the MSWP, except on a much larger scale. Within Fox River, the silt/clay fraction is only 65 percent and the sand fraction is 35 percent (Lammers, 2009). As shown in Figure 5.18, the mechanical processing system becomes the overwhelmingly favorable alternative when the sand fraction is higher, as more uncontaminated sediments are diverted from being transported to a landfill and are available for reuse. In general, as the sand fraction becomes higher, the mechanical processing system becomes more efficient and its use increases impact avoidance compared with the natural dewatering system.

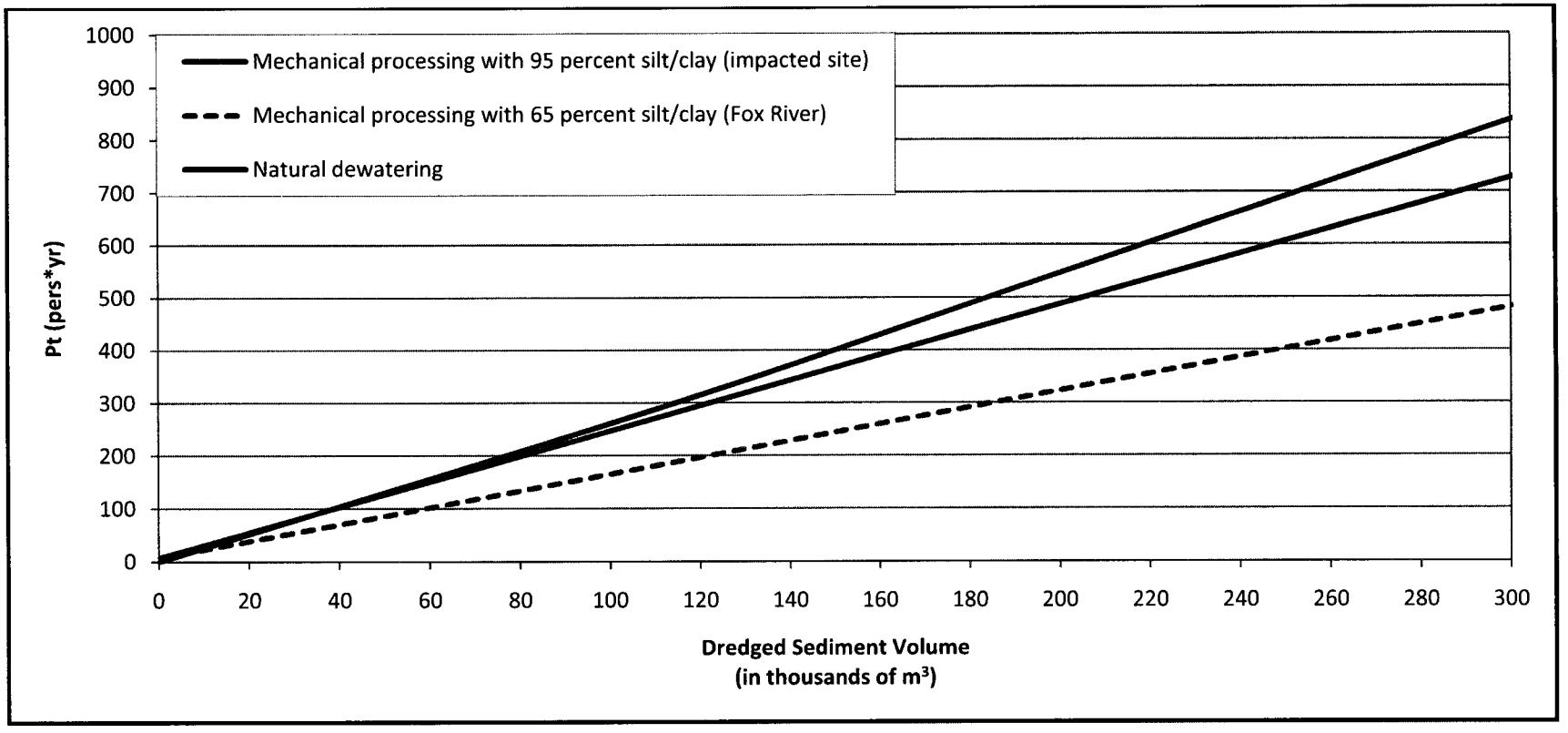

Figure 5.18: Comparison of Impacts for Both Systems for Different Scenarios of Silt/Clay and Sand Proportions in Sediments. The sediments of the impacted site are known to be approximately 95 percent silt/clay and 5 percent sand, and although the mechanical processing system results in less impact than the natural dewatering system, the difference is not dramatic. This is because relatively little sand is diverted from being transported to landfill (and are available for reuse) by the grain size separation process used by the MSWP. However, if the impacted site had 65 percent silt/clay and 35 percent sand, similar to the Fox River cleanup in Green Bay, WI, where the soil washing process is being used, the mechanical processing system is dramatically more favorable than the natural dewatering system. This is because a large fraction of the sediments are diverted from transport to landfill and are available for reuse.

5.5.5 Conclusion

As modeled in this LCA, the mechanical processing system will result in fewer environmental impacts than the natural dewatering system for volumes of dredged sediment greater than 33,000 m^3. However, the divergence in total impact between the two systems is slight; the point at which the total impact of the natural dewatering system begins to exceed a 10-percent increase over the mechanical processing system is at 160,000 m^3. In comparing damage assessment results, the mechanical processing system has higher impacts to resources, while the natural dewatering system has higher impacts to human health, climate change and ecosystem quality.

The mechanical processing system is sensitive to different MSWP acquisition and release scenarios. As more MSWP transportation impacts are present within the mechanical processing system, the more sediment must be processed in the MSWP before this system become less environmentally impactful than the natural dewatering system. A similar result exists as the distance increases that dredged sediments must be hauled to the site MSWP processing.

The LCA methodology is an effective tool to assess environmental impacts from alternative methods for dewatering and disposing of dredged sediments. Although a dramatic difference was not found between the mechanical processing system and the natural dewatering system (within the dredged sediment volume interval that is likely for the Kingston project), this LCA has shown how sensitive the results are to the equipment and sediment transportation assumptions that have been made, as well as the natural characteristics of the impacted area. In locations where dredged sediments have a higher proportion of sand that can be separated by a MSWP (or similar process), the benefits from using mechanical processing systems can become substantial.

5.5.6 Future Work

Assumptions made in this LCA could be verified and refined to increase its accuracy. The most important data that could be verified are:

i. if the dewatered contaminated sediments can be disposed of entirely at the Moose Creek landfill;

ii. if the current dewatering location at Knox Farm could be expanded to suit the needs of the project, and if not, where the dewatering location would potentially be for additional sediment volumes;

iii. the site-specific density of the soil to be excavated for the expansion of the Knox Farm dewatering location;

iv. if the dewatering location at Knox Farm was to be expanded, what is the destination for the excavated soils;

v. the precise water content of the sediments that have been dewatered at Knox Farm for two years;

vi. what material(s) is it best to model the construction of the MSWP on;

vii. what are the MSWP-specific power requirements;

viii. what volume of water does the water-based processing of the MSWP require, and will the MSWP treat its own wastewater if used on impacted area sediments;

ix. if the Kingston project were to use the MSWP, and no other subsequent project was identified, what is the location to which it would be shipped back to the owning company;

x. if additional contaminated soils and sediments, not originating from the impacted area, would be processed in the MSWP if this technology was available in Kingston. A potentially large source of additional soils that could be processed in the MSWP may originate from remediation of the former tannery brownfield.

CHAPTER 6: CONCLUSIONS

Historical industrial activities within the Kingston Inner Harbour have left behind a legacy of contamination that remains to the current day. The most heavily impacted area includes the Orchard Street Marsh and the portion of the Great Cataraqui River that is located south of Belle Island and east of the former Davis Tannery property. Although the surface water quality within this impacted area is generally good, sediments at this aquatic site are known to exceed CCME sediment quality guidelines for many organic and inorganic contaminants.

A semi-quantitative ERA, conducted in accordance with guidance literature from CCME (1996) and ASWG (Chapman, 2010) was performed for the impacted area to assess risk to various receptors classes. Because they are the most dominant and widespread contaminants within the sediments of the impacted area, ecological impacts to receptors were evaluated due to the following CoPCs: As, Cr, Cu, Pb, Hg, Zn, and PCBs. This ERA showed that muskrat are a species at high risk because of Cr(III) ingestion, and mink are at intermediate risk because of PCBs. Depending on their actual feeding characteristics within the impacted area, great blue herons and osprey may be at intermediate risk because of MeHg. In comparison to CRTGs and IJC criteria developed for mammalian and avian piscivorous wildlife, tissue residues of Hg and PCBs from selected fish species living in the impacted area (brown bullhead, yellow perch, and northern pike) often significantly exceeded the specified thresholds, especially for PCBs.

While CRTGs and IJC criteria are conservative in nature, impacted area field observations of brown bullhead revealed a substantial presence of morphological abnormalities, which are both much less severe and much less frequent at reference sites. Although brown bullhead tissue residues were found to be low in comparison to fish toxicity thresholds for all CoPCs, the available fish toxicity thresholds are not specific to brown bullhead. The brown bullhead has a particularly intimate relationship with the sediment, and unique toxicity thresholds may be required for this species to properly assess its risk to contaminants. In addition, toxicity thresholds do not account for possible additive or synergistic effects due to complex mixtures of contaminants, such as those found within the impacted area, and therefore risk may be further underestimated.

Ultimately, the observation of vastly disproportionate numbers of deformities within a single location is compelling evidence of adverse conditions.

Previous studies, including those studying bioaccumulation of contaminants, sediment toxicity tests, and analyses of benthic community structure, have identified other adverse biological effects occurring within the impacted area as a result of contaminated sediments. The result of the semi-quantitative ERA has provided a further line of evidence for adverse biological effects. Consequently, a remediation strategy options and feasibility analysis was conducted for the river portion of the impacted area. This options analysis concluded that, given the natural characteristics of this aquatic area, dredging is the most appropriate sediment remediation strategy to achieve short-term and long-term human health and ecological risk reduction[1]. Chromium speciation analysis on sediment pore water from the impacted area determined that there exists no Cr(VI) that could be liberated into the water column during dredging operations. The result of this pore water analysis is particularly valuable, as there is very little available literature on chromium speciation in pore water that has been contaminated with tannery effluent, and because peepers were demonstrated to be a simple and reliable method for pore water sampling.

The use of LCA in assessing remediation alternatives is presently novel, but is emerging as a powerful tool for use by ecological decision-makers. LCA was found be an impressive and effective tool for distinguishing the environmental impacts of potential alternatives for the dewatering and disposal of dredged sediments. LCA allowed the identification of dredged sediment volume intervals over which specific alternatives result in fewer impacts. Specifically, the LCA conducted for the mechanical processing system and the natural dewatering system identified that, given the assumptions and available data for the assessment, the mechanical processing system results in fewer impacts for dredged sediment volumes in excess of 33,000 m^3. In general, the natural dewatering system has higher impacts to human health, climate change, and ecosystem quality, while the mechanical processing system has higher impacts to resources. The utility of the LCA methodology in assessing these alternatives was further evidenced by

[1] Preceding any dredging operations, however, an archeological survey of the impacted area is recommended as this site may contain historically significant submerged vessels.

its capability to identify the sensitivity of the results to equipment and sediment transport assumptions, as well as the grain size distribution present within the river portion of the impacted area.

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Appendix A: Maps

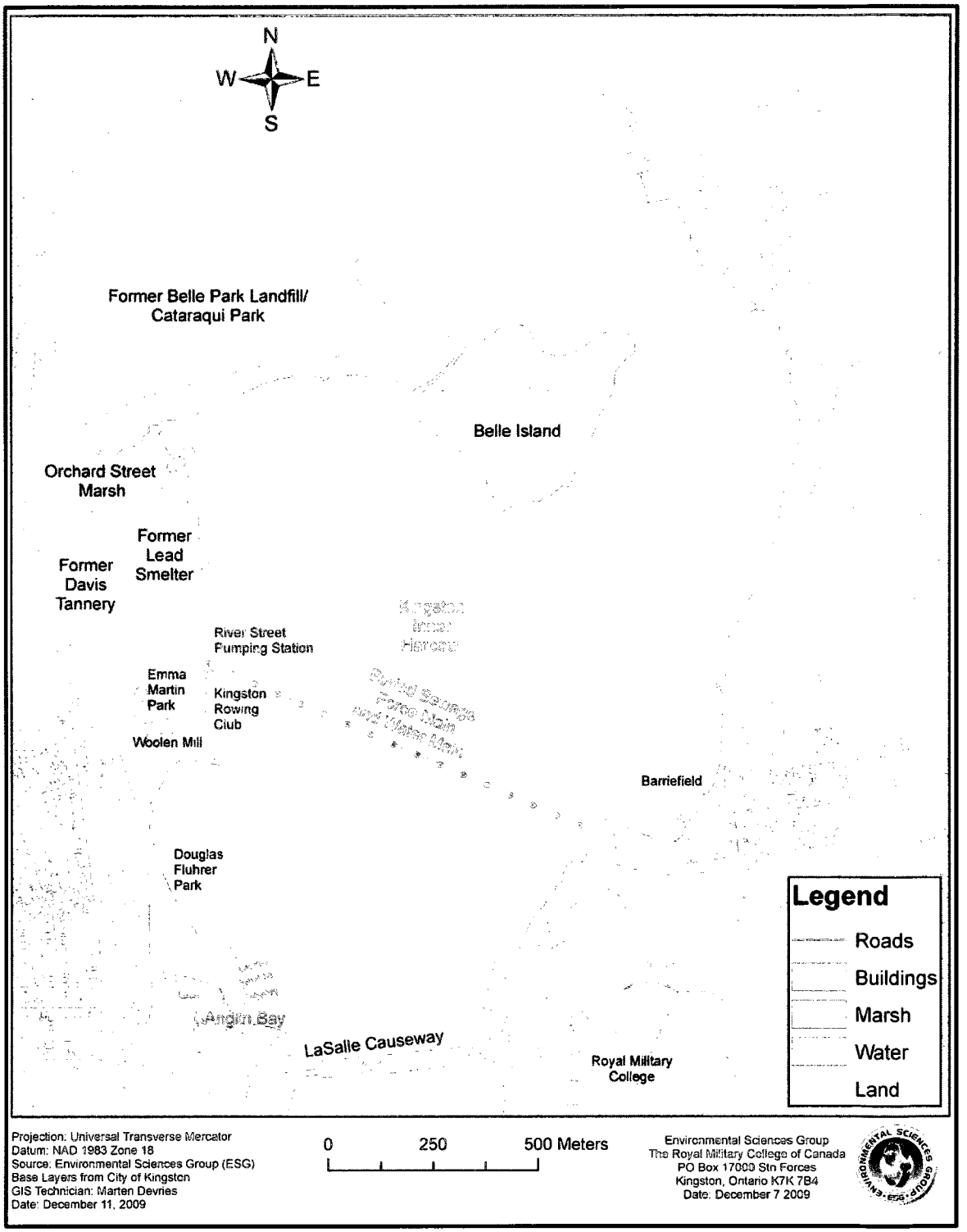

Figure A.1: Geographical Features and Land Use within the Kingston Inner Harbour (ESG, 2009b)

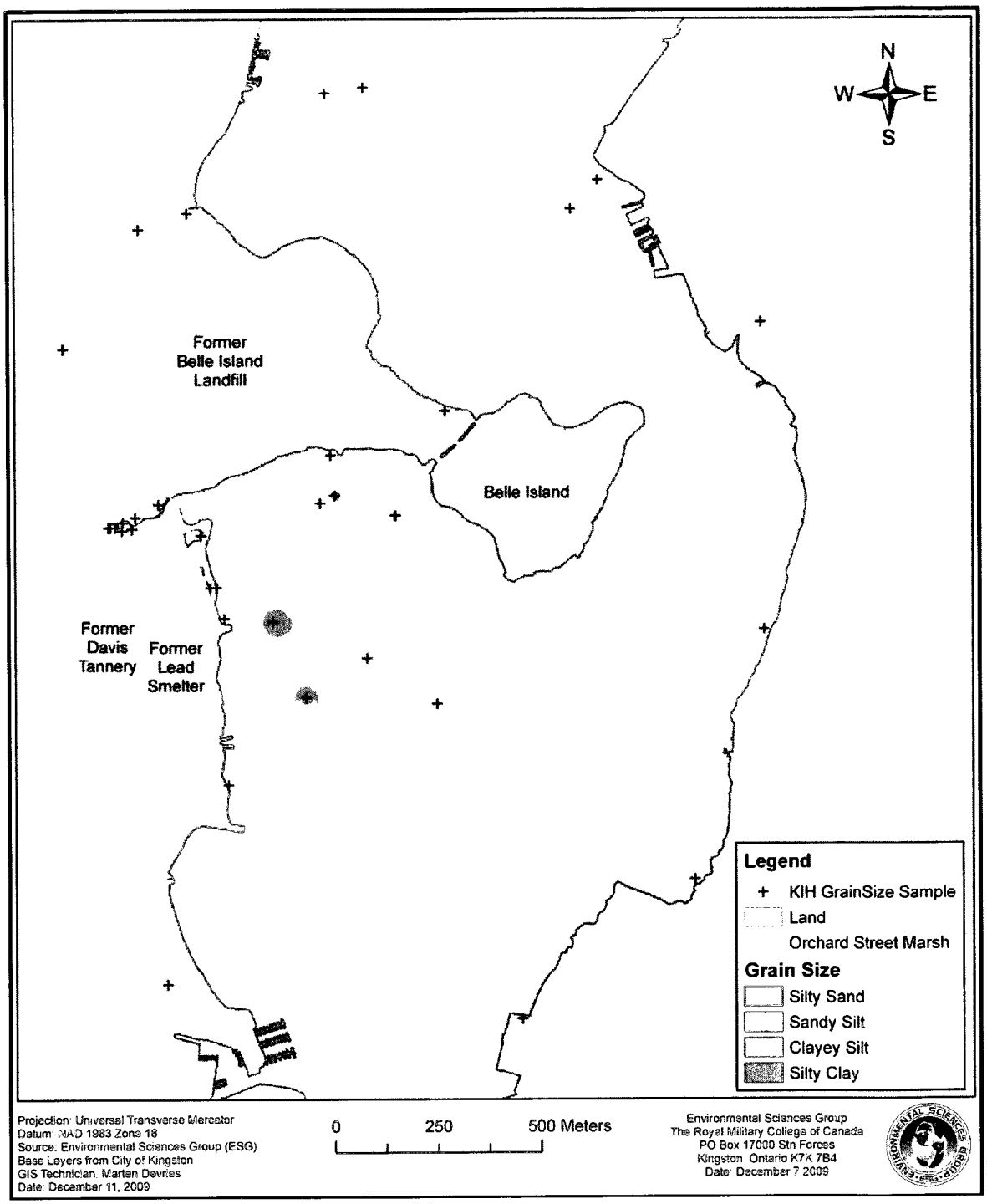

Figure A.2: Distribution of Fine-grained Surface Sediments within the Kingston Inner Harbour (ESG, 2009b)

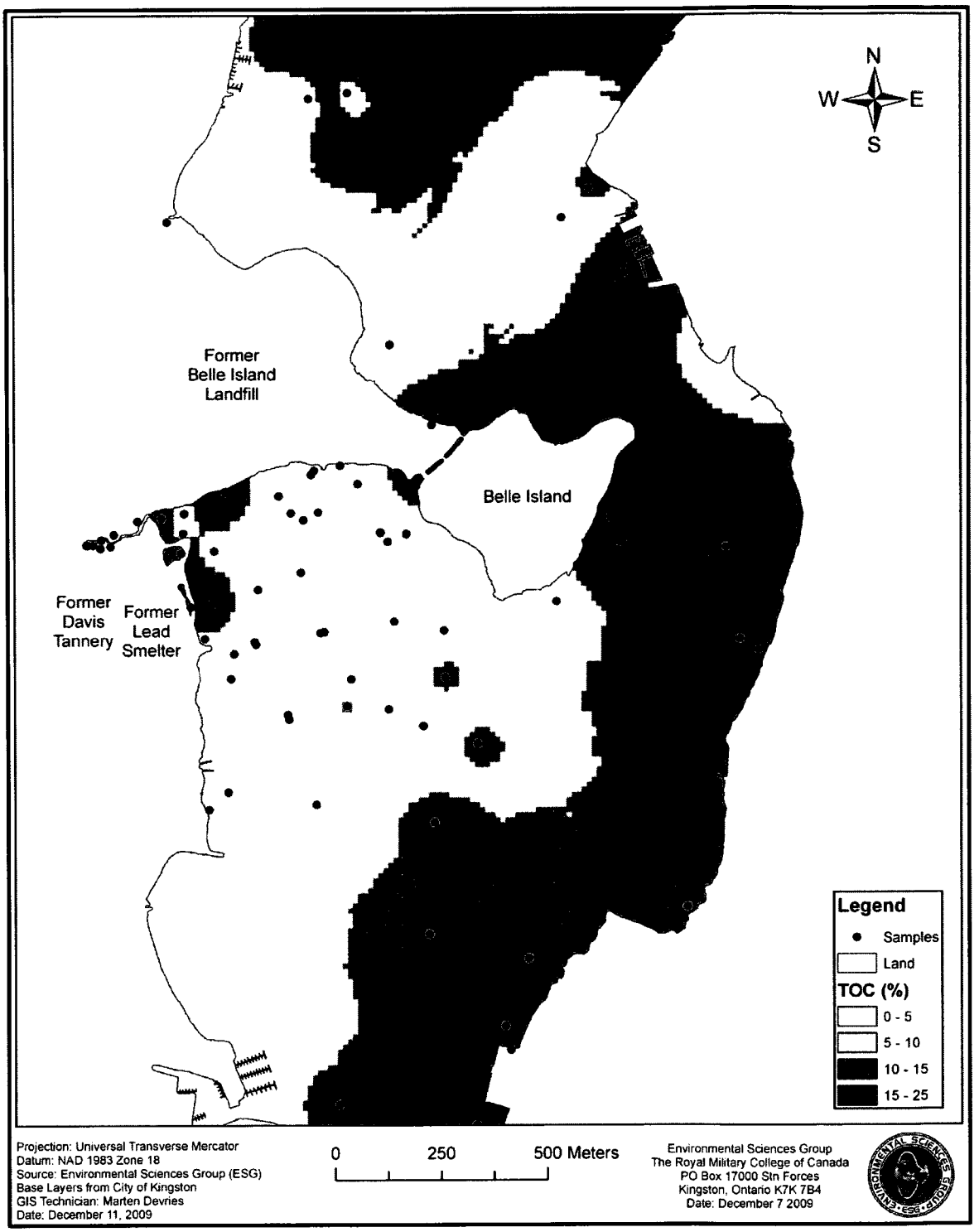

Figure A.3: Distribution of Total Organic Carbon in Surface Sediments within the Kingston Inner Harbour (ESG, 2009b)

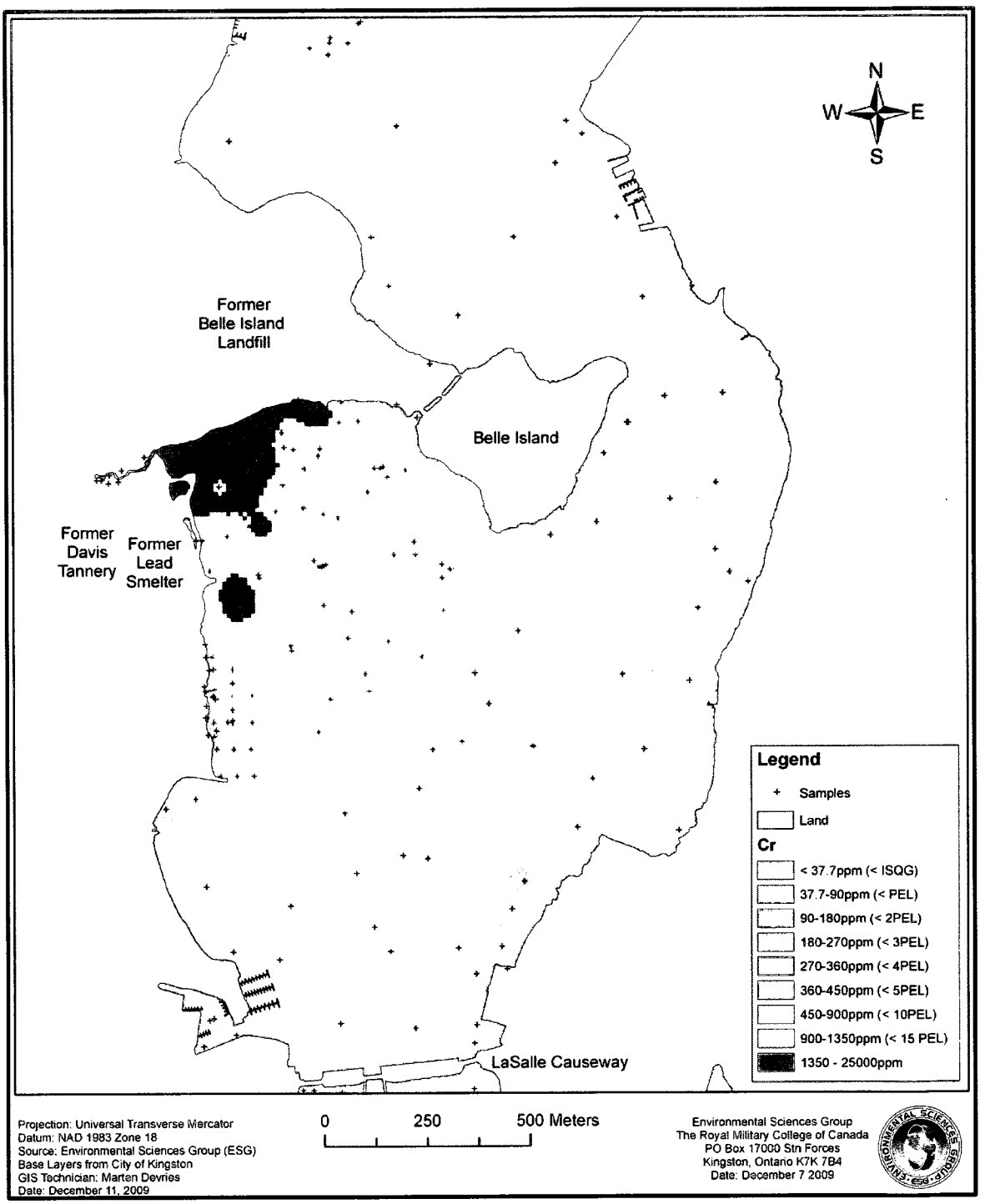

Figure A.4: Distribution of Chromium within Surface Sediments of the Kingston Inner Harbour (ESG, 2009b)

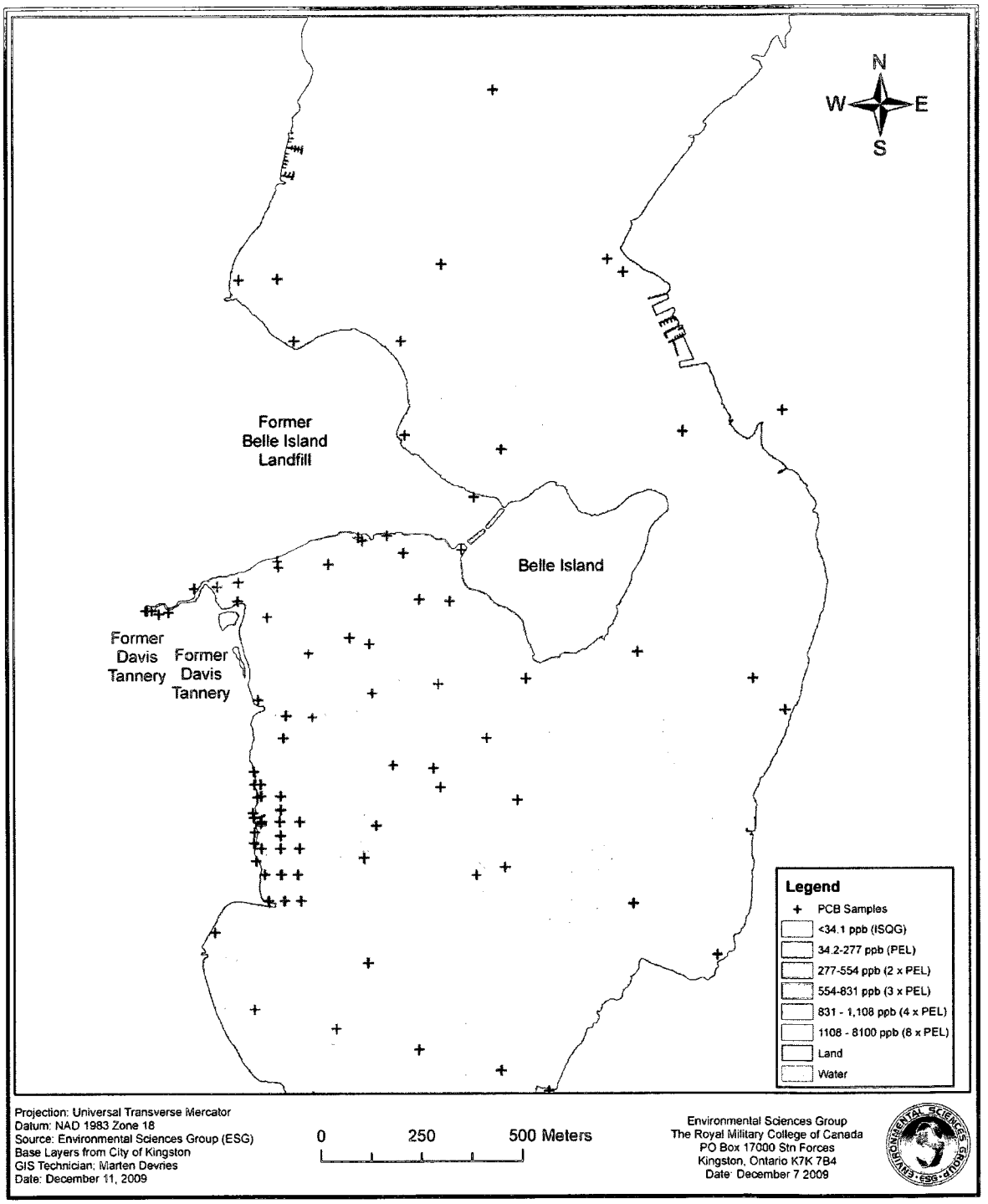

Figure A.5: Distribution of PCBs within Surface Sediments of the Kingston Inner Harbour (ESG, 2009b)

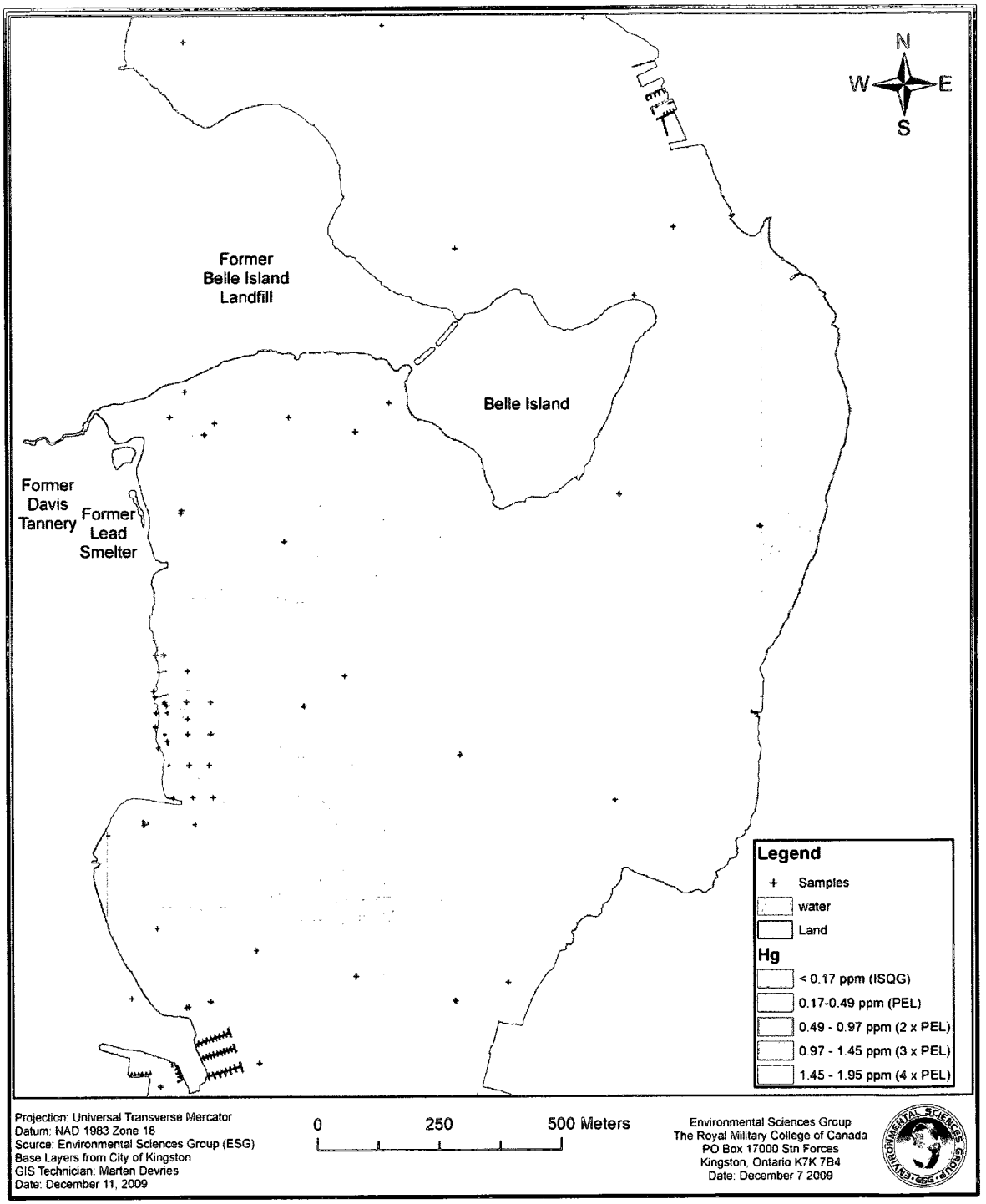

Figure A.6: Distribution of Mercury within Surface Sediments of the Kingston Inner Harbour (ESG, 2009b)

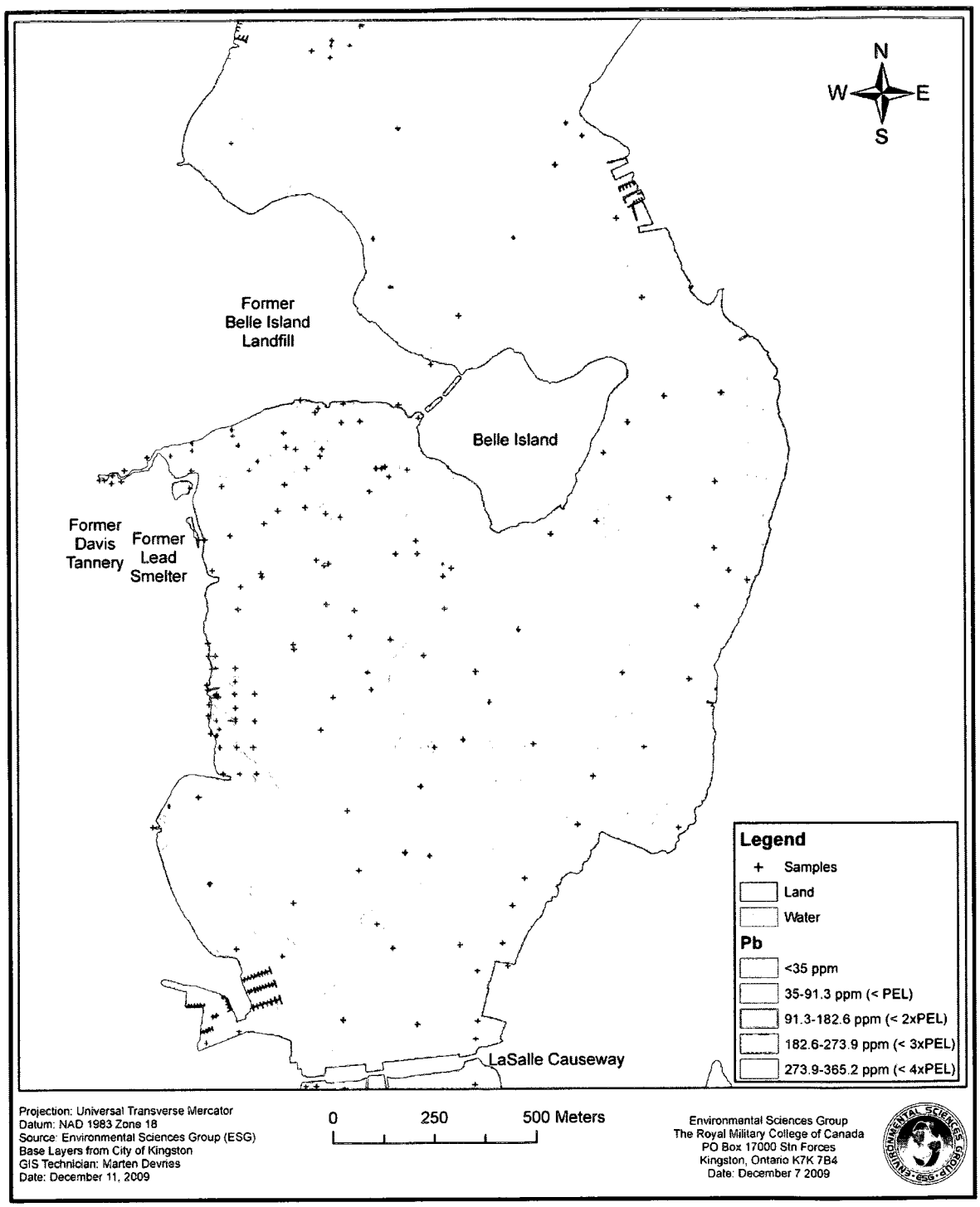

Figure A.7: Distribution of Lead within Surface Sediments of the Kingston Inner Harbour (ESG, 2009b)

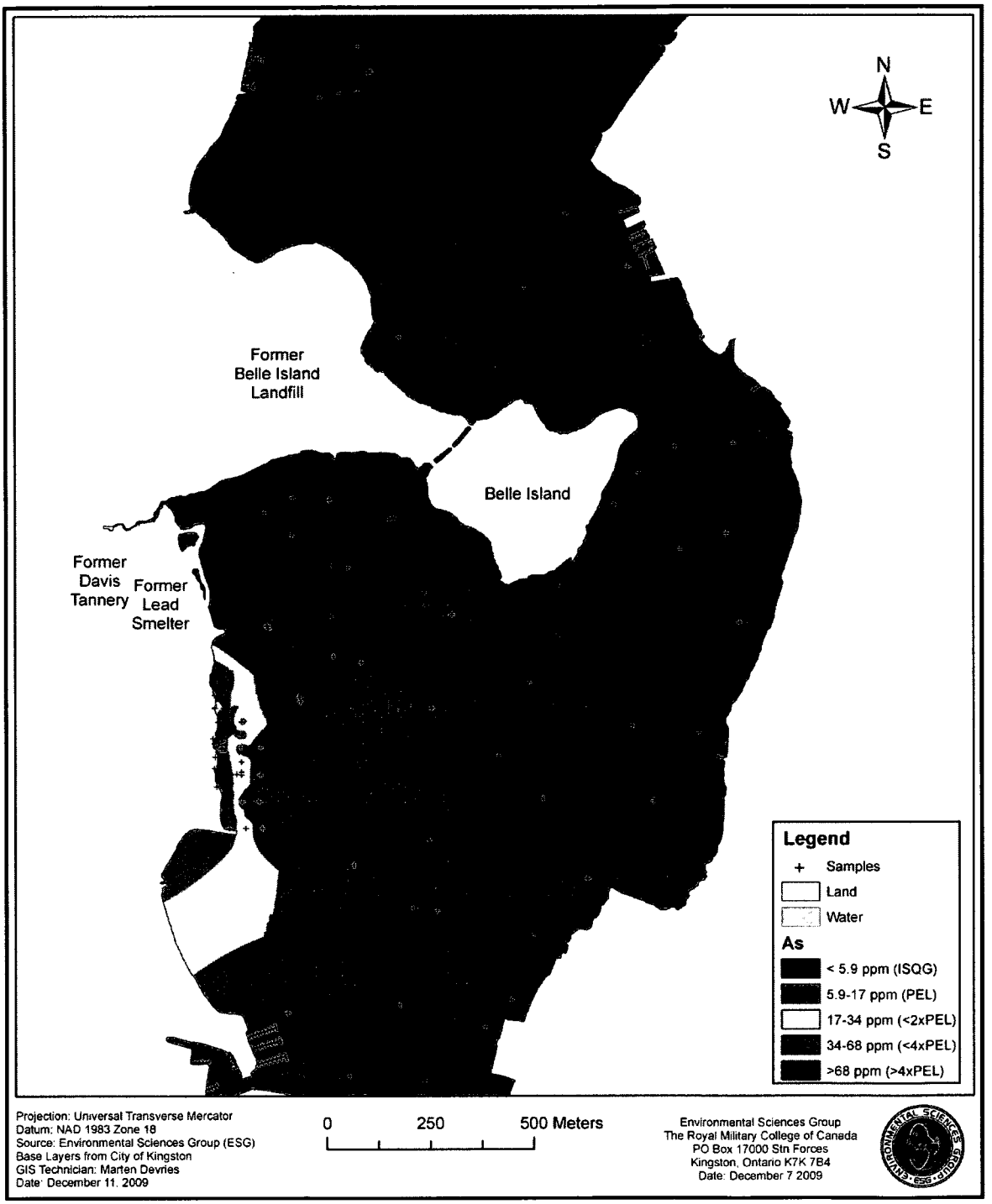

Figure A.8: Distribution of Arsenic within Surface Sediments of the Kingston Inner Harbour (ESG, 2009b)

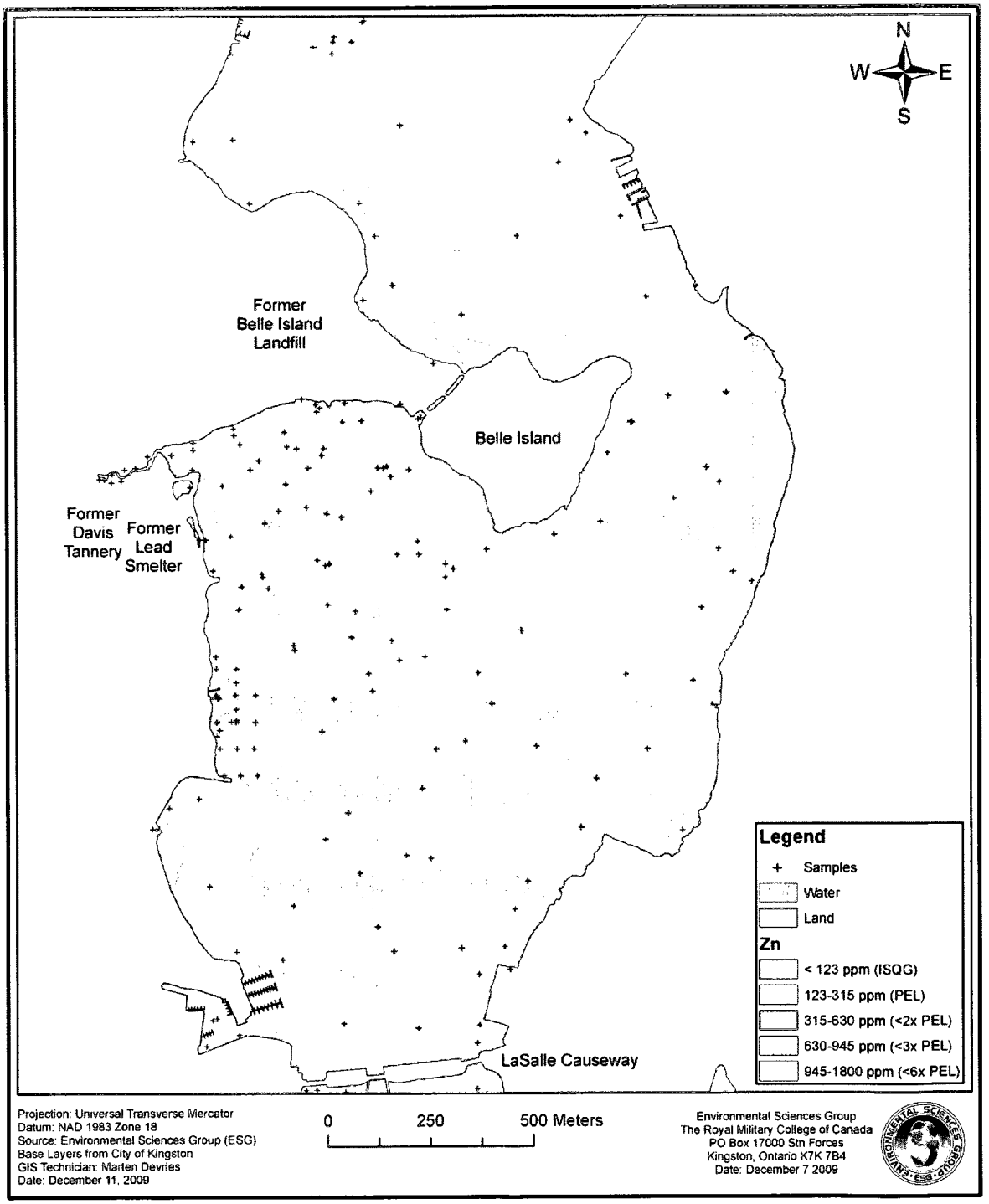

Figure A.9: Distribution of Zinc within Surface Sediments of the Kingston Inner Harbour (ESG, 2009b)

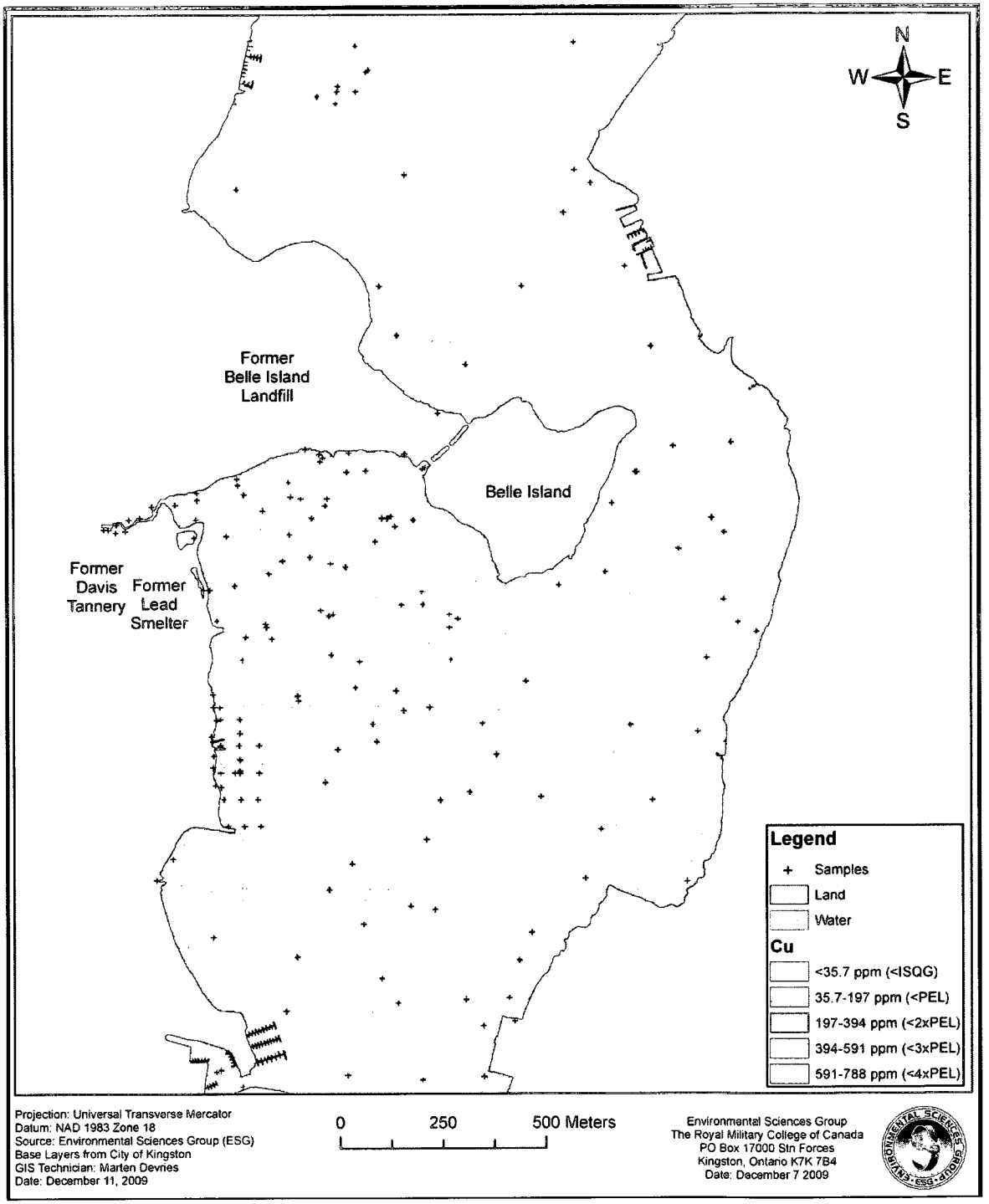

Figure A.10: Distribution of Copper within Surface Sediments of the Kingston Inner Harbour (ESG, 2009b)

Appendix B: ERA Data

Table B.1: Orchard Street Marsh Cattail Root Data

Sample	Percent moisture*	As (ppm, dw)	Cr (ppm, dw)	Cu (ppm, dw)	Pb (ppm, dw)	Zn (ppm, dw)	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)
Marsh Root 1	0.70	<1.0	40	6.7	5.7	80	0.30	12	2.0	1.7	24
Marsh Root 2	0.70	1.1	182	7.1	7.9	54	0.33	55	2.1	2.4	16
Marsh Root 3	0.70	<1.0	21	3.4	6.3	22	0.30	6.3	1.0	1.9	6.6
Marsh Root 4	0.70	<1.0	16	5.3	3.8	32	0.30	4.8	1.6	1.1	9.6
Marsh Root 5	0.70	<1.0	40	9.0	3.9	61	0.30	12	2.7	1.2	18

* Conservative estimate based on value of 74.9 percent in Vetayasuporn (2009)

Table B.2: Orchard Street Marsh Sediment Data

Sample	Percent moisture*	As (ppm, dw)	Cr (ppm, dw)	Cu (ppm, dw)	Pb (ppm, dw)	Zn (ppm, dw)	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)
Marsh Sed 1	0.80	7.3	16,400	28.2	267	169	1.5	3,300	5.6	53	34
Marsh Sed 2	0.80	12.3	40,700	72.6	233	212	2.5	8,100	15	47	42
Marsh Sed 3	0.80	<1.0	1370	13.0	33.0	94	0.20	270	2.6	6.6	19
Marsh Sed 4	0.80	4.3	8,920	30.2	254	145	0.86	1,800	6.0	51	29
Marsh Sed 5	0.80	5.9**	13,000**	28.8**	273**	181**	1.2	2,600	5.8	55	36

* Conservative estimate based on Tinney (2006) and Asquini *et al.* (2007)

** Value is result of average of triplicates

Table B.3: South Belle Park Cattail Root Data

Location	% mois-ture*	As (ppm, dw)	Cr (ppm, dw)	Cu (ppm, dw)	Pb (ppm, dw)	Zn (ppm, dw)	Aroclor 1242 (ppb, dw)	Aroclor 1254 (ppb, dw)	Aroclor 1260 (ppb, dw)	Total PCB (ppb, dw)	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)	Total PCB (ppb, ww)
South Belle Park Root 1	0.70	2.1	42	4.2	14.7	25.4	<3.0	6.30	9.6	18.9	0.62	13	1.3	4.4	7.6	5.7
South Belle Park Root 2	0.70	4.1**	50**	2.4**	5.6**	20.3**	<3.0**	7.48**	27.7**	38.2**	1.2	15	0.71	1.7	6.1	12
Root Reference	0.70	<1.0	1	<2.0	1.0	22.2	<3.0	3.00	2.07	8.07	0.30	0.30	0.60	0.30	6.7	2.4

* Conservative estimate based on value of 74.9 percent in Vetayasuporn (2009)
** Values is result of average of duplicates

Table B.4: South Belle Park Sediment Data

Location	% mois-ture*	As (ppm, dw)	Cr (ppm, dw)	Cu (ppm, dw)	Pb (ppm, dw)	Zn (ppm, dw)	Aroclor 1242 (ppb, dw)	Aroclor 1254 (ppb, dw)	Aroclor 1260 (ppb, dw)	PCB Total (ppb, dw)	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)	Total PCB (ppb, ww)
South Belle Park Sed 1	0.80	9.1	3600	105	426	429	< 3.0	44.0	54.0	101	1.8	720	21	85	86	20
South Belle Park Sed 2	0.80	4.6	1560	61.7	76.8	152	< 3.0	51.0	130	184	0.92	310	12	15	30	37
Cattail Sed Reference	0.80	4.7	10	21.1	50.9	98.5	< 3.0	1.50	1.50	6.00	0.94	2.0	4.2	10	20	1.2

* Estimate based on Tinney (2006) and Asquini *et al.* (2007)

Table B.5: Marsh Cattail Inflorescence Data

Sample	Percent moisture*	As (ppm, dw)	Cr (ppm, dw)	Cu (ppm, dw)	Pb (ppm, dw)	Zn (ppm, dw)	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)
Marsh Inflor 1	0.70	<1.0	<2.0	5.7	<2.0	17	0.30	0.60	1.7	0.60	5.1
Marsh Inflor 2	0.70	<1.0	<2.0	5.3	<2.0	17	0.30	0.60	1.6	0.60	5.2
Marsh Inflor 3	0.70	<1.0	<2.0	6.5	<2.0	21	0.30	0.60	2.0	0.60	6.3
Marsh Inflor 4	0.70	<1.0	<2.0	4.7	<2.0	14	0.30	0.60	1.4	0.60	4.2
Marsh Inflor 5	0.70	<1.0**	<2.0**	4.7**	<2.0**	21**	0.30	0.60	1.4	0.60	6.3

* Conservative estimate based on value of 74.9 percent in Vetayasuporn (2009)
** Value is result of average of duplicates

Table B.6: Fish Sample Data from the Impacted Site and Reference Site (all samples collected on 18 Nov 09)

Sample	Whole or partial fish	Species	Location**	Total length (mm)	Fork Length (mm)	Standard length (mm)	Body weight (g)	Age (yrs)	Lipid percentage	Percent moisture
09-07703	W	Brown bullhead	IMP	236	234	202	204.6	4	11.4	71.9
09-07721	W	Brown bullhead	IMP	315	312	268	421.3	5	3.7	75.4
09-07736	W	Brown bullhead	IMP	233	230	198	163.8	4	6.0	74.6
09-07793	W	Brown bullhead	IMP	233	230	197	139.7	4	13.5	70.2
09-07796	W	Brown bullhead	IMP	329	325	297	438.0	6	14.4	72.9
09-07646	P	Yellow perch	IMP	193	186	164	76.9	5	9.6	71.4
09-07649	P	Yellow perch	IMP	133	128	114	26.7	3	1.9	67.2
09-07652	P	Yellow perch	IMP	157	151	132	43.2	4	9.1	66.9
09-07826	P	Yellow perch	IMP	131	126	410	27.0	3	5.0	73.8
09-07879	P	Yellow perch	IMP	147	142	126	36.2	3	1.6*	72.6
09-07787	P	Northern pike	IMP	641	621	579	170.1	5	5.6	71.8*
09-07802	P	Northern pike	IMP	449	428	399	495.9	4	0.12	75.7
09-07805	P	Northern pike	IMP	400	379	350	390.2	4	0.80	74.6
09-07811	P	Northern pike	IMP	462	436	404	584.9	4	0.12*	74.1*
09-07873	P	Northern pike	IMP	416	389	354	413.3	4	2.7	73.8
09-07676	W	Brown bullhead	REF	253	246	227	224.5	5	2.5	70.1
09-07685	W	Brown bullhead	REF	255	249	220	302.9	5	15.4	73.1
09-07739	W	Brown bullhead	REF	261	255	223	234.4	5	8.8	77.5
09-07700	P	Yellow perch	REF	207	204	180	141.6	5	5.0	71.8*
09-07778	P	Yellow perch	REF	153	149	131	40.2	4	0.75	73.6
09-07784	P	Yellow perch	REF	154	149	131	47.5	4	2.0	72.3
09-07667	P	Northern Pike	REF	680	630	610	1725.4	5	2.9*	73.1
09-07670	P	Northern Pike	REF	469	447	413	585.5	4	17.4	74.7
09-07831	P	Northern Pike	REF	392	372	340	345.3	3	1.3	74.6

* Value is result of average of duplicates. Note that samples were not analyzed in the order in which they are listed above.

** IMP: impacted site; REF: reference site

Table B.7: Metals Data from Fish Sampled at the Impacted Site and Reference Site (all samples collected on 18 Nov 09)

Sample	Species	Location**	Percent moisture	As (ppm, dw)	Cr (ppm, dw)	Cu (ppm, dw)	Pb (ppm, dw)	Zn (ppm, dw)	As (ppm, ww)	Cr (ppm, ww)	Cu (ppm, ww)	Pb (ppm, ww)	Zn (ppm, ww)
09-07703	Brown bullhead	IMP	71.9	<1.0	3.9	2.4	<0.5	63.4	0.28	1.1	0.67	0.01	18
09-07721	Brown bullhead	IMP	75.4	<1.0*	2.2*	4.9*	5.3*	52.5*	0.25	0.54	1.2	1.3	13
09-07736	Brown bullhead	IMP	74.6	<1.0	4.8	4.9	<0.5	54.9	0.25	1.2	1.2	0.13	14
09-07793	Brown bullhead	IMP	70.2	<1.0	1.3	3.8	<0.5	70.3	0.30	0.39	1.1	0.15	21
09-07796	Brown bullhead	IMP	72.9	<1.0*	1.8*	4.8*	<0.5*	50.1*	0.27	0.49	1.3	0.11	14
09-07646	Yellow perch	IMP	71.4	<1.0*	1.4*	2.6*	<0.5*	81.1*	0.29	0.40	0.73	0.15	23
09-07649	Yellow perch	IMP	67.2	<1.0	1.9	2.3	<0.5	120	0.33	0.61	0.75	0.17	39
09-07652	Yellow perch	IMP	66.9	<1.0	1.4	3.2	<0.5	75.2	0.33	0.47	1.1	0.17	25
09-07826	Yellow perch	IMP	73.8	<1.0	<3.0	1.5	<0.5	94.1	0.26	0.78	0.40	0.13	25
09-07879	Yellow perch	IMP	72.6	<1.0*	3.1*	1.7*	<0.5*	77.5*	0.27	0.85	0.47	0.14	21
09-07787	Northern pike	IMP	71.8*	<1.0	1.2	1.8	<0.5	121	0.28	0.35	0.50	0.14	34
09-07802	Northern pike	IMP	75.7	<1.0	1.5	1.7	<0.5	88.4	0.24	0.36	0.42	0.12	21
09-07805	Northern pike	IMP	74.6	<1.0	<1.0	2.5	<0.5	131	0.25	0.25	0.64	0.13	33
09-07811	Northern pike	IMP	74.1*	<1.0	<1.0	2.5	<0.5	91.6	0.26	0.26	0.65	0.13	24
09-07873	Northern pike	IMP	73.8	<1.0	<1.0	2.2	<0.5	92.4	0.26	0.26	0.58	0.13	24
09-07676	Brown bullhead	REF	70.1	<1.0	1.0	6.2	<0.5	49.9	0.30	0.31	1.9	0.15	15
09-07685	Brown bullhead	REF	73.1	<1.0	1.1	2.7	<0.5	53.2	0.27	0.29	0.73	0.14	14
09-07739	Brown bullhead	REF	77.5	<1.0	<1.0	5.2	<0.5	52.7	0.23	0.23	1.2	0.12	12
09-07700	Yellow perch	REF	71.8*	<1.0	1.1	2.7	<0.5	60.0	0.28	0.31	0.76	0.14	17
09-07778	Yellow perch	REF	73.6	<1.0	1.2	2.4	<0.5	94.0	0.26	0.32	0.63	0.13	25
09-07784	Yellow perch	REF	72.3	<1.0	1.5	1.7	<0.5	86.9	0.28	0.42	0.46	0.14	24
09-07667	Northern Pike	REF	73.1	<1.0	<1.0	2.3	<0.5	79.2	0.27	0.27	0.62	0.14	21
09-07670	Northern Pike	REF	74.7	<1.0	<1.0	1.4	<0.5	131	0.25	0.25	0.36	0.13	33
09-07831	Northern Pike	REF	74.6	<1.0	<1.0	2.7	<0.5	137	0.25	0.25	0.69	0.13	35

* Value is result of average of duplicates. Note that samples were not analyzed in the order in which they are listed above.

** IMP: impacted site; REF: reference site

Table B.8: PCB Data from Fish Sampled at the Impacted Site and Reference Site (all samples collected on 18 Nov 09)

Sample	Species	Location	% Moisture	Aroclor 1242 (ppm, dw)	Aroclor 1254 (ppm, dw)	Aroclor 1260 (ppm, dw)	Total PCBs (ppm, dw)	Total PCBs (ppm, ww)	Mammalian PCB TEQ, all Aroclors** (ng TEQ·kg^{-1})	Avian PCB TEQ, all Aroclors** (ng TEQ·kg^{-1})	Mammalian PCB TEQ, Aroclors 1254 and 1260 (ng TEQ·kg^{-1})	Avian PCB TEQ, Aroclors 1254 and 1260 (ng TEQ·kg^{-1})
09-07703	Brown bullhead	IMP	71.9	<0.05	0.43	2.30	2.78	0.78	39	90	39	78
09-07721	Brown bullhead	IMP	75.4	<0.05	<0.05	0.74	0.84	0.21	10	33	9.9	21
09-07736	Brown bullhead	IMP	74.6	<0.05	<0.05	1.10	1.20	0.30	14	42	14	30
09-07793	Brown bullhead	IMP	70.2	<0.05	<0.05	1.90	2.00	0.60	23	62	23	51
09-07796	Brown bullhead	IMP	72.9	<0.05	<0.05	1.30	1.40	0.38	16	47	16	35
09-07646	Yellow perch	IMP	71.4	<0.05	0.42	0.96	1.43	0.41	24	55	23	43
09-07649	Yellow perch	IMP	67.2	<0.05	0.70	1.20	1.95	0.64	35	73	35	62
09-07652	Yellow perch	IMP	66.9	<0.05	0.29	0.53	0.87	0.29	15	38	15	26
09-07826	Yellow perch	IMP	73.8	<0.05	0.06	<0.05	0.07	0.02	2.6	16	2.4	4.0
09-07879	Yellow perch	IMP	72.6	<0.05	0.43	0.54	1.02	0.28	19	45	19	33
09-07787	Northern pike	IMP	71.8*	<0.05*	0.38*	1.9*	2.33	0.66	33	77	33	65
09-07802	Northern pike	IMP	75.7	<0.05	0.23	0.71	0.99	0.24	15	40	15	28
09-07805	Northern pike	IMP	74.6	<0.05	0.43	1.00	1.48	0.38	25	56	24	45
09-07811	Northern pike	IMP	74.1*	<0.05*	<0.05*	<0.05*	0.15	0.04	2.3	15	2.1	3.5
09-07873	Northern pike	IMP	73.8	<0.05	0.19	1.20	1.44	0.38	19.5	51	19	39
09-07676	Brown bullhead	REF	70.1	<0.05	<0.05	<0.05	0.15	0.04	2.3	15	2.1	3.5
09-07685	Brown bullhead	REF	73.1	<0.05	<0.05	<0.05	0.15	0.04	2.3	15	2.1	3.5
09-07739	Brown bullhead	REF	77.5	<0.05	<0.05	<0.05	0.15	0.03	2.3	15	2.1	3.5
09-07700	Yellow perch	REF	71.8*	<0.05*	0.05*	0.08*	0.18	0.05	2.7	16	2.4	4.3
09-07778	Yellow perch	REF	73.6	<0.05	0.09	0.08	0.22	0.06	3.9	18	3.6	6.1
09-07784	Yellow perch	REF	72.3	<0.05	<0.05	0.06	0.16	0.04	2.4	15	2.2	3.8
09-07667	Northern Pike	REF	73.1	<0.05	0.14	0.36	0.55	0.15	8.5	27	8.3	15
09-07670	Northern Pike	REF	74.7	<0.05	0.05	0.13	0.23	0.06	3.2	17	3.0	5.5
09-07831	Northern Pike	REF	74.6	<0.05	<0.05	0.11	0.23	0.06	3.0	17	2.8	5.0

* Value is result of average of duplicates. Note that samples were not analyzed in the order in which they are listed above.

** Sum of Aroclors 1242, 1254, and 1260

Table B.9: Impacted Site MeHg and PCB Fish Data from Scheider (2009)

Species	Year Sampled	Length (mm)	Body weight (g)	Sex	Lipid %age	Methyl mercury, fillet (ppm, ww)	Total PCBs, fillet (ppm, ww)	Methyl mercury, whole-body (ppm, ww)*	Total PCB, whole-body (ppm, ww)**	Mammalian Aroclor 1260 TEF (ng TEQ·kg^{-1})	Avian Aroclor 1260 TEF (ng TEQ·kg^{-1})
Brown bullhead	2002	199	104	M	2.5	0.03	0.18	0.023	--	--	--
		229	150	M	3.5	0.03	0.12	0.023	--	--	--
		239	170	M	3.0	0.02	0.08	0.016	--	--	--
		255	210	M	3.6	0.04	0.16	0.030	--	--	--
		258	220	M	3.8	0.03	0.16	0.023	--	--	--
		263	234	M	1.8	0.05	0.24	0.036	--	--	--
		266	236	F	0.9	0.04	0.10	0.030	--	--	--
		271	236	M	0.6	0.04	0.54	0.030	--	--	--
		275	298	M	0.1	0.03	0.04	0.023	--	--	--
		280	261	M	1.5	0.03	0.16	0.023	--	--	--
		314	416	M	1.9	0.03	0.26	0.023	--	--	--
	1999	212	121	M	1.0	0.03	0.14	0.023	--	--	--
		219	128	M	1.5	0.02	0.14	0.016	--	--	--
		241	195	F	3.9	0.03	0.28	0.023	--	--	--
		244	174	F	2.2	0.02	0.36	0.016	--	--	--
		247	169	M	1.7	0.03	0.24	0.023	--	--	--
		253	202	M	1.0	0.04	0.08	0.030	--	--	--
		254	210	M	1.5	0.04	0.22	0.030	--	--	--
		256	220	M	0.9	ND	0.14	0.009	--	--	--
		259	197	M	0.8	0.03	0.22	0.023	--	--	--
		259	227	M	1.6	0.03	0.26	0.023	--	--	--

* Conversion based on method of Peterson *et al.* (2005)

** From USEPA (2006), conversion based on whole-body:fillet ratio of PCBs of 5.5:1 for yellow perch and 4.1:1 for northern pike. No conversion factor was reported for brown bullhead.

Table B.9 (cont)

Species	Year Sampled	Length (mm)	Body weight (g)	Sex	Lipid %age	Methyl mercury, fillet (ppm, ww)	Total PCBs, fillet (ppm, ww)	Methyl mercury, whole-body (ppm, ww)*	Total PCB, whole-body (ppm, ww)**	Mammalian Aroclor 1260 TEF (ng TEQ·kg^{-1})	Avian Aroclor 1260 TEF (ng TEQ·kg^{-1})
Yellow perch	2002	145	38	F	1.3	0.09	0.06	0.061	0.33	3.7	8.4
		162	53	M	1.1	0.1	0.14	0.067	0.77	8.7	20
		165	57	F	1.9	0.06	0.06	0.043	0.33	3.7	8.4
		168	59	F	1.4	0.16	0.04	0.10	0.22	2.5	5.6
		175	72	F	0.6	0.09	0.06	0.061	0.33	3.7	8.4
		182	84	F	0.3	0.06	0.06	0.043	0.33	3.7	8.4
		185	75	F	0.8	0.09	0.06	0.061	0.33	3.7	8.4
	1999	156	40	M	0.4	0.14	0.30	0.091	1.7	19	42
		165	40	F	0.5	ND	0.10	0.009	0.55	6.2	14
		165	57	F	1.4	0.08	0.10	0.055	0.55	6.2	14
		174	58	F	0.6	0.07	0.12	0.049	0.66	7.5	17
		175	61	F	0.5	0.08	0.10	0.055	0.55	6.2	14
		189	81	F	0.5	0.08	0.08	0.055	0.44	5.0	11
Northern pike	2002	301	171	F	0.1	0.11	0.06	0.073	0.25	2.8	6.3
		335	204	M	0.4	0.09	0.10	0.061	0.41	4.6	10
		376	264	F	0.2	0.09	0.12	0.061	0.49	5.6	13
		507	531	M	0.4	0.4	1.40	0.24	5.7	65	150
		558	652	M	0.3	0.5	0.54	0.29	2.2	25	57

* Conversion based on method of Peterson *et al.* (2005)

** From USEPA (2006), conversion based on whole-body:fillet ratio of PCBs of 5.5:1 for yellow perch and 4.1:1 for northern pike. No conversion factor was reported for brown bullhead.

Table B.9 (cont)

Species	Year Sampled	Length (mm)	Body weight (g)	Sex	Lipid percentage	Methyl mercury, fillet (ppm, ww)	Total PCBs, fillet (ppm, ww)	Methyl mercury, whole-body (ppm, ww)*	Total PCB, whole-body (ppm, ww)**	Mammalian Aroclor 1260 TEF (ng TEQ·kg^{-1})	Avian Aroclor 1260 TEF (ng TEQ·kg^{-1})
Northern pike	1999	329	203	F	0.3	0.09	0.16	0.061	0.66	7.4	17
		360	240	F	0.2	0.09	0.12	0.061	0.49	5.6	13
		379	296	M	0.2	0.08	0.12	0.055	0.49	5.6	13
		382	346	F	0.3	0.08	0.12	0.055	0.49	5.6	13
		413	445	M	0.7	0.13	0.10	0.085	0.41	4.6	10
		425	393	F	0.6	0.14	0.06	0.091	0.25	2.8	6.3
		483	659	F	0.7	0.12	0.14	0.079	0.57	6.5	15
		570	1108	M	0.4	0.29	0.28	0.18	1.2	13	29
		571	1052	M	0.3	0.23	0.18	0.14	0.74	8.3	19
		712	2152	F	0.2	0.31	0.14	0.19	0.57	6.5	15

* Conversion based on method of Peterson *et al.* (2005)

** From USEPA (2006), conversion based on whole-body:fillet ratio of PCBs of 5.5:1 for yellow perch and 4.1:1 for northern pike. No conversion factor was reported for brown bullhead.

Table B.10: Reference Site (Colonel By Lake) MeHg and PCB Fish Data From Scheider (2009)*

Species	Date sampled	Length (mm)	Body weight (g)	Sex	Lipid percentage	Methyl mercury, fillet (ppm, ww)	Total PCBs, fillet (ppm, ww)	Methyl mercury, whole-body (ppm, ww)**	Total PCB, whole-body
Brown bullhead	15-Jul-97	195	119	F	0.4	0.04	ND	0.030	--
		299	449	F	0.6	0.20	ND	0.13	--
Yellow perch	15-Jul-97	146	45	M	0.4 (composite)	0.07	ND	0.049	--
		163	58	F		0.05	ND	0.036	--
		170	58	F		0.08	ND	0.055	--
		172	67	F		0.05	ND	0.036	--
		174	67	M		0.07	ND	0.049	--
		175	64	F		0.08	ND	0.055	--
		175	65	F		0.06	ND	0.043	--
		179	72	F		0.08	ND	0.055	--
		193	93	F		0.07	ND	0.049	--
		202	112	F		0.07	ND	0.049	--
		220	135	F		0.11	ND	0.073	--
		226	158	F		0.13	ND	0.085	--

* Data from Scheider (2006) did not report any data for northern pike from Colonel By Lake

** Conversion based on method of Peterson *et al.* (2005)

Appendix C: Calculation of Food Ingestion Rates for ERA

Food ingestion rates (FIRs) of captive animals do not reflect FIRs of free-ranging animals as energy is not expended in such activities as foraging for food and water, eluding predators, and defending territory (USEPA, 1993). However, FIRs for free-ranging wildlife are seldom found in the literature due to the practical difficulties in empirically measuring these values. When free-ranging FIRs are unavailable, this information can be developed from allometric equations modeling the free metabolic rate (FMR) of free-ranging animals. These allometrically-derived FIRs can be calculated using Equation C.1 (USEPA, 1993):

$$FIR = \frac{FMR \times CF}{\sum_{i=1}^{n}[P_i \times GE_i \times AE_i]} \quad \textbf{(C. 1)}$$

where FMR is determined by the equation of Nagy (1987) (Equation 4.2):

$$FMR = a \times (BW)^b \quad \textbf{(C.2)}$$

The right hand side of Equation C.2 is assumed to be in the units of ($kJ \cdot d^{-1}$). The constants "a" and "b" can be found in the literature, as well as:

i. BW: is the body weight of the receptor for which the FIR is being derived; this is expressed in (g);

ii. CF: is a conversion factor, equal to (0.239 $kcal \cdot kJ^{-1}$);

iii. P_i: is the proportion of total food that the *i*th food item comprises; this is a dimensionless quantity;

iv. GE_i: is the gross energy of the *i*th food item, which is expressed in ($kcal \cdot kg^{-1}$ (ww)); and

v. AE_i: is the assimilation efficiency; this is a dimensionless quantity.

Gross energy values could not be located for cattails. As a result, the most conservative free-ranging FIR has been taken from the literature for the muskrat. Though the allometrically-derived FIR could not be derived here for the red-winged blackbird, Sample *et al.* (1996) performed the calculation himself using Nagy (1987). The data used to calculate the allometric FIRs for the remaining receptors is displayed in Table C.1 and Table C.2.

Table C.1: Receptor Data used to Calculate Allometrically-Derived FIR Values

Receptor	a (unitless)	b (unitless)	BW (g)	Food Item	P_i (unitless)	GE_i (kcal·kg^{-1} (ww))	AE_i (unitless)
Mink	2.582[a]	0.862[a]	1040[c]	Fish	1.0	1200[c]	0.91[c]
Great blue heron	10.5[b]	0.681[b]	2400[d]	Fish	1.0	1200[c]	0.79[c]
Osprey	10.5[b]	0.681[b]	1500[d]	Fish	1.0	1200[c]	0.79[c]

[a] Nagy (1987)
[b] Nagy (1999)
[c] USEPA (1993)
[d] Sample *et al.* (1996)

Based on the values in Table C.1, and Equation C.1 and Equation C.2, the FIR values for the mink, great blue heron, and osprey were calculated. These FIRs are presented in Table C.2; Appendix E.1 contains a sample calculation of a FIR.

Table C.2 – Allometrically-derived FIR Values

Receptor	FIR (kg·d^{-1})
Mink	0.23
Great blue heron	0.53
Osprey	0.39

Appendix D: Data for Chromium Speciation Study

D.1 ICP-MS Data for Cr(total)

Table D.1: LOD and LOQ for Cr(total) Analysis

Value	Cr(total) (ppb)
LOD	0.82
LOQ	2.73

Table D.2: QC Sample Results for Cr(total) Analysis

Sample	Percent difference from 54.3 ppb (%)
QC 1	-1.7
QC 2	-4.6
QC 3	-7.6
QC 4	10
QC 5	-17
QC 6	-9.1
QC 7	-0.073
QC 8	8.6
QC 9	-15
QC 10	12
QC 11	20
QC 12	19
QC 13	13
Average of Absolute Values	11

Table D.3: Blank Sample Results for Cr(total) Analysis

Sample	Cr(total) (ppb)
B1	0.74 (non-detect)
B2	0.26 (non-detect)
B3	0.19 (non-detect)
B4	0.12 (non-detect)
B5	0.17 (non-detect)
B6	0.09 (non-detect)
B7	0.16 (non-detect)
B8	0.15 (non-detect)
B9	0.18 (non-detect)
B10	0.26 (non-detect)
B11	0.21 (non-detect)
B12	0.81 (non-detect)
B13	0.97 (trace)
B14	0.28 (non-detect)
B15	0.34 (non-detect)

Table D.4: Spike Sample Results for Cr(total) Analysis

Sample	Measured spike concentration (ppb)	Theoretical spike concentration (ppb)	Percent recovery (%)
SPK1	8.4	9.2	86
SPK2	8.8	9.2	90
SPK3	5.7	9.2	59
SPK4	4.1	9.2	42
SPK5	4.5	9.2	47
SPK6	3.2	9.2	33
SPK7	5.9	9.2	61
SPK8	5.2	9.2	54
SPK9	8.6	9.2	89

Table D.5: Depth Profile Results for Cr(total) Analysis

Peeper	Cell depth (cm)	Cr(total) concentration, left cell (ppb)	Cr(total) concentration, right cell (ppb)	RPD of analytical duplicate (%)	Average field duplicate Cr(total) concentration (ppb)	RPD of field duplicates (%)
Reference	-2.0	2.2	1.5		1.8 (trace)	38
	-6.5	1.8	1.2		1.5 (trace)	38
	-11.0	1.6	1.6		1.6 (trace)	3.0
	-15.5	1.3*	1.6	2.7	1.4 (trace)	-22
	-20.0	1.5	1.2		1.4 (trace)	18
	-24.5	1.0	0.93		0.96 (trace)	5.6
	-29.0	0.87	1.1		0.99 (trace)	-25
	-33.5	0.92	0.81		0.87 (trace)	13
	-38.0	0.87*	0.95	2.2	0.91 (trace)	-9.5
Peeper 1	-2.0	1.5	2.1		1.8 (trace)	-35
	-6.5	5.4	5.5		5.5	-2.2
	-11.0	5.8	5.2		5.5	12
	-15.5	6.0	6.6		6.3	-9.4
	-20.0	6.5*	6.3	0.14	6.4	3.1
	-24.5	6.6	6.1		6.3	7.3
	-29.0	5.2	6.0		5.6	-14
	-33.5	5.4	5.9		5.7	-9.1
	-38.0	5.9	5.8		5.9	1.9
Peeper 2	-2.0	4.3*	4.2	-7.8	4.3	0.52
	-6.5	4.9	4.2		4.6	18
	-11.0	4.6	4.5		4.6	1.6
	-15.5	4.6	4.9		4.8	-7.4
	-20.0	5.1*	5.1	1.4	5.1	1.6
	-24.5	5.3	5.5		5.4	-3.3
	-29.0	5.9	6.9		6.4	-15
	-33.5	5.9	5.6		5.7	5.7
	-38.0	5.9	6.2		6.1	-3.9
Peeper 3	-2.0	3.6*	3.1	-18	3.3	17
	-6.5	3.5	2.6		3.1	29
	-11.0	3.1	2.8		3.0	8.3
	-15.5	3.6	3.7		3.7	-3.4
	-20.0	4.2	3.8*	-1.5	4.0	8.3
	-24.5	4.0	3.0		3.5	28
	-29.0	3.1	2.9		3.0	3.9
	-33.5	3.9	3.0		3.5	27
	-38.0	2.9	3.3		3.1	-13
Peeper 4	-2.0	2.1	2.9*	-0.16	2.5 (trace)	-32
	-6.5	1.9	1.6		1.7 (trace)	12
	-11.0	1.2	1.9		1.5 (trace)	-48
	-15.5	1.6	1.9		1.7 (trace)	-18
	-20.0	2.0	1.4		1.7 (trace)	38
	-24.5	2.1	1.8		2.0 (trace)	17
	-29.0	2.1	1.7		1.9 (trace)	25
	-33.5	2.2	2.2		2.2 (trace)	0.42
	-38.0	2.2	2.7		2.4 (trace)	20

* Value is average of duplicates

D.2 ICP-MS-HPLC Data for Cr Speciation Analysis Without EDTA

Table D.6: LOD and LOQ for Cr Speciation Analysis without EDTA

Species	Cr(III) (ppb)	Cr(VI) (ppb)
LOD	0.23	0.14
LOQ	0.76	0.45

Table D.7: QC Sample Results for Cr Speciation Analysis without EDTA

Sample	% Diff from 54.3 ppb (%)	% Diff from 50.7 ppb (%)
QC 1	-0.82	-3.8
QC 2	2.0	4.1
QC 3	11	5.1
QC 4	14	9.8
QC 5	-23	-25
QC 6	23	22
QC 7	-15	-19
QC 8	-11	-9.0
QC 9	-13	-11
QC 10	-7.7	-11
QC 11	-6.0	-4.2
QC 12	-12	-14
Average of absolute values	12	11

Table D.8: Blank Sample Results for Cr Speciation Analysis without EDTA

Sample	Cr(III) (ppb)	Cr(VI) (ppb)
B1	0.0 (non-detect)	0.0 (non-detect)
B2	0.018 (non-detect)	0.078 (non-detect)
B3	0.0081 (non-detect)	0.068 (non-detect)
B4	0.10 (non-detect)	0.18 (trace)
B5	0.013 (non-detect)	0.11 (non-detect)
B6	0.016 (non-detect)	0.12 (non-detect)
B7	0.018 (non-detect)	0.10 (non-detect)
B8	0.034 (non-detect)	0.15 (trace)
B9	0.029 (non-detect)	0.13 (non-detect)
B10	0.039 (non-detect)	0.084 (non-detect)
B11	0.040 (non-detect)	0.093 (non-detect)
B12	0.053 (non-detect)	0.12 (non-detect)
B13	0.039 (non-detect)	0.13 (non-detect)
B14	0.036 (non-detect)	0.12 (non-detect)
B15	0.35 (trace)	0.12 (non-detect)
B16	0.034 (non-detect)	0.10 (non-detect)
B17	0.11 (non-detect)	0.055 (non-detect)
B18	0.068 (non-detect)	0.16 (trace)
B19	0.027 (non-detect)	0.12 (non-detect)
B20	0.061 (non-detect)	0.21 (trace)

Table D.9: Spike Sample Results for Cr Speciation Analysis without EDTA

Sample	Cr(III)			Cr(VI)		
	Measured spike concentration (ppb)	Theoretical spike concentration (ppb)	Percent recovery (%)	Measured spike concentration	Theoretical spike concentration	Percent recovery (%)
SPK1	4.7	4.4	110	4.3	4.8	90
SPK2	5.3	4.4	120	3.6	4.8	76
SPK3	6.1	4.4	140	0.010	4.8	0.21
SPK4	5.6	4.4	130	0.043	4.8	0.90
SPK5	5.7	4.4	130	-0.076	4.8	0.0
SPK6	3.4	4.4	77	-0.0034	4.8	0.0
SPK7	4.1	4.4	93	-0.071	4.8	0.0
SPK8	4.2	4.4	94	-0.056	4.8	0.0
SPK9	4.5	4.4	100	3.0	4.8	62

Table D.10: Cr(III) Depth Profile Results for Cr Speciation Analysis without EDTA

Peeper	Cell depth (cm)	Cr(III) concentration, left cell (ppb)	Cr(III) concentration, right cell (ppb)	RPD of analytical duplicate (%)	Average field duplicate Cr(III) concentration (ppb)	RPD of field duplicates (%)
Reference	-2.0	< 0.23	< 0.23		< 0.23	---
	-6.5	< 0.23	< 0.23		< 0.23	---
	-11.0	< 0.23	< 0.23		< 0.23	---
	-15.5	< 0.23*	< 0.23	---	< 0.23	---
	-20.0	< 0.23	< 0.23		< 0.23	---
	-24.5	< 0.23	< 0.23		< 0.23	---
	-29.0	< 0.23	< 0.23		< 0.23	---
	-33.5	< 0.23	< 0.23		< 0.23	---
	-38.0	< 0.23*	< 0.23	---	< 0.23	---
Peeper 1	-2.0	< 0.23	< 0.23		< 0.23	---
	-6.5	< 0.23	< 0.23		< 0.23	---
	-11.0	< 0.23	< 0.23		< 0.23	---
	-15.5	< 0.23	< 0.23		< 0.23	---
	-20.0	< 0.23*	< 0.23	---	< 0.23	---
	-24.5	< 0.23	0.26		< 0.23	---
	-29.0	0.26	0.24		0.25 (trace)	7.6
	-33.5	0.28	< 0.23		< 0.23	---
	-38.0	0.29	0.37		0.33 (trace)	-25
Peeper 2	-2.0	< 0.23*	< 0.23	---	< 0.23	---
	-6.5	< 0.23	< 0.23		< 0.23	---
	-11.0	< 0.23	< 0.23		< 0.23	---
	-15.5	< 0.23	< 0.23		< 0.23	---
	-20.0	< 0.23*	< 0.23	---	< 0.23	---
	-24.5	< 0.23	< 0.23		< 0.23	---
	-29.0	< 0.23	< 0.23		< 0.23	---
	-33.5	< 0.23	< 0.23		< 0.23	---
	-38.0				< 0.23	---
Peeper 3	-2.0	< 0.23*	< 0.23	---	< 0.23	---
	-6.5	< 0.23	< 0.23		< 0.23	---
	-11.0	< 0.23	< 0.23		< 0.23	---
	-15.5	< 0.23	< 0.23		< 0.23	---
	-20.0	< 0.23	< 0.23*	---	< 0.23	---
	-24.5	< 0.23	< 0.23		< 0.23	---
	-29.0	< 0.23	< 0.23		< 0.23	---
	-33.5	< 0.23	< 0.23		< 0.23	---
	-38.0	< 0.23	< 0.23		< 0.23	---
Peeper 4	-2.0	< 0.23	< 0.23*	---	< 0.23	---
	-6.5	< 0.23	< 0.23		< 0.23	---
	-11.0	< 0.23	< 0.23		< 0.23	---
	-15.5	< 0.23	< 0.23		< 0.23	---
	-20.0	< 0.23	< 0.23		< 0.23	---
	-24.5	< 0.23	< 0.23		< 0.23	---
	-29.0	< 0.23	< 0.23		< 0.23	---
	-33.5	< 0.23	< 0.23		< 0.23	---
	-38.0	< 0.23	< 0.23		< 0.23	---

Table D.11: Cr(VI) Depth Profile Results for Cr Speciation Analysis without EDTA

Peeper	Cell depth (cm)	Cr(VI) concentration, left cell (ppb)	Cr(VI) concentration, right cell (ppb)	RPD of analytical duplicate (%)	Average field duplicate Cr(VI) concentration (ppb)	RPD of field duplicates (%)
Reference	-2.0	< 0.14	< 0.14		< 0.14	---
	-6.5	< 0.14	< 0.14		< 0.14	---
	-11.0	< 0.14	< 0.14		< 0.14	---
	-15.5	< 0.14	< 0.14	---	< 0.14	---
	-20.0	< 0.14	< 0.14		< 0.14	---
	-24.5	< 0.14	< 0.14		< 0.14	---
	-29.0	< 0.14	< 0.14		< 0.14	---
	-33.5	< 0.14	< 0.14		< 0.14	---
	-38.0	< 0.14	< 0.14	---	< 0.14	---
Peeper 1	-2.0	< 0.14	< 0.14		< 0.14	---
	-6.5	< 0.14	< 0.14		< 0.14	---
	-11.0	< 0.14	< 0.14		< 0.14	---
	-15.5	< 0.14	< 0.14		< 0.14	---
	-20.0	< 0.14	< 0.14	---	< 0.14	---
	-24.5	< 0.14	< 0.14		< 0.14	---
	-29.0	< 0.14	< 0.14		< 0.14	---
	-33.5	< 0.14	< 0.14		< 0.14	---
	-38.0	0.14 (trace)	< 0.14		< 0.14	---
Peeper 2	-2.0	< 0.14	< 0.14	---	< 0.14	---
	-6.5	< 0.14	< 0.14		< 0.14	---
	-11.0	< 0.14	< 0.14		< 0.14	---
	-15.5	< 0.14	< 0.14		< 0.14	---
	-20.0	< 0.14	< 0.14	---	< 0.14	---
	-24.5	< 0.14	< 0.14		< 0.14	---
	-29.0	< 0.14	< 0.14		< 0.14	---
	-33.5	< 0.14	< 0.14		< 0.14	---
	-38.0	< 0.14	< 0.14		< 0.14	---
Peeper 3	-2.0	< 0.14	< 0.14	---	< 0.14	---
	-6.5	< 0.14	< 0.14		< 0.14	---
	-11.0	< 0.14	< 0.14		< 0.14	---
	-15.5	< 0.14	0.30 (trace)		0.19 (trace)	---
	-20.0	< 0.14	< 0.14	---	< 0.14	---
	-24.5	< 0.14	< 0.14		< 0.14	---
	-29.0	0.16 (trace)	< 0.14		< 0.14	---
	-33.5	< 0.14	< 0.14		< 0.14	---
	-38.0	< 0.14	< 0.14		< 0.14	---
Peeper 4	-2.0	< 0.14	< 0.14	---	< 0.14	---
	-6.5	< 0.14	< 0.14		< 0.14	---
	-11.0	< 0.14	< 0.14		< 0.14	---
	-15.5	< 0.14	< 0.14		< 0.14	---
	-20.0	< 0.14	< 0.14		< 0.14	---
	-24.5	< 0.14	< 0.14		< 0.14	---
	-29.0	< 0.14	0.24 (trace)		0.16 (trace)	---
	-33.5	< 0.14	0.23 (trace)		0.15 (trace)	---
	-38.0	< 0.14	< 0.14		< 0.14	---

D.3 ICP-MS-HPLC Data for Cr Speciation Analysis with EDTA

Table D12: LOD and LOQ for Cr Speciation Analysis with EDTA

Species	Cr(III) (ppb)	Cr(VI) (ppb)
LOD	0.10	0.11
LOQ	0.33	0.36

Table D.13: QC Sample Results for Cr Speciation Analysis with EDTA

Sample	% Diff from 54.3 ppb (%)	% Diff from 50.7 ppb (%)
QC 1	16	14
QC 2	17	14
QC 3	6.0	0.44
QC 4	6.2	1.2
QC 5	8.1	2.4
QC 6	5.5	3.8
QC 7	7.9	3.8
QC 8	21	18
QC 9	1.0	-3.2
QC 10	17	14
QC 11	9.2	3.8
QC 12	2.6	1.1
QC 13	3.4	1.8
Average of absolute values	9.2	5.7

Table D.14: Blank Sample Results for Cr Speciation Analysis with EDTA

Sample	Cr(III) (ppb)	Cr(VI) (ppb)
B1	0.0 (non-detect)	0.048 (non-detect)
B2	0.0 (non-detect)	0.064 (non-detect)
B3	0.0 (non-detect)	0.032 (non-detect)
B4	0.0 (non-detect)	0.094 (non-detect)
B5	0.0 (non-detect)	0.075 (non-detect)
B6	0.0 (non-detect)	0.036 (non-detect)
B7	0.0 (non-detect)	0.077 (non-detect)
B8	0.0 (non-detect)	0.13 (trace)
B9	0.023 (non-detect)	0.12 (trace)
B10	0.040 (non-detect)	0.16 (trace)
B11	0.0 (non-detect)	0.051 (non-detect)
B12	0.015 (non-detect)	0.10 (non-detect)
B13	0.043 (non-detect)	0.089 (non-detect)
B14	0.13 (trace)	0.083 (non-detect)
B15	0.00 (non-detect)	0.064 (non-detect)
B16	0.026 (non-detect)	0.13 (trace)

Table D.15: Spike Sample Results for Cr Speciation Analysis with EDTA

Sample	Cr(III)			Cr(VI)		
	Measured spike concentration (ppb)	Theoretical spike concentration (ppb)	Percent recovery (%)	Measured spike concentration (ppb)	Theoretical spike concentration (ppb)	Percent recovery (%)
SPK1	6.9	4.0	170	-0.064	4.3	0.0
SPK2	7.0	4.0	180	-0.070	4.3	0.0
SPK3	5.9	4.0	150	-0.013	4.3	0.0
SPK4	6.3	4.0	160	-0.047	4.3	0.0
SPK5	5.3	4.0	130	0.014	4.3	3.2
SPK6	6.7	4.0	170	-0.063	4.3	0.0
SPK7	8.1	4.0	2.0	-0.004	4.3	0.0
SPK8	4.9	4.0	1.2	-0.027	4.3	0.0
SPK9	6.0	4.0	150	0.317	4.3	7.4

Table D.16: Cr(III) Depth Profile Results for Cr Speciation Analysis with EDTA

Peeper	Cell depth (cm)	Cr(III) concentration, left cell (ppb)	Cr(III) concentration, right cell (ppb)	RPD of analytical duplicate (%)	Average field duplicate Cr(III) concentration (ppb)	RPD of field duplicates (%)
Reference	-2.0	0.20	0.22		0.21 (trace)	-7.4
	-6.5	0.22	0.22		0.22 (trace)	1.3
	-11.0	0.23	0.18*	-23	0.21 (trace)	27
	-15.5	0.19	0.20		0.19 (trace)	-3.7
	-20.0	0.29	0.27		0.28 (trace)	7.5
	-24.5	0.33	0.25		0.29 (trace)	28
	-29.0	0.18	0.25		0.21 (trace)	-34
	-33.5	0.21	0.23*	-31	0.22 (trace)	-9.9
	-38.0	0.34	0.23		0.28 (trace)	40
Peeper 1	-2.0	0.49	0.56		0.52	-14
	-6.5	N/A**	0.37		0.37	---
	-11.0	0.54	0.45		0.49	19
	-15.5	0.63	0.61*	-76	0.62	1.7
	-20.0	0.80	0.92		0.86	-14
	-24.5	0.82	0.72		0.77	13
	-29.0	0.94	0.83		0.88	11
	-33.5	0.99	0.68		0.83	37
	-38.0	1.3	1.1	-39	1.2	18
Peeper 2	-2.0	0.57	0.42		0.49	30
	-6.5	0.47	0.58		0.51	-17
	-11.0	0.40	0.43		0.42	-6.2
	-15.5	0.38	0.55*	-13	0.47	-38
	-20.0	0.65	0.65		0.65	0.50
	-24.5	0.62	0.53		0.57	16
	-29.0	0.95	0.76		0.86	23
	-33.5	0.92	0.83		0.88	8.6
	-38.0	1.1	1.5*	-46	1.3	-28
Peeper 3	-2.0	0.32	0.36		0.34	-12
	-6.5	0.26	0.21		0.24 (trace)	20
	-11.0	0.20	0.25		0.23 (trace)	-20
	-15.5	0.21	0.24		0.23 (trace)	-14
	-20.0	0.26*	0.24	18	0.35	6.4
	-24.5	0.23	0.16		0.19 (trace)	38
	-29.0	0.21	0.22		0.22 (trace)	-5.1
	-33.5	0.34	0.36		0.35	-7.0
	-38.0	0.31	0.24		0.28 (trace)	25
Peeper 4	-2.0	0.64*	0.62	15	0.63	16
	-6.5	0.58	0.56		0.57	3.2
	-11.0	0.38	0.40		0.39	-6.2
	-15.5	0.42	0.34		0.38	22
	-20.0	0.54	0.33		0.43	49
	-24.5	0.44*	0.30	-6.2	0.37	37
	-29.0	0.44	0.66		0.55	-39
	-33.5	0.53	0.45		0.49	17
	-38.0	0.44	0.53		0.49	-19

Table D.17: Cr(VI) Depth Profile Results for Cr Speciation Analysis with EDTA

Peeper	Cell depth (cm)	Cr(VI) concentration, left cell (ppb)	Cr(VI) concentration, right cell (ppb)	RPD of analytical duplicate (%)	Average field duplicate Cr(VI) concentration	RPD of field duplicates (%)
Reference	-2.0	< 0.11	< 0.11		< 0.11	---
	-6.5	< 0.11	< 0.11		< 0.11	---
	-11.0	0.15	< 0.11*	---	< 0.11	---
	-15.5	0.19	0.19		0.19 (trace)	-5.3
	-20.0	0.22	< 0.11		0.14 (trace)	---
	-24.5	< 0.11	0.11		< 0.11	---
	-29.0	< 0.11	< 0.11		< 0.11	---
	-33.5	< 0.11	< 0.11*	---	< 0.11	---
	-38.0	< 0.11	< 0.11		< 0.11	---
Peeper 1	-2.0	< 0.11	< 0.11		< 0.11	---
	-6.5	< 0.11	< 0.11		< 0.11	---
	-11.0	< 0.11	< 0.11		< 0.11	---
	-15.5	< 0.11	< 0.11*	---	< 0.11	---
	-20.0	< 0.11	< 0.11		< 0.11	---
	-24.5	< 0.11	< 0.11		< 0.11	---
	-29.0	< 0.11	< 0.11		< 0.11	---
	-33.5	< 0.11	< 0.11		< 0.11	---
	-38.0	< 0.11	< 0.11*	---	< 0.11	---
Peeper 2	-2.0	< 0.11	< 0.11		< 0.11	---
	-6.5	< 0.11	< 0.11		< 0.11	---
	-11.0	< 0.11	< 0.11		< 0.11	---
	-15.5	< 0.11	< 0.11*	---	< 0.11	---
	-20.0	< 0.11	< 0.11		< 0.11	---
	-24.5	< 0.11	< 0.11		< 0.11	---
	-29.0	< 0.11	< 0.11		< 0.11	---
	-33.5	< 0.11	< 0.11		< 0.11	---
	-38.0	< 0.11	< 0.11*	---	< 0.11	---
Peeper 3	-2.0	< 0.11	< 0.11		< 0.11	---
	-6.5	< 0.11	< 0.11		< 0.11	---
	-11.0	< 0.11	< 0.11		< 0.11	---
	-15.5	< 0.11	< 0.11		< 0.11	---
	-20.0	< 0.11*	< 0.11	---	< 0.11	---
	-24.5	< 0.11	< 0.11		< 0.11	---
	-29.0	< 0.11	< 0.11		< 0.11	---
	-33.5	< 0.11	< 0.11		< 0.11	---
	-38.0	< 0.11	< 0.11		< 0.11	---
Peeper 4	-2.0	< 0.11*	< 0.11	---	< 0.11	---
	-6.5	< 0.11	< 0.11		< 0.11	---
	-11.0	< 0.11	< 0.11		< 0.11	---
	-15.5	< 0.11	< 0.11		< 0.11	---
	-20.0	< 0.11	< 0.11		< 0.11	---
	-24.5	< 0.11*	< 0.11	---	< 0.11	---
	-29.0	< 0.11	< 0.11		< 0.11	---
	-33.5	< 0.11	< 0.11		< 0.11	---
	-38.0	< 0.11	< 0.11		< 0.11	---

Appendix E: Derivations and Sample Calculations

E.1 Calculation of Mink FIR and HQ for PCBs

The FIR of mink is calculated using Equation C.1:

$$FIR = \frac{FMR \times CF}{\sum_{i=1}^{n}[P_i \times GE_i \times AE_i]}$$

and Equation C.2:

$$FMR = a \times (BW)^b$$

Therefore, using mink data from Table C.1:

$$FIR\ (mink) = \frac{\left\{\frac{(2.582 \times (1040)^{0.862})kJ}{day}\right\} \times 0.239\frac{kcal}{kJ}}{1.0 \times 1200\frac{kcal\ (ww)}{kg} \times 0.91}$$

$$FIR\ (mink) = 0.23\frac{kg}{day}$$

To calculate the HQ, the following formula is used:

$$HQ = \frac{ADD\left(\frac{mg}{kg \times day}\right)}{TRV\left(\frac{mg}{kg \times day}\right)}$$

where the ADD is calculated using Equation 3.1:

$$ADD = \left\{\left[\sum_{i=1}^{n} EPC_{fi} \times F_i\right] + (EPC_{sed} \times F_{sed})\right\} \times \frac{FIR \times F_{site} \times ED}{BW}$$

Calculating the ADD of PCBs for mink using receptor data from Table 3.1, and the UCL95 for PCBs in fish from Table 3.4:

$$ADD\ (mink, PCBs) = \left\{\left(0.652\frac{mg}{kg} \times 1.0\right) + 0\right\} \times \frac{0.225\frac{kg}{day} \times 1.0 \times 1.0}{1.04\ kg}$$

$$ADD\ (mink, PCBs) = 0.14\frac{mg}{kg \times day}$$

Taking the quotient of the ADD (mink, PCBs) with the TRV for PCBs in mink (Table 3.6):

$$HQ\ (mink, PCBs) = \frac{0.14\frac{mg}{kg \times day}}{0.053\frac{mg}{kg \times day}}$$

$$HQ\ (mink, PCBs) = 2.6$$

E.2 Calculation of Quantities for Use in the LCA

E.2.1 Deriving Equations that Calculate the Mass of Dry Solids and Mass of Water in a Saturated Sediment Sample

Consider a mass (M) of wet sediment in its natural state (within the river), which occupies a given volume (V). The *unit weight* (γ_s) of that sediment is given by (Craig, 1987):

$$\gamma_s = \frac{Mg}{V} \qquad (\boldsymbol{E.1})$$

where g is the gravitational constant (9.81 $m \cdot s^{-2}$). Equation E.1 can be rearranged to the form:

$$M = \frac{\gamma_s V}{g} \qquad (\boldsymbol{E.2})$$

For the purposes of this section, the term *water content (w)*, as defined within soil mechanics, will be used. In soil mechanics, water content of a wet soil or sediment sample is defined as the ratio of the mass of the water (M_w) to the mass of the dry solids (M_s) in the sample, as given by Equation E.3 (Craig, 1987). It will be assumed that the sediments within the impacted area are two-phase, fully saturated sediments (*i.e.* there is no air in the sediments), thus the total mass (M) of the sediments is given by Equation 3.4 (Craig, 1987):

$$w = \frac{M_w}{M_s} \qquad (\boldsymbol{E.3})$$

$$M = M_w + M_s \qquad (\boldsymbol{E.4})$$

Developing Equation E.3:

$$w + 1 = \frac{M_w}{M_s} + 1$$

$$w + 1 = \frac{M_w}{M_s} + \frac{M_s}{M_s}$$

$$w + 1 = \frac{M_w + M_s}{M_s}$$

Using Equation E.4, and then rearranging:

$$M = M_s(w + 1) \qquad (\boldsymbol{E.5})$$

Combining Equation E.2 and Equation E.5, and then rearranging, Equation E.6 is obtained:

$$M_s = \frac{\gamma_s V}{(w+1)g} \qquad (\boldsymbol{E.6})$$

Using a similar process, an equation for M_w can be obtained. Beginning with Equation E.3:

$$w = \frac{M_w}{M_s}$$

$$\frac{1}{w} = \frac{M_s}{M_w}$$

$$\frac{1}{w} + 1 = \frac{M_s}{M_w} + 1 \qquad where \ \frac{1}{w} + 1 = \frac{(1+w)}{w}$$

$$\frac{(1+w)}{w} = \frac{M_s + M_w}{M_w}$$

Using Equation E.4, and rearranging:

$$M_w = \frac{w\gamma_s V}{(1+w)g} \qquad (\boldsymbol{E.7})$$

In summary, it has been assumed that the sediments within the river are fully saturated, and given the parameters γ_s and w for a sediment volume (V), the total mass of dry solids (M_s) and total mass of water (M_w) within this volume are given by Equation E.6 and Equation E.7, respectively.

E.2.2 Calculation of Unit Weight for Impacted Area Sediments

The equation to calculate the unit mass of a sample of soil or sediment is given by Equation E.8 (Craig, 1987):

$$\gamma_s = \frac{G_s + S_r e}{1 + e}\ \gamma_w \qquad (\boldsymbol{E.8})$$

where G_s is the specific gravity of the solid particles, S_r is the degree of saturation, e is the void ratio, and γ_w is the unit weight of water. Table E.1 is a summary of relevant data that will be needed for making calculations in this appendix.

Table E.1: Summary of Data and Constants Needed for Sediment Calculations

Quantity	Value	Reference
G_s	2.06	Inspect-Sol (2003)
S_r	1.0	Assumption
w	4.0	Tinney (2006)
γ_w	9.8 kN·m^{-3} (constant)	Craig (1987)
e	8.2	Calculated from other quantities
γ_s	11 kN·m^{-3}	Calculated from other quantities

The void ratio (e) was calculated from known quantities of the impacted area sediments, using Equation E.9 (Craig, 1987):

$$S_r = \frac{wG_s}{e} \qquad (\boldsymbol{E.9})$$

The unit weight (γ_s) was calculated from Equation E.8:

$$\gamma_s = \frac{2.06 + (1.0)(8.2)}{1 + 8.2}\left(9.8\frac{kN}{m^3}\right)$$

$$\gamma_s = 11\frac{kN}{m^3}$$

E.2.3 Calculation of Mass of Water and Mass of Dry Solids of Dredged Sediments

Equation E.6 and Equation E.8, with the data summarized in Table E.1, to calculate M_s and M_w found within the functional unit, 200,000 m^3 of sediment. The sum of M_s and M_w represents the dredged mass of sediments (M_d), as defined in Chapter 5.

$$M_s = \frac{\gamma_s V}{(w+1)g} = \frac{\left(11\frac{kN}{m^3}\right)(200{,}000\ m^3)}{(4.0+1)\left(9.81\frac{m}{s^2}\right)} = 44{,}900\ t$$

$$M_w = \frac{w\gamma_s V}{(1+w)g} = \frac{(4.0)\left(11\frac{kN}{m^3}\right)(200{,}000\ m^3)}{(4.0+1)\left(9.81\frac{m}{s^2}\right)} = 179{,}000\ t$$

E.2.4 Calculation of Input Mass of Sediments

As detailed in Section 5.2.3(iii), the volume of dredged sediment will be reduced by 50 percent, through dewatering of these sediments during dredging processes. Assuming that this volume reduction is due entirely from lost water, the total mass of dredged sediments (M_d) for the initial 200,000 m^3 of will be reduced by the mass of 100,000 m^3 of water, which results in the input mass of sediments (M_i).

$$M_i = M_d - \rho_w(100{,}000\ m^3)$$

$$M_i = (44{,}900\ t + 179{,}000\ t) - \left(1000\frac{kg}{m}\right)(100{,}000\ m^3)$$

$$M_i = 123{,}000\ m^3$$

E.2.5 Calculation of Mass of Sediments Exiting the MSWP

After the sediments are processed by the MSWP, of the total mass of the wet sediments, 25 percent is water (Wevers, 2009). Therefore, knowing M_s, the mass of the wet sediments that exit the MSWP after processing can be calculated:

$$Mass\ of\ Sediments\ that\ Exit\ the\ MSWP = \frac{M_s}{0.75} = \frac{44{,}900\ t}{0.75} = 59{,}900\ t$$

E.2.6 Calculation of Mass of Sediments after Dewatering for Two Years

After the input sediments have dewatered at Knox Farm for two years, it has been assumed that, of the total mass of the dewatered sediments, 15 percent of this mass is water. Therefore, knowing M_s, the mass of the dewatered sediments can be calculated:

$$Mass\ of\ Dewatered\ Sediments = \frac{M_s}{0.85} = \frac{44{,}900\ t}{0.85} = 52{,}800\ t$$