DOCUMENTING SPATIAL & TEMPORAL VARIATIONS OF SUB-SURFACE CONTAMINANTS USING TREE CORES: IMPLICATIONS FOR THE DESIGN OF EFFECTIVE WASTE MANAGEMENT STRATEGIES

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Documenting spatial and temporal variations of subsurface contaminants using tree cores: Implications for the design of effective waste management strategies

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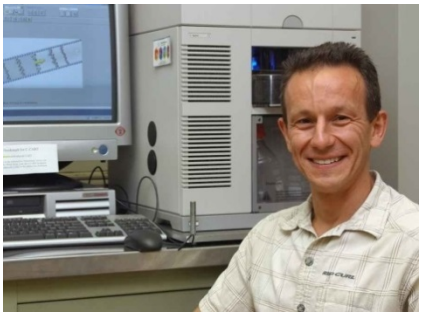

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EXECUTIVE SUMMARY

This report is the output of a multidisciplinary research initiative at the Labrador Institute of Memorial University, funded by the Harris Centre-MMSB Waste Management Applied Research Fund 2014–2015. It is part of a much larger project entitled “the use of trees to delineate subsurface contaminants in Canada’s northern environment”, which brings together faculty, researchers and students at Memorial University of Newfoundland (Canada) and Technical University of Denmark (Denmark).

The research presented here was undertaken at the former landfill site of the Canadian Air Force Base, 5 Wing Goose Bay, in the remote community of Happy Valley-Goose Bay, Labrador. Contamination at the former landfill site is the result of environmentally unsound pre-1990’s disposal of households and industrial solid wastes. This research is first to use tree cores to study the presence of organic and inorganic contaminants in soil and groundwater, and then to evaluate how this innovative method can be of aid in efficient environmental assessment and monitoring in the early stages of site characterization. When compared with traditional techniques that commonly involve drilling boreholes and monitoring wells for soil and groundwater sampling, the tree-core method is very simple, fast and inexpensive to implement, and requires minimal field equipment.

Many communities across Labrador and elsewhere in northern Canada are now investigating contaminated sites, particularly those associated with community waste disposal, past military activities or waste rocks and/or tailings from past mineral exploration and mine’s operations. Tree-core analysis may therefore be a broadly useful and important method for long-term environmental assessment and monitoring efforts. Such analysis will support good decision-making to ensure that proper waste management plans are put in place to prevent or control impact on water quality and the environment. If implemented, the tree-core method could be also of use to other types of facilities (e.g. mineral exploration and mining wastes, leaking of petroleum storage tanks, etc.) and environmental protection organizations.

In this study, core samples were taken from mature and healthy-looking trembling aspen, black spruce and white birch trees growing at a former landfill site. One set of core samples was stored in 20 mL glass vials, kept cool at about 4˚C and analyzed within 3 to 5 days for petroleum hydrocarbons (benzene, toluene, ethylbenzene and m, p, o-xylenes or collectively BTEX and methyl tertiary-butyl ether or MTBE) and chlorinated ethenes (perchloroethene or PCE, trichloroethene or TCE, 1,1 dichloroethene or1,1-DCE, *cis*-1,2-dichloroethene or *cis*-DCE and *trans*-1,2-

dichloroethylene or *trans*-DCE), using headspace-gas chromatography-mass spectrometry (HS-GC-MS). A second set was air dried at room temperature in the laboratory, under protection from possible contaminants, then cross-dated, divided into two 9-year core segments, and washed and acid digested before analysis for major and trace elements by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS).

MTBE, 1,1-DCE, *cis*-DCE and *trans*-DCE were not found in any of the core samples of tree species growing at the landfill site and are considered to be absent in the groundwater. However continue monitoring for these organic contaminants is suggested until site clean-up is complete. TCE was detected in only few trees. On the other hand, BTEX compounds and PCE were detected in most tree cores, and contamination is the most likely explanation for the elevated levels found in the trees. In addition, two zones of anomalously high concentrations of total BTEX constituents and PCE, respectively, were identified and recommended for monitoring by groundwater wells. Tree species exhibit different concentrations of BTEX constituents and PCE, indicating selective uptake and accumulation. Some majors or essential elements (Ca, K and Mg) and trace elements (Ag, Ba, Cd, Ce, Co, Cr, Cs, Cu, Fe, Mn Mo, Nb, Nd, Ni, Pb, Rb, Sb, Sm, Sr, Ti, U, Y, Zn and Zr) were detected in the selected tree-ring segments. However, their concentrations don’t show any sufficiently regular patterns to confidently infer chemical changes or contamination in the environment.

The tree-core method has great potential to become a common tool for detecting subsurface contaminants and locating elevated areas of contamination at initial stages of site assessment and monitoring in Canada northern environment. It can therefore aid in the proper management of contamination during landfill operations and after site closures, and may also be used at other types of facilities, in efforts to minimize negative impacts on the environment and public health.

1. INTRODUCTION

1.1. Overview

Proper waste management has become a worldwide humanitarian topic, because of increased awareness of potential risks posed by unsound waste disposal to human health and the environment (El-Fadel et al., 1997; Rowe et al., 1997). In remote communities in Canada's North, here defined as the part north of the southern limit of discontinued permafrost zone, landfills and/or dumps remain the most common methods employed for the disposal of solid waste, much as they do elsewhere (Bright et al., 1995; Zagozewski et al., 2011). In northern communities, landfills or dumps have received typically household and commercial/industrial wastes or waste rocks from mineral exploration and mining activities (Bright et al., 1995; ROLES, 2014; Government of Canada, 2015). Modern engineered landfills are designed to mitigate or prevent the adverse impacts of waste on the surrounding environment. However, the generation of leachate and gas remains an inevitable consequence of existing waste disposal practices and at any future landfill sites, and risks to public health and environment may arise if sites are not well-controlled (Sawhney and Kozloski, 1984; Allen, 2001; Christensen et al., 2001; Eggen et al., 2010). Consequently, the development of innovative locality-specific strategies and methods is crucial to ensuring efficient solid waste management and environmental protection (Department of Municipal Affair, 2002; Municipalities Newfoundland and Labrador, 2010).

1.1.1. Leachate contaminants and gases from solid waste landfills and open dumpsites

Landfill leachate is produced by excess water (from rainfall, snowmelt and decomposition of the wastes) percolating through layers of deposited waste and migrating into surrounding areas (e.g. Christensen et al., 2001; Kanmani et al., 2013). The chemical qualities of leachate are very complex and extremely variable (Fatta et al., 1999). In general, leachate quality depends mainly on the types of solid wastes deposited, the chemical and biochemical reactions that occur as the waste material decomposes, and the age of deposited wastes (Christensen et al., 2001). In a typical landfill receiving a mixture of municipal, commercial and industrial waste, leachate pollution plume contains inorganic macrocomponents (e.g. Ca, Mg, Na, K, Fe, Mn and Cl), heavy metals (e.g. Pb, Hg, Cr, Cd, As, Cu, Ni and Zn), and organic compounds, including chlorinated ethenes such as perchloroethene (PCE) and trichloroethene (TCE), polychlorinated biphenyls (PCBs) and petroleum hydrocarbons like benzene, toluene, ethylbenzene and m, p, o-xylenes (collectively referred to as BTEX) and methyl tertiary-butyl ether (MTBE) and potentially other volatile organic compounds

(e.g. Sawhney and Kozloski, 1984; Christensen et al., 2001). Additionally, the decomposition of organic components inside solid waste landfills generates greenhouse gases (CO_2, CH_4 and N_2O), contributing to climate change (e.g. Manfredi et al., 2009). Therefore, inadequate waste management entails considerable risks, particularly including the contamination of surface water, groundwater, soils and air (Fatta et al., 1999; Christensen et al., 2001).

1.1.2. *Evaluation of contaminated sites: traditional methods for site assessment and monitoring*

Substantial resources are spent in the assessment and cleanup of former landfill sites and surrounding areas that have become contaminated or polluted due to past disposal practices now known to adversely affect human health and the environment, and also due to poor site monitoring and maintenance plans (Christensen et al., 2001). As a result, environmental assessment and monitoring practices have been receiving increasing attention not only for effective evaluation of pollution potential and detection of contaminated soil and groudwater, but also as decision-support tools for sustainable approaches to the long-term protection of the environment at extant and future landfills (e.g. Cifrian et al., 2013). Effective site assessment requires data on historical and current transport of subsurface contaminants, and a chronological record of contamination or pollution. Historical information, although critical in assessing the potential future migration of contaminants and temporal changes in the variability of contaminants released into the environment, is frequently missing or incomplete.

There is an extensive tradition of drilling boreholes and monitoring wells for soil and groundwater sampling to assess and monitor sites. But, drilling processes are not only expensive and time-consuming, but also requires heavy equipment, which is invasive and causes ecological damage. These drawbacks often limit the extent of investigated areas. Moreover, in remote northern communities, traditional methods are often difficult to apply, due to site remoteness, limited local logistical capacity, and harsh climatic conditions (Rutter et al., 2003; Government of Canada, 2015: 2014). Moreover, data collected by this method of analyzing soil and groundwater has no time dimension, and does not permit the reconstruction of site pollution history requires for better design of waste management strategies in general, and assessment, remediation or containment plans in particular. These shortcomings indicate a crucial need for innovative methods to carry out extensive monitoring surveys and produce reliable historical information. In recognition of this need, this research evaluates the feasibility of using tree-core analysis to detect the presence of subsurface

contamination by volatile organic compounds and trace elements to complement traditional drilling methods.

1.2. Research rationale: The use of tree-core analysis to support decision-making in waste management

Despite the controversy surrounding landfill practices, landfills are an important method of organised waste disposal, and will continue to be so until feasible alternatives are developed. At present, landfills inevitably generate leachate, and when that leachate is uncontrolled or improperly managed, it pollutes nearby groundwater, surface water, soil, and air. This environmental pollution poses a risk to human health. Such risks necessitate careful control of spatial and temporal variations in environmental conditions during a landfill's operational lifespan and after its closure. Because the chemistry of the leachate for a given landfill cannot be predicted from data in the literature, since the parameters influencing its composition vary extremely both within sites (old and new areas of the fill) and between sites, environmental impact assessments and monitoring of individual landfill sites are essential to the development of effective environmental waste management strategies. Site impact assessment and monitoring using traditional methods (soil and groundwater sampling through drilling) are often limited by high costs and difficulties in carrying out extensive monitoring surveys.

Tree-core analysis, offers a critical decision-support tool for waste management and can help ensure that environmental and other sustainability aspects are considered effectively in policy, plan and program making for three major reasons: (1) it represents a unique strategy to assess the present state of pollution and/or the changes of environmental conditions with time, and thus to reconstruct a site's pollution history, providing the necessary data for better projections of variations in contaminant concentrations; (2) it is fast and inexpensive and involves sampling with a tree corer, which is rapid, simple and non-destructive, causing negligible damage to the ecological systems being protected; and (3) it is a valuable subsurface screening method for quickly detecting sites of unknown subsurface contamination or for identifying contamination patterns, particularly in remote locations or urban settings where it is complicated and expensive to install monitoring wells. Moreover, trees have the potential to magnify variations in pollutant levels even in cases where the concentrations of target elements are low in soils, if the elements of interest occur in gaseous or liquid forms. Given that historically, landfills have been the most commonly-used option for waste

disposal, and that they remain so in the remote northern communities, trees could be used broadly useful for assessing subsurface environmental pollution.

Although tree-core analysis has become an integral part of environmental investigations worldwide because of the high cost of environmental cleanups, it has yet to be implemented in a waste management context in Newfoundland and Labrador (and at other remote northern communities). Moreover, the provincial economy is fuelled substantially by the ore extraction and electricity generation industries, and tree-core analysis may also be applied to the wastes generated by mineral exploration and mining activities, and mineral processing operations (waste-rock, tailings and dust) and hydropower plants (waste water sludge and residues). The tree-core method of assessing environmental baselines and/or identifying the timing and sources of contamination is therefore of broad strategic benefits to Newfoundland and Labrador's socio-economic development.

1.3. Research objectives

This research addresses the manner in which trees provide essential environmental data to assist the development of waste management strategies for minimizing and preventing environmental damages caused by historical unsound waste disposal practices. The tree-core method was applied at the former solid waste landfill of the Canadian Air Force Base, 5 Wing Goose Bay in the remote community of Happy Valley-Goose Bay, Labrador, to test for known organic and inorganic contaminants in soil and groundwater. The research involves the following tasks:

(1) Consulting with community members and local organizations at various stages of the research project.

(2) Selecting a sampling area with tree species and features that satisfy the requirements for use in tree-core analysis.

(3) Performing test analyses of tree-core samples for organic compounds by gas chromatography-mass spectrometry (GC-MS) by headspace extraction at the Stable Isotope Laboratory of Memorial University of Newfoundland, and select a reference laboratory for the analysis of trace elements using High Resolution-Inductively Coupled Plasma-Mass Spectrometry (HR-ICP-MS).

(4) Sampling, preparing and analysing tree cores from different tree species for different contaminants, including petroleum hydrocarbons (benzene, toluene, ethylbenzene and m, p, o-xylenes or BTEX and methyl tertiary-butyl ether or MTBE), chlorinated ethenes

(perchloroethene or PCE, trichloroethene or TCE, 1,1 dichloroethene or1,1-DCE, *cis*-1,2-dichloroethene or *cis*-DCE and *trans*-1,2-dichloroethylene or *trans*-DCE), and major and trace elements (62 elements).

(5) Investigating spatial and temporal changes in the variability of contaminants among tree species, as well as within individual trees; identifying the most appropriate tree species for managing long-term spatial contamination; and establishing the baseline concentrations for organic compounds and major and trace elements in tree-cores.

(6) Distinguishing pollution-growth responses in tree-ring series from responses to climate change and tree biology, as well as from natural background signals.

The outcomes of this research and the application of tree-core method will contribute to: (1) designing efficient, site-specific solid waste management approaches to prevent or control impacts on water quality and the environment; (2) reducing the overall costs and duration of initial stages of site contamination investigation (phase I site assessments) and monitoring of subsurface contamination at open/closed landfill sites; and (3) training highly qualified personnel (HQP).

1.4. Knowledge mobilization and deliverables

The development and implementation of this research project involved several consultations with local community members and meetings with community and government organizations. Research findings have been presented to audiences in the local community at Labrador Institute of Memorial University in Happy Valley-Goose Bay and at the Department of Chemistry of Memorial University in St. John's. Moreover, one manuscript was submitted in November 2015 to an international peer-reviewed journal for publication and two additional manuscripts are in advanced stages of development and preparation. Copies of all papers will be given to the Harris Centre upon their publications:

(1) Sean Murphy (research assistant) and Merline Fonkwe (2014): Using tree-core samples to detect subsurface contamination. The Labrador Institute of Memorial University, Happy Valley-Goose Bay, NL *(August 22, 2014).*

(2) Merline Fonkwe (2015): Documenting spatial and temporal variations of subsurface contaminants using tree cores: Implications for the design of effective waste management strategies. Midterm Project Report to the Harris Centre of Memorial University *(March 27, 2015).*

(3) Merline Fonkwe and Sean Murphy (2015): Geo-chemistry and assessment of environmental contamination. Visiting Speaker at the Department of Chemistry of Memorial University, St. John's *(April 25, 2015).*

(4) Merline Fonkwe and Stefan Trapp (*submitted*): Analyzing tree cores to detect petroleum hydrocarbon-contaminated groundwater at a former landfill site in the community of Happy Valley-Goose Bay, eastern Canadian subarctic. *Environmental Science and Pollution Research, November 2015*.

2. POLLUTANTS UPTAKE AND ACCUMULATION BY TREES

During their lifetimes, trees uptake pollutants present in their surrounding directly through their roots, bark or leaves (Cutter and Guyette, 1993; Padilla and Anderson, 2002; Trapp, 2007). Most importantly, the extensive and deep roots and large canopies of trees allow them to absorb a variety of pollutants (as water and nutrients) from large volumes of soil, groundwater and air. Chemical elements accumulate in all of a tree's organs, with most elements taken up by the roots. Tree roots uptake elements in solid, liquid and gaseous forms, with the most efficient accumulation occurring during plant-gas interaction (Padilla and Anderson, 2002). Thus, the chemistry of tree tissues should be a reflection of soil, groundwater and/or air chemical conditions. Pollutants that entered a tree from the roots are transported upward to the tree truck and branches by water along with nutrients (sap). Figure 1 illustrates the major mechanisms by which trees accumulate environmental contaminants from their surroundings (Burken et al., 2011). Contaminant uptake and accumulation are functions of physicochemical properties, the nature and concentration of specific contaminants, environmental conditions, such as seasons and soil properties, and tree species and specific physiology (Cutter and Guyette, 1993; Padilla and Anderson, 2002; Trapp, 2007). A tree may act either as an "accumulator", concentrating contaminants in its aerial tissues or as "excluder", restricting uptake of contaminants potentially deleterious to its health (Baker, 1981; Watmough, 1997). Therefore, the applicability of the tree-core method must be evaluated site by site if meaningful results are to be obtained.

Environmental scientists have measured the chemical composition of tree cores for over 40 years to measure the amounts of inorganic and organic compounds in the tree growth surroundings at numerous sites in temperate, subtropical and mediterranean regions (e.g. Watmough, 1997; Vroblesky et al., 1999; Balouet and Oudijk, 2006; Balouet et al., 2007; St-Laurent et al., 2009; Bruken et al., 2011; Algreen, 2015; Algreen et al. 2015; Rein et al., 2015; Fonkwe and Trapp,

submitted). They have met with some success in providing the semi-quantitative data needed for preliminary site evaluations and environmental monitoring. These studies investigate the response of trees to air, soil and groundwater pollution caused by human activities, such as solid waste disposal among others.

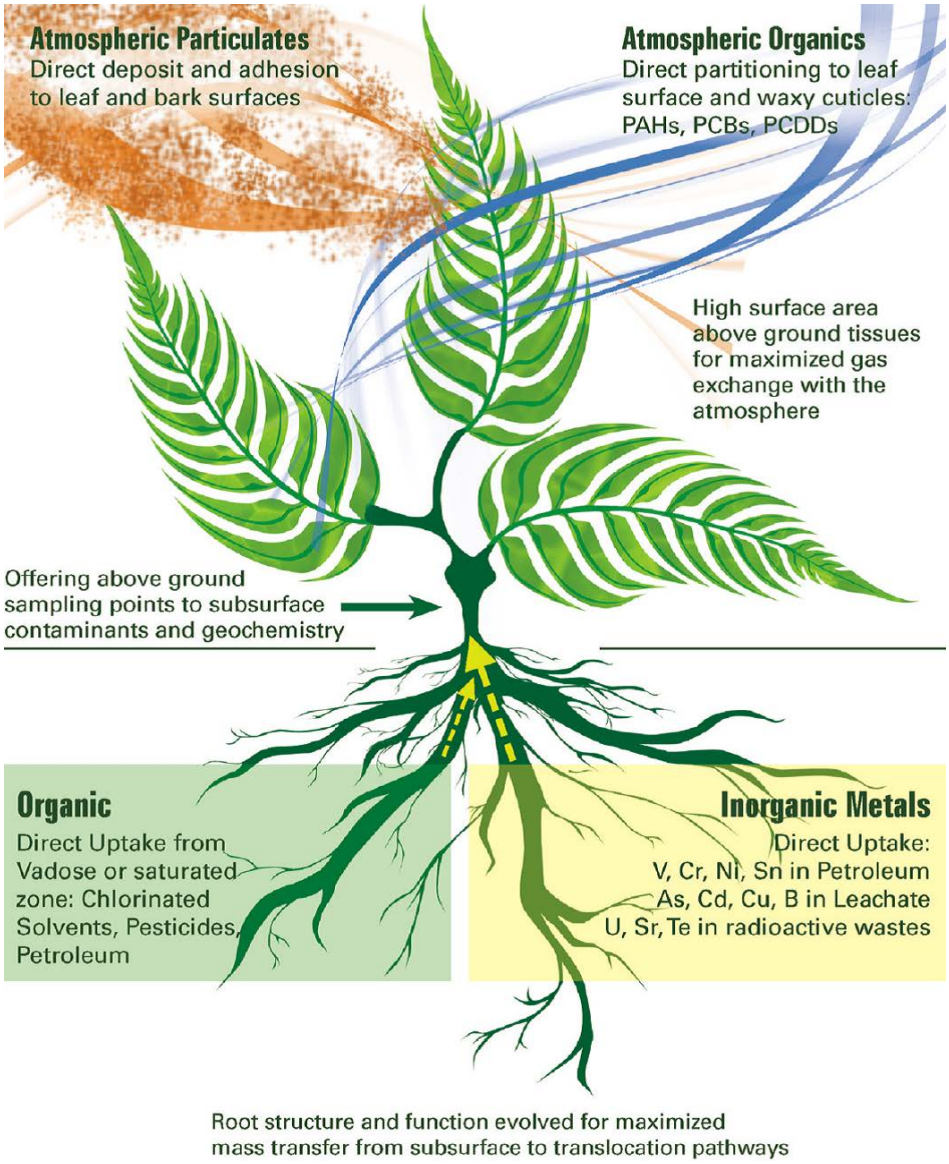


Figure 1: Major processes by which environmental pollutants are accumulated into trees. Soil and groundwater pollutants are taken up through the roots. Atmospheric pollutants diffuse into the leaves or adhere to plant surfaces (Figure from Burken et al., 2011).

3. TREE-CORE METHOD IN POLLUTION EVALUATION AND MONITORING

Most trees growing in temperate regions have annual growth patterns, which produce rings in their trunks (e.g. Cutter and Guyette, 1993). A yearly growth ring is composed of early, wide and light colored wood during the spring and summer, and late, narrow and dark wood during fall/winter

months, representing the end of the tree's annual growth (Fig. 2). The width of tree rings varies from year to year and is directly related to the growing environmental conditions during the time of their formation. The tree sap transporting contaminants or pollutants and nutrients circulates through the youngest, outermost annual rings which represent the sapwood, the living portion of the tree truck, whereas heartwood is the dead, inner part of the tree trunk. The layer of sapwood varies in thickness and number of growth rings between tree species.

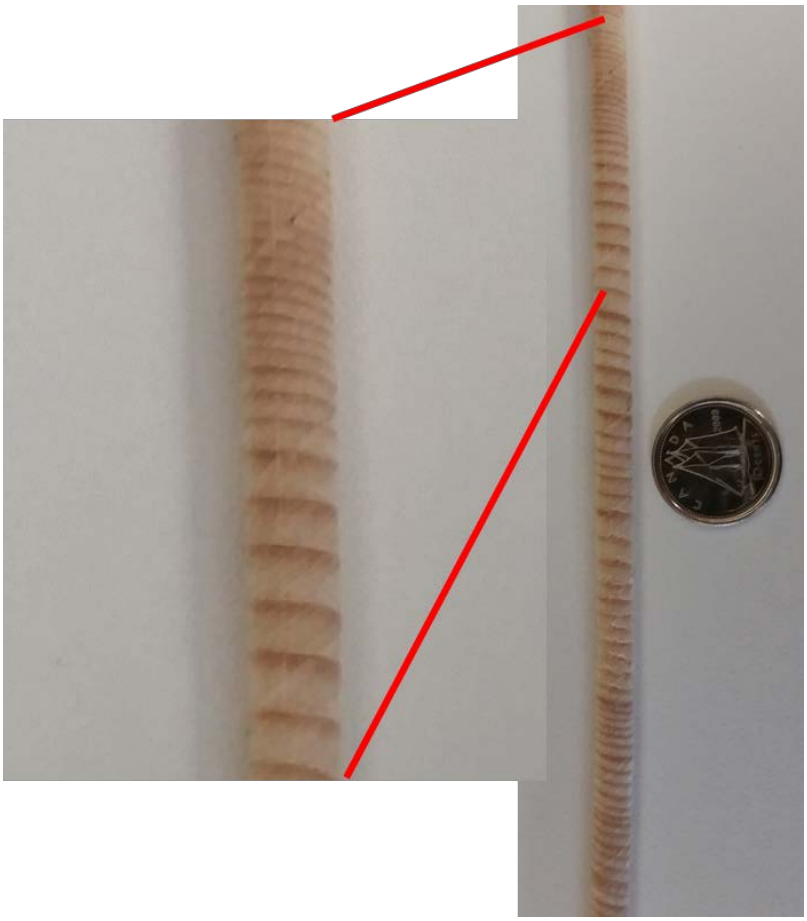


Figure 2: Tree core sample of a black spruce tree showing alternating rings consisting of light-colored summer growth band and dark, fall/winter growth bands. Each pair of light and dark bands represents a year's growth or annual growth ring. Note the variations in widths of annual tree rings, which might be explain by changes in the environmental conditions during tree growth *(Figure prepared by Sean Murphy).*

3.1. Dendrochronological approach

Dendrochronology or tree-ring dating examines events as they have been recorded over time in the tree-ring structures (e.g. in wood density and ring width patterns). Counting the dark ring segments may indicate the age of a tree and identifying tree-ring growth patterns and wood structures is useful in several disciplines, such as climatology, ecology, geomorphology and

archaeology (e.g. Speer, 2010; Malik and Wisturba, 2012). The main principle of dendrochronology suggests that variations in tree-ring width and wood density indicate a response to conditions in the surrounding environment. When environmental stress (e.g. pollution, drought, etc.) appears during growth, trees typically grow poorly and develop narrower rings (e.g. Speer, 2010; Trapp et al., 2001). Dendrochronology has been also applied to the reconstruction of different types of environmental events, such as climate changes, fires, glacier movements, mass-movements, floods, earthquakes, and volcanic activity (Malik and Wisturba, 2012). However, growth ring anomalies, such as missing, false and wedging rings, can complicate and impede reliable tree-ring crossdating.

3.2. Dendrochemical approach

Dendrochemistry is the study of elemental concentrations (major and trace elements) in a tree's annual growth rings. A yearly record of groundwater, soil and atmospheric conditions can be preserved in the annual growth rings as active transport of elements through pores in the rings stops during the conversion of sapwood to heartwood. This element fixation is useful for studying pollution histories and provides information about past events that is typically unattainable from other sources (e.g. Watmough, 1997; Watmough and Hutchinson, 2003; Balouet et al., 2007; St-Laurent et al., 2009). Therefore, dendrochemistry can be used to date the contamination events. Because metals may translocate between tree-rings inside the sapwood, sapwood sampling should be avoided when applying dendrochemical approach (Cutter and Guyette, 1993). Not all tree species are useful in dendrochemical studies because of the reported "barrier mechanism" at the root/soil interface that excludes pollutants from entering some trees and thereby accumulating in the rings, and also because of the lateral movement of some elements across growth-ring boundaries in other tree species (e.g. Watmough, 1997).

3.3. Phytoscreening approach

Phytoscreening is a much more recent approach to tree-core analysis, focusing mainly on the examination of concentrations of volatile organic compounds (VOCs) confined in the outermost and youngest annual ring, mainly sapwood, providing the current state of contamination in the tree growing zone (e.g. Vroblesky et al., 1999: 2004: 2008; Larsen et al., 2008; Sorek et al., 2008; Burken et al., 2011; Algreen et al., 2015; Rhein et al., 2015). Phytoscreening has been applied with success mainly in temperate, subtropical, or mediterranean regions to detect and delineate contamination by moderately hydrophobic VOCs with low octanol-water partition coefficients (log *Kow* = 1 - 3), commonly chlorinated ethenes, such as PCE, TCE and cis- and trans-DCE (e.g.

Vroblesky et al., 1999: 2004:2008; Larsen et al., 2008; Gopalakrishnan et al., 2007; Sorek et al., 2008; Ma and Burken, 2002; Schumacher et al., 2004; Wittlingerova et al., 2013; Limmer et al., 2014) and to a lesser extent petroleum hydrocarbon constituents, such as BTEX and MTBE (Landmeyer et al., 2000; Schumacher et al., 2004; Sorek et al., 2008; Wilson et al., 2013; Algreen, 2015; Algreen et al., 2015; Fonkwe and Trapp, *submitted*). Most recently, phytoscreening has been used for emerging contaminants, commonly explosives and munitions compounds, such as 2,4,6-trinitrotoluene (or TNT), pentaerythritoltetranitrate or PETN, hexahydro-1,3,5-trinitro-1,3,5-triazine or RDX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine or HMX, 2-amino-4,6-dinitrotoluene or 2ADNT, 2,4-Dinitroanisole or DNAN and perchlorate (ClO_4^-) (Karnjanapiboonwong et al., 2012; Limmer et al., 2015) and persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) (Balouet et al., 2014; Balouet and Chalot, 2015). Phytoscreening has been tested for heavy metals and found to be less reliable than for volatile organic compounds (Algreen et al., 2012; 2014).

4. MATHERIAL AND METHODS

4.1. Description of the study area

Happy Valley-Goose Bay is a small, remote community in the province of Newfoundland and Labrador in Canada, at the western extremity of Lake Melville, an inlet of the Labrador Sea (53˚30' N and 60˚41' W; Fig. 3). It covers an area of 306 km^2 and has a population of about 8000. The climate is subarctic, marked by heavy snowfall from November to March with snow covering the ground from November to May and high rainfall from June to September (average annual precipitation of 762 mm). The average daily temperatures remain below freezing from November to April and vary between –17.6˚C and 15.5˚C.

Surficial geology is composed of Quaternary marine and fluvial sediments to a depth of about 100 m, consisting dominantly of fine- to medium-grained sands and interbedded marine silts and clay, overlying a conglomerate and sandstone sequence (Liverman, 1997; Nunn and van Nosttrand, 1996; Wardle and Ash, 1986). Bedrock is composed of a Paleoproterozoic anorthosite-mangerite-charnockite-granite suite and the massif anorthosite of the Cape Caribou River Allochthon (Valvasori et al., 2015; Wardle and Ash, 1986).

The community of Happy Valley-Goose Bay is home of the Canadian Force Base (CFB) 5 Wing Goose Bay. This military air force base was constructed in 1941 on a flat-lying terrace, which has an elevation between 40 to 50 m (a.s.l.) and is bordered by the Terrington Basin to the north and

the Churchill River to the south (Fig. 3). It played an important role as a refuelling base to facilitate transatlantic flights during World War II and afterwards supported low-level flight training, air-defence exercises and bombing practices for the North Atlantic Treaty Organization (Wells, 2013). CFB 5 Wing Goose Bay remained a strategic military air base until 1987 and still continues today to support allied low-level flight training and multinational flying operations. Before 1990, a variety of residential and industrial wastes generated at CFB 5 Wing Goose Bay were disposed of on-site at several dumping areas making up a poorly-regulated and unlined landfill along the escarpment at the south-southeast boundary of the military property (AMEC, 2009; JWEL, 1992; see Fig. 3).

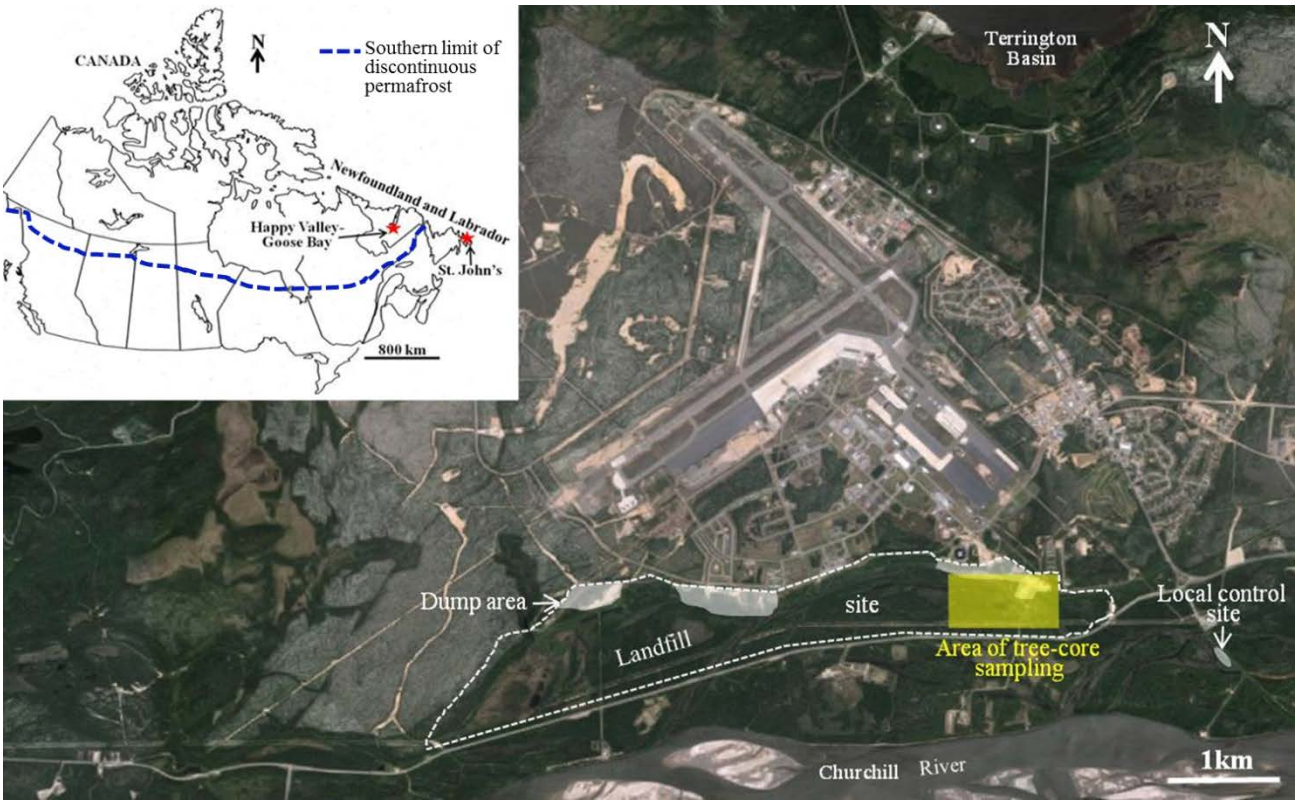


Figure 3: Map (from Google Earth) showing the former landfill site and major dump areas along the south boundary of Canadian Force Base 5 Wing Goose Bay; the area of tree-core sampling is outlined. The local control site located outside the landfill site is indicated. An inset map of Canada shows the location of the study area, the remote community of Happy Valley-Goose Bay, which lies north of the discontinuous permafrost in Canada Eastern subarctic (Labrador) and the city of St. John's where tree-core samples were freighted for analysis of organic components in tree-core samples. *(Figure prepared by Daniel Frawley).*

4.2. Characteristics of the former landfill site

The former landfill site covers approximately 6 km2 of low-lying land at an average elevation of 10 m, above sea level (a.s.l.) (Figs. 3 and 4). It has received mainly drums/containers of

motor oil, petroleum hydrocarbons, such as gasoline, jet and diesel fuels, lubricants and pesticides, and also construction and demolition debris and household wastes (JWEL, 1992; BFA, 1996; Curtis and Lammey, 1998). The refuse was covered at different points of time with sand (JWEL, 1992); however, surface metallic debris is still visible (see Appendix Figs. A1, A2, A3). The vegetation is dominated by grasses and locally forested areas, which consist of a mixture of coniferous and deciduous trees. Depth to groundwater averages 2.5 m and in several locations, groundwater intercepts the land surface and forms wetlands (swamps and marshes) with a number of elongated surface water bodies, collectively called stillwater (AMEC, 2009; Fig. 4; Appendix Fig. A4). Groundwater is unconfined and flows south to southeast towards the Churchill River, following low topography (see Fig. 4). The hydraulic conductivity of saturated subsurface layers at the landfill site ranges from 3.6 x·10-5 m/s to 1.0 x·10-2 m/s (AMEC, 2009: 2011).

Assessments of the landfill site since 1991 have revealed that it is contaminated by petroleum products, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and heavy metals (AMEC, 2011: 2009; BFA, 1996; JWEL, 1992). Clean-up activities have been undertaken since 1993 with the removal of several thousands of drums/containers, many still with residual contents; however, an unknown number of drums remains buried at the site (AMEC, 2009; BFA, 1996; Curtis and Lammey, 1998; Wells, 2013). Total BTEX concentrations up to 2744 mg/L have been obtained from discarded fuel drums (JWEL, 1992). Nests of groundwater monitoring wells have been installed at selected parts of the landfill site (Fig. 4). Two separate plumes of BTEX compounds and TCE have been identified cross-cutting stillwater #4 (AMEC, 2009: 2011; FEI, 2006). There, measured groundwater samples have indicated concentration ranges of 2.0 – 990.0 µg/L for benzene, 6.5 – 27.9 µg/L for toluene, 0.7 – 27.9 µg/L for ethylbenzene and 2.0 – 17.1 µg/L for total xylenes; MTBE was not detected (AMEC, 2011: 2009; FEI, 2006). In the other hand, TCE concentrations ranged from 23 to 180 mg/L. Furthermore, TCE daughter products *cis*-DCE and *trans*-DCE were detected at concentrations 1 µg/L and 0.3 µg/L, respectively. Groundwater samples were also measured for their metal content (AMEC, 2011). Aluminium (102 – 638 µg/L), Cadmium (0.018 – 0.028 µg/L), Copper (6 µg/L) and Iron (520 – 53200 µg/L) exceeded the Maximum Contaminant Level (MCL) of Fresh Water Aquatic Life Guidelines settled by the Canadian Council of Ministers of the Environment (CCME) for Aluminium (5 – 100 µg/L), Cadmium (0.017 µg/L), Copper (2 – 4 µg/L) and Iron (300 µg/L) (AMEC, 2011). The presence of extensive wetland hampers monitoring well installation and therefore, effective site assessments with groundwater sampling.

4.3. Field sampling

Tree-core samples were taken in the eastern portion of the landfill site (Fig. 4). This area is of concern because initial site investigations found VOCs, PAHs, heavy metals, and pesticides in both groundwater (from test pits) and surface water; VOCs and PAHs in groundwater exceeded the applicable Groundwater Quality Standards (AMEC, 2009: 2011; FEI, 2006). Therefore, continued monitoring is necessary for risk management and/or mitigation. This area is easy to access and has experienced only minimally invasive remediation activities, which have preserved mature trees, suitable for use in tree-core analysis approach (Cutter and Guyette, 1993).

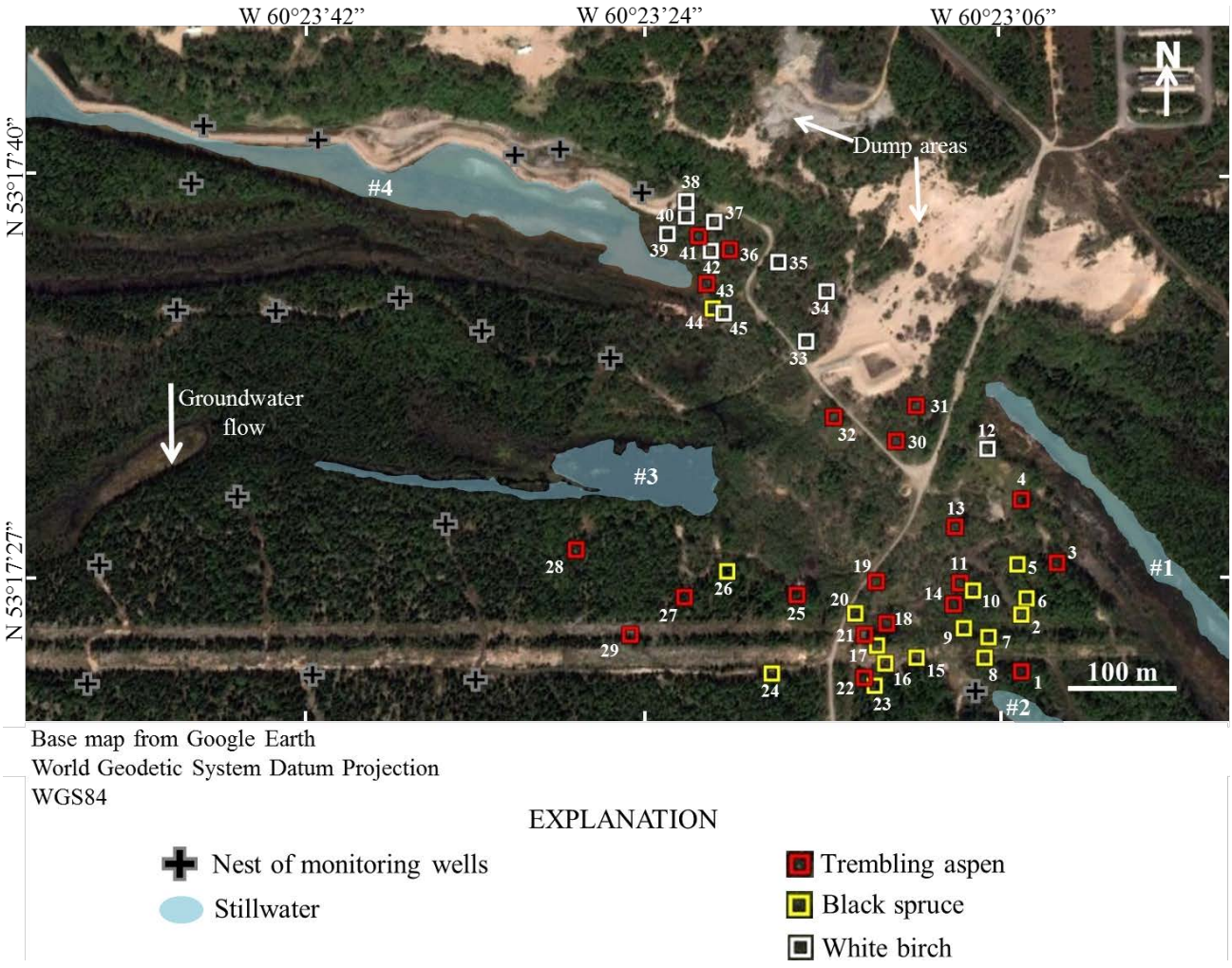


Figure 4: Map of the area of tree-core sampling showing the locations of sampled trees by species; the numbers represent of the tree-core samples. Locations of major stillwaters and monitoring well, in the vicinity of the sampling area are also shown. The direction of groundwater flow is indicated. *(Figure prepared by Daniel Frawley).*

The site-specific background conditions (i.e. diffuse anthropogenic influences) of the subsurface environment are unknown, as are those of the study area in general. Moreover, it was

impossible to confidently assign a typical background location within the study area where the physical and environmental characteristics were representative of the site overall. Nonetheless, a local control site located outside of the landfill site at about 2 km downstream towards the south-southeast was selected for the collection of additional tree-core samples (Fig.3), to assess the possibility of the landfill site contributing to off-site contaminant levels nearby.

4.4. Tree-core collection and handling

Tree-core samples were collected on three days, between 18 August 2014 and 2 September 2014, according to the criteria and established procedures by Cutter and Guyette (1993), Vroblesky (2008) and Holm et al. (2011) by summer students at the Labrador Institute, Memorial University (Daniel Frawley and Sean Murphy) under the supervision of Dr. Merline Fonkwe and Mr. Morgon Mill, a personnel member of the Labrador institute, Memorial University. During sampling, the weather was dry with low wind (6 – 22 km/h) and daily temperatures ranged between 14˚C and 24˚C. Mature (stem diameter between 18 and 39 cm) and visibly healthy trees were sampled randomly at the landfill site, including 20 trembling aspens (Populus tremuloides), 15 black spruces (Picea mariana) and 9 white birches (Betula papyrifera) (Fig. 4). In addition, tree-core samples were taken from 3 trembling aspens and 4 black spruces at the local control site. Core samples from the tree trunk were extracted from the north or northwest side of each tree (the side facing the direction of groundwater flow), using a 35.5 cm long, 5.15 mm diameter increment Haglöf® tree-corer (Fig. 5). Trees have a defence mechanism for sealing off the damaged area (hole in the trunk) caused by the extraction of core samples, even after extensive core sampling (Shigo, 1984; Algreen and Trapp, 2014).

Three to four core samples were collected per tree. For dendrochronology and dendrochemistry approaches, two long core samples were extracted through the entire trunk of every tree at chest height (about 1.4 m above ground). The core samples were stored into plastic straws (Western Plastics Inc.), both end of each straw were sealed with packing tape for transport back to the laboratory until preparation for analysis; the core samples were labeled with a number and coring orientation (Fig. 6A). For phytoscreening, tree cores 8 cm in length were taken at a height of about 1 m above the ground surface and quickly broken into several smaller pieces, then placed into 20 mL Gerstel® glass screw-top vials sealed with PTFE-lined septum caps (Fig. 6B). The vials were immediately stored in an iced cooler container in the field and transferred into a 4˚C refrigerator at the end of each day for overnight storage. The following day, the core samples were freighted by air

in an iced cooler box at Memorial University of Newfoundland in St. John's (see Fig. 3) for analysis of petroleum hydrocarbons and chlorinated ethenes.

Figure 5: Tree-core sampling process. **(A)** The tree-corer used in this study, also known as an increment borer (the T-shaped metal instrument), and the tree-core extractor device. **(B)** The tree corer is drilled through the center of the trunk of the tree by pressing the tip of the corer firmly against the bark of tree trunk and turning the handles clockwise. **(C)** The extractor device is inserted into the corer from the handle end to carry and pull out the tree-core sample, a small cylinder of wood from the tree; the corer is withdrawn from the tree by turning the handle in counter clockwise direction. *(Figure prepared by Sean Murphy).*

Figure 6: Core samples after removal from the tree-corer extractor and storage in **(A)** plastic straws for dendrochronological and dendrochemical analyses and **(B)** A glass screw-top 20 mL vial for phytoscreening, and transported to the North West River Research Station of the Labrador Institute. *(Figure prepared by Sean Murphy).*

4.5. Preparation of tree-core samples and laboratory methods

4.5.1. Dendrochronology

In the laboratory, the packing tape was removed from both ends of each straw and the core samples were left to dry at room temperature for few months. When dry, the ends of each straw

were sealed again and the core samples were sent in November 2014 to the dendrochronological laboratory at Station de Recheche FERLD, Université du Québec en Abitibi-Témiscamingue for analysis to assess possible periods of stress in the trees during the operation of the military base. This involved counting annual growth rings and measuring growth ring widths using WinDENDRO, a semi-automated tree-ring image processing system (Guay et al., 1992). The data were not received by the time of this report's preparation, despite numerous requests for the analytical data. As a consequence of this situation, the results of dendrochronological analysis are not presented here, nor discussed further in this report. Once the data are received, a separate report will be submitted at a later date to the Harris Center of Memorial University.

4.5.2. Dendrochemistry

The core samples were kept free of all possible contaminants and were air dried at room temperature. The preparation of core samples for analysis was done by the summer students Daniel Frawley and Sean Murphy under the supervision of Dr. Merline Fonkwe at the North West River Research Station of the Labrador Institute. For each core sample, annual growth rings were counted and dates were ascribed to each growth ring based on the characteristic pattern with lighter and darker layers that represent summer and winter growth (Fig. 7A).

Depending on the age of the tree, two core segments of 9-year growth ring intervals, 1984–1993 and 1974–1983 or 1962–1973 or 1954–1963 or 1953–1944 were selected to evaluate whether any elements showed abnormal concentration changes across the majority of the trees, as the result of contamination due to unsound solid waste disposal practices until 1990 at the former landfill site. Annual growth rings from the sapwood were not selected, because of the expected high variability of their chemical compositions (Cutter and Guyette, 1993; Algreen et al, 2012: 2014). The selected core sections were stored in 4 mL glass vials (Fisher Scientific) (Fig. 7B) and sent for further preparation/transformation, which includes washing the core samples, total acid digestion to bring core samples into liquid form and dilution, before total elemental analysis (for inorganic components, including target pollutants) by Activation Laboratories Ltd. in Hamilton (Canada), using High Resolution Inductively coupled plasma mass spectrometry (HR-ICP-MS). A total of 62 elements were simultaneously quantified: Ag, As, Au, Bi, Ba, Be, Ca, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Lu, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Pd, Pt, Rb, Re, Sb, Sc, Se, Sm, Sn, Ta, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr.

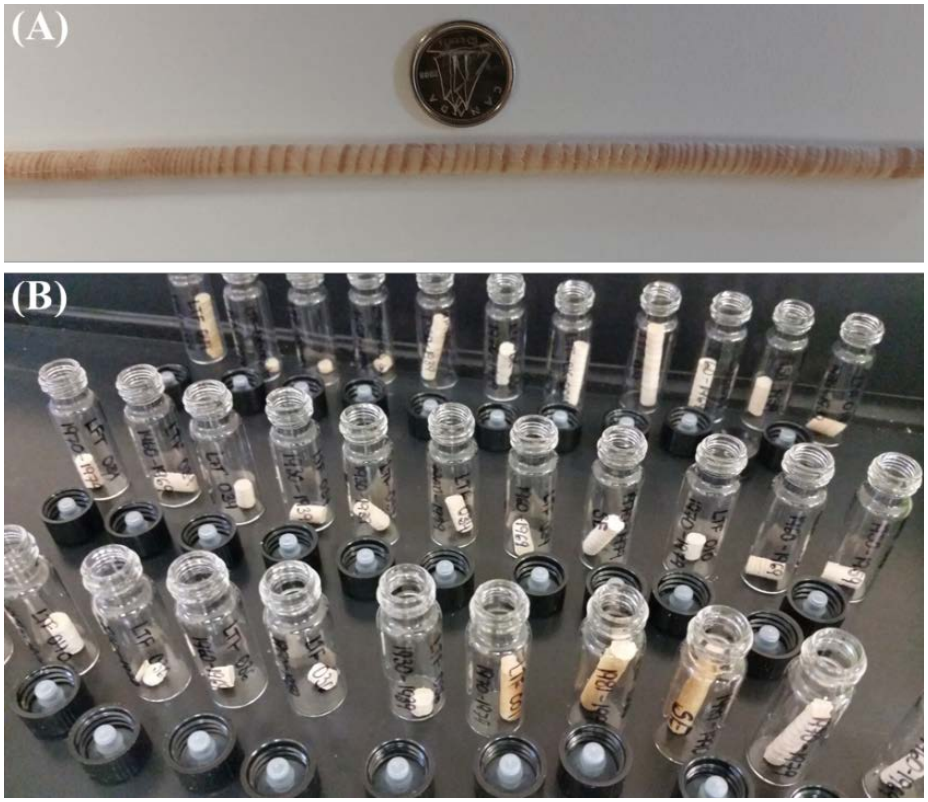


Figure 7: Tree-core sample for dendrochemical analysis. **(A)** A tree core prepared and ready for age dating. **(B)** Selected 9-year core segments in 4 mL glass vials to send for the analysis of major and trace elements by HR-ICP-MS. Note the variations in widths of annual tree rings and in the size of the core segments. *(Figure prepared by Sean Murphy).*

4.5.2. Phytoscreening

Tree-core samples were analysed for VOCs, including petroleum hydrocarbons, including BTEX compounds and MTBE, and chlorinated ethenes, PCE, TCE, 1,1-DCE, *cis*-DCE and *trans*-DCE. All the analyses of the target organic contaminants were done at the CREAIT-Stable Isotope Laboratory of Memorial University by headspace-gas chromatography-mass spectrometry (HS-GC-MS), using an Agilent 6890N gas chromatograph equipped with a 5975C mass selective detector and a DB-624 capillary column (Fig. 8). Upon receipt in the laboratory the same or next shipping day, the core samples were either prepared for immediate analysis or stored at 4˚C until analysis within 3 to 5 days of sampling. Before analysis, core samples were allowed to equilibrate in the vials for 24 hours at room temperature (21˚C). The vials were heated at 70˚C in an incubator for 30 minutes under gentle shaking and 200 µL volume of headspace was extracted from each vial using a heated gas-tight syringe (Fig. 8A) and immediately injected into the GC instrument for analysis (Figs. 8B and C). The BTEX compounds, m-and p-xylenes could not be separated and were , therefore measured together.

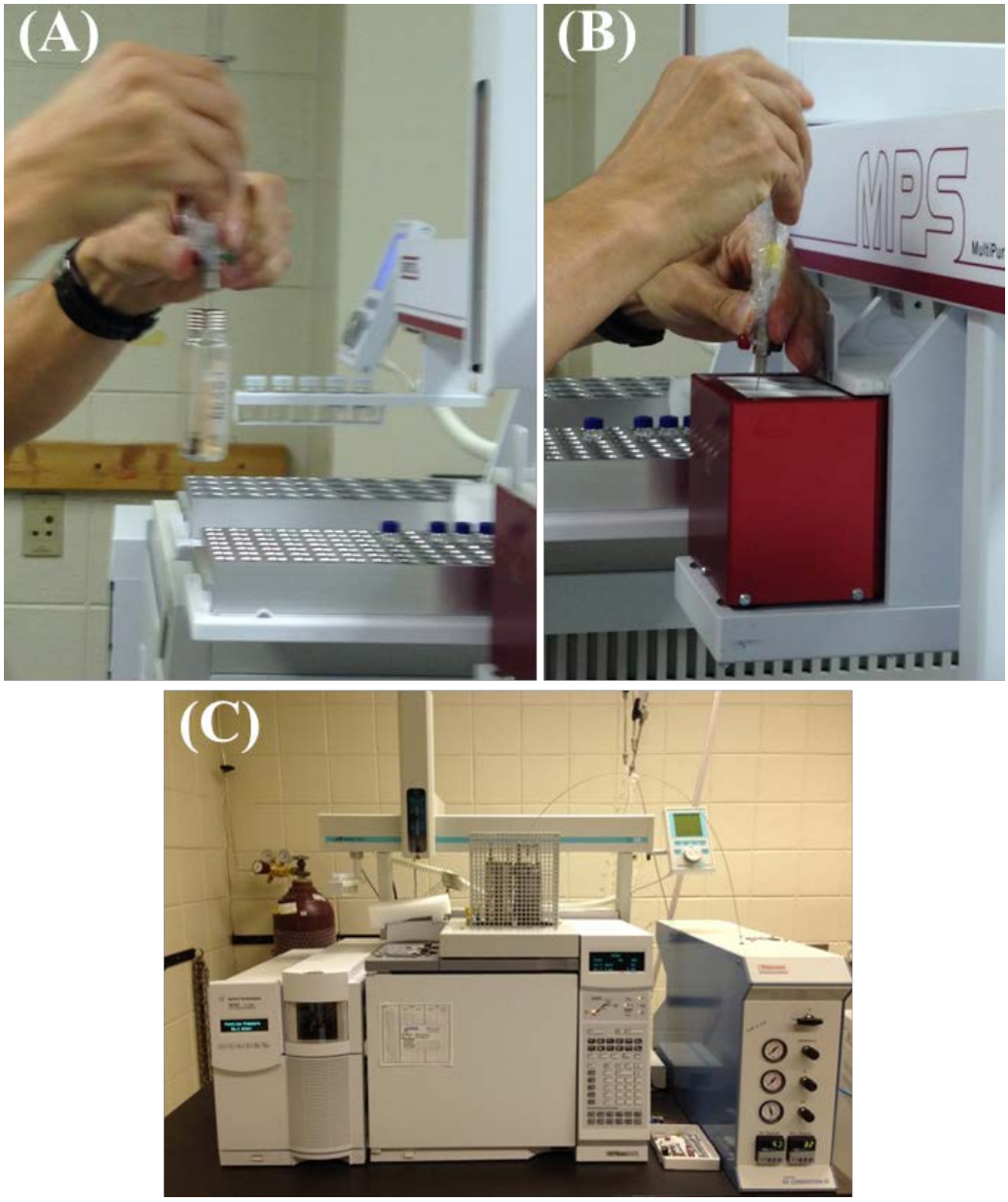


Figure 8: Analytical procedures for organic contaminants. **(A)** Headspace extraction of gas containing organic compounds, including target organic contaminants with a syringe. **(B)** Injection of the gas into the GC instrument. **(C)** Agilent 6890N gas chromatograph used for the analysis of the target organic compounds *(Photos by M. Fonkwe)*.

5. RESULTS AND DISCUSSION

5.1. Petroleum hydrocarbons

A more detailed presentation of the tree-core analytical results was submitted in November 2015 for publication in a peer-reviewed journal, *Environmental Science and Pollution Research,* and this manuscript is under revision for resubmission (Fonkwe and Trapp, *submitted*).

5.1.1. Concentrations of the BTEX compounds in tree cores and spatial distribution

At the landfill site, all tree species contained detectable concentrations of all or selected BTEX compounds in varied proportions: Benzene (0.20 – 2.3 µg/L), toluene (0.20 – 137 µg/L), ethylbenzene (0.2 – 0.93 µg/L), m- and p-xylene (0.40 – 1.13 µg/L) and o-xylene (0.20 µg/L). This finding is supported by prior measurement tests of groundwater and surface water in the sampling area (AMEC, 2009). Moreover, although low, the concentrations of BTEX in tree-core samples were correlated with groundwater concentrations in the vicinity of the sampling area (Fig. 9: AMEC, 2011: 2009). This is expected because plants such as trees are passive samplers of subsurface contaminants and they have the ability to sample a much larger area than that afforded by groundwater samples. This suggests that groundwater BTEX concentration is the primary factor governing the concentrations obtained from tree-core samples.

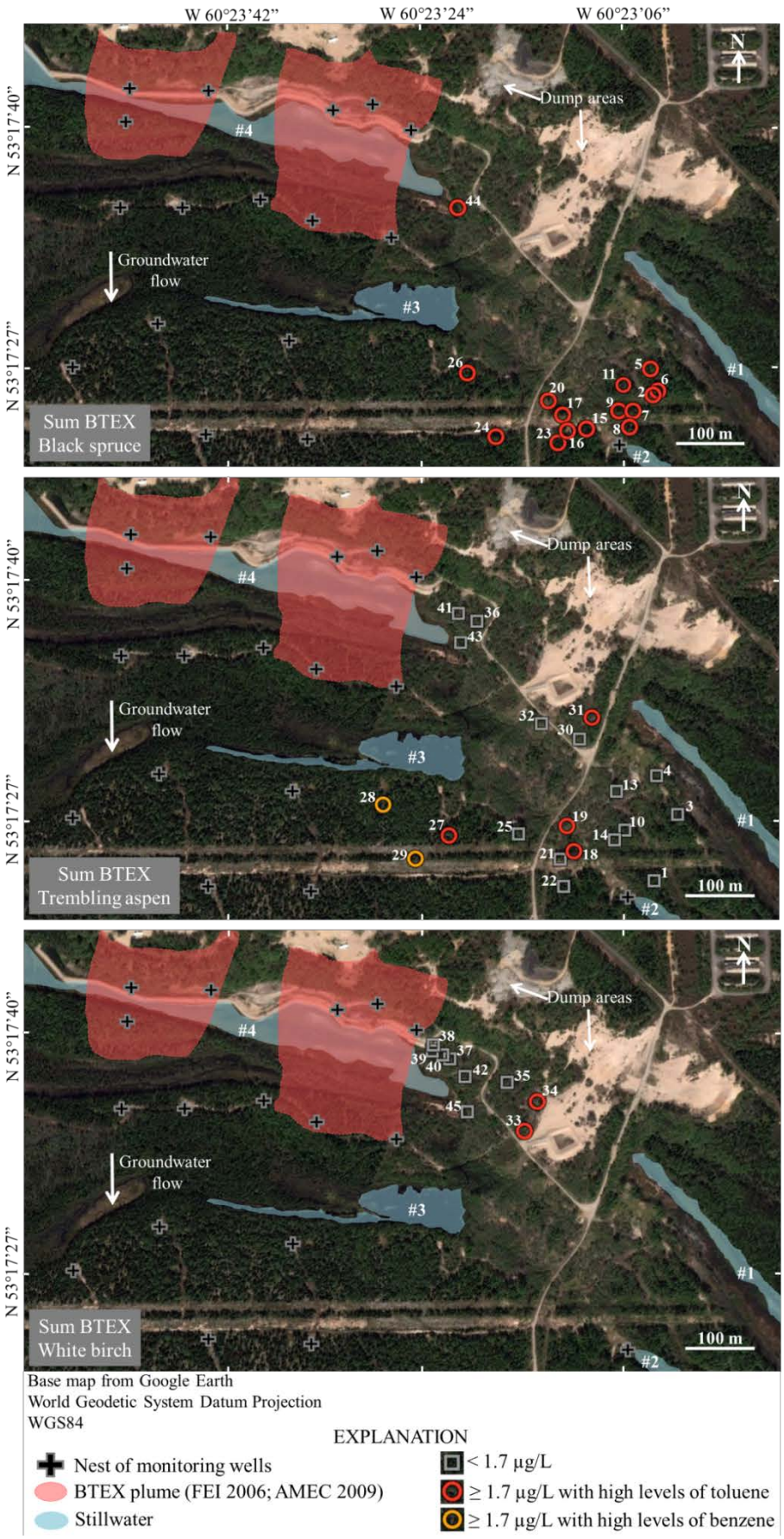
At the local control site, on the other hand, the BTEX concentrations were low but similar to those obtained at the landfill site. Toluene was found at the highest concentration when compared with the other BTEX constituents. The presence of BTEX compounds in tree-core samples indicates the possible migration of contaminants from the landfill site. Probable contaminant migration off-site has previously been mentioned by the appropriate authorities (in newspaper archives), which has led to the abandonment of agricultural lands adjacent to the local control area.

These findings demonstrate that tree-core analysis can indeed be used to detect BTEX contaminated shallow groundwater (~2.5 m deep) in subarctic environments, much as in mediterranean and temperate environments, as shown by Algreen et al. (2015) and Sorek et al. (2008). The low content of BTEX in the tree cores might be due to BTEX degradation (Sorek et al., 2008; Wilson et al., 2013; Nichols et al., 2014).

The concentrations of the BTEX compounds in each tree-core sample were sum and the total BTEX concentrations of all core samples were divided in three different populations, which were identified using the probability plot (not shown here). The values less than 1.7 µg/L represent

See next page

Figure 9: Spatial distribution maps of sum BTEX concentrations in tree-core samples for each tree species: black spruce (top), trembling aspen (middle) and white birch (bottom). The numbers represent the sampled trees. Also shown are the nearby stillwaters, monitoring wells and contours of BTEX plumes in groundwater collected in summer 2005 and September-October 2006 (FEI, 2006; AMEC, 2009). Note that the clustering of anomalous values of sum BTEX compounds in tree-core samples is observed between stillwater #2 and #3 and at the vicinity of stillwater #4. *(Figure prepared by Daniel Frawley).*


W 60°23'42"
W 60°23'24"
W 60°23'06"
N 53°17'40"
N 53°17'27"
N
Dump areas
Groundwater flow
#1
#2
#3
#4
100 m
Sum BTEX Black spruce
Sum BTEX Trembling aspen
Sum BTEX White birch
Base map from Google Earth
World Geodetic System Datum Projection
WGS84
EXPLANATION
Nest of monitoring wells
BTEX plume (FEI 2006; AMEC 2009)
Stillwater
< 1.7 µg/L
≥ 1.7 µg/L with high levels of toluene
≥ 1.7 µg/L with high levels of benzene

background values, while values above 1.7 µg/L are anomalous. The distribution maps of the total BTEX compounds in presented per tree species, black spruce, trembling aspen and white birch in Figure 9. The clustering of anomalous values of sum BTEX compounds in tree-core samples is observed between stillwater #2 and #3 and at the vicinity of stillwater #4. These delineated zones of elevated sum BTEX concentrations are optimal for the installation of groundwater monitoring wells for further investigations of the site.

The uptake of BTEX compounds varies between tree species. For example, toluene concentrations are clearly higher in black spruce than in aspen or birch. Pine trees have been observed to emit elevated levels of toluene under stress (Heiden et al., 1999), so an endogenous, natural source in black spruce cannot be excluded beforehand. However, the measured concentrations are more likely originate from external sources, i.e. groundwater, because of: (1) the wide range of values does not indicate production of toluene by black spruce; (2) Most importantly, the highest concentrations of toluene in black spruce (sample 26) are closely neighbored by the highest concentrations of toluene in aspen (sample 27) (Fig. 9). Moreover, the next samples in this direction (nos. 28 and 29) have the highest levels of benzene measured in aspen wood (Fig. 9). Thus, contamination is the most likely explanation for the elevated levels found in the trees.

5.1.2. Concentrations of MTBE in tree cores

None of the tree-core samples collected at the landfill site or local control area contained a detectable concentration of MTBE. At the landfill site, MTBE results corroborate with available groundwater data within or at the vicinity of the sampling area (AMEC, 2012: 2011: 2009; Fig. 2). Although MTBE was not found in monitoring wells, assessment of subsurface MTBE contamination in this work was prompted by the fact that MTBE and the BTEX compounds are commonly associated with petroleum hydrocarbon-contaminated groundwater, and by evidence that tree-core analysis is sometimes able to identify subsurface contamination undetected by traditional groundwater monitoring (e.g. Larsen et al., 2008). Experiments conducted by Burken and Schnoor (1998) and Ma et al. (2004), have indicated uptake of MTBE by poplar (*Populus* spp.) and eucalyptus (*Eucalyptus* spp.) trees. These laboratory findings were later corroborated by the identification of MTBE in mature oak trees (*Quercus virginiana*) growing above gasoline-contaminated groundwater <3.9 m bgs (Landmeyer et al., 2000). Therefore, the absence of MTBE in core samples is an indication of the absence of groundwater MTBE contamination. Given that buried drums are still present at the landfill site and may leak their contents at any time, constituting

a possible source of MTBE in subsurface soil and groundwater, continuous monitoring remain necessary until cleanup is complete at the landfill site.

5.2. Chlorinated ethenes in tree cores

The concentrations of chlorinated ethenes were determined in tree-core samples. The compounds 1,1-DCE, *cis*-DCE and *trans*-DCE, were not found in any of the core samples of tree species growing at the Landfill site. PCE was the most detected contaminant in the tree-core samples at concentration levels, reaching 58.5 µg/L. It was detected primarily in white birch, followed by trembling aspen and black spruce. In contrast, TCE was less frequent, detected in very limited number of core samples from trembling aspen and white birch concentration levels. A map of the PCE concentration in the collected tree-core samples is shown a cluster of detected PCE is observed north of the sampling area (Fig. 10).

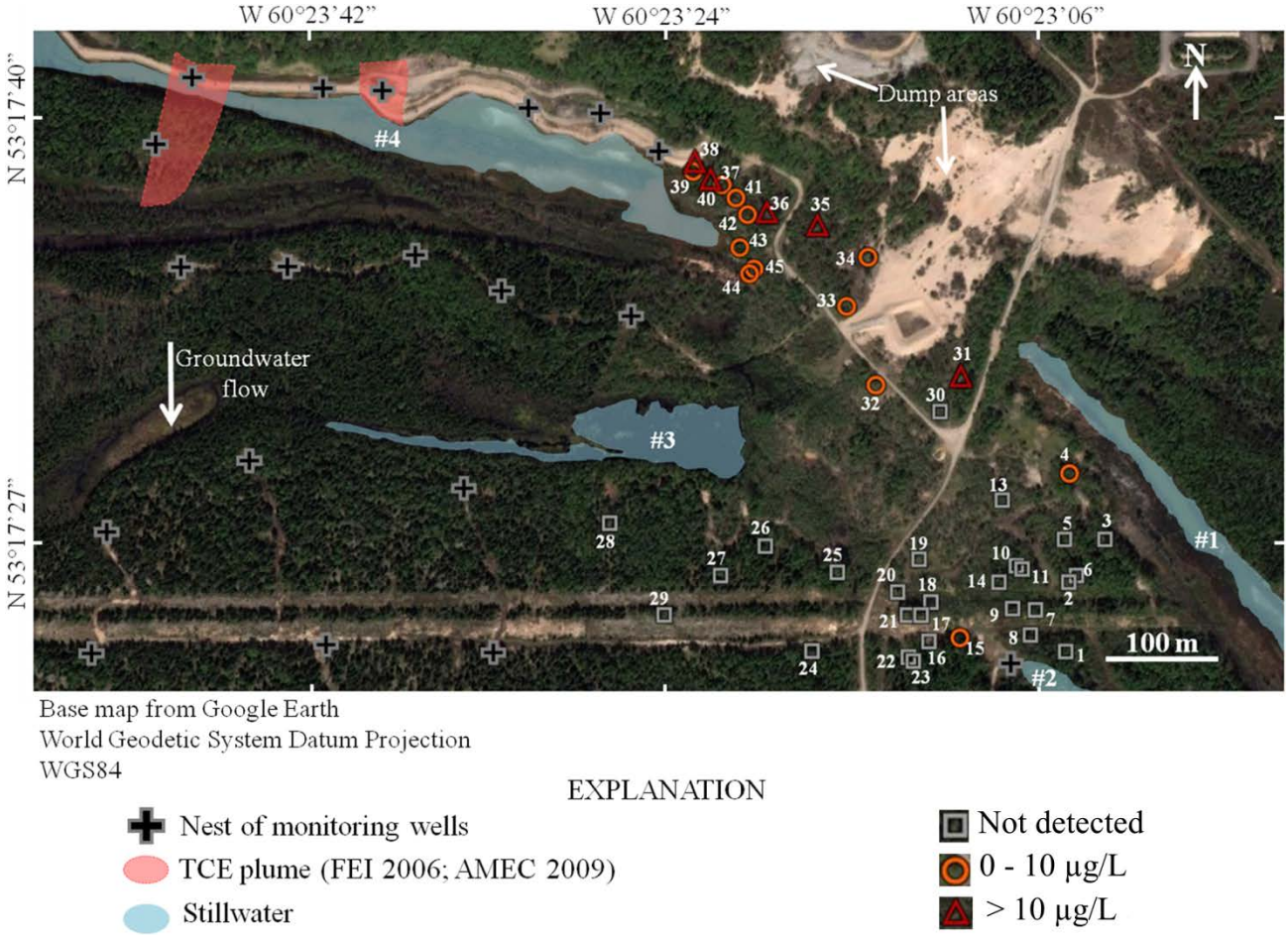


Figure 10: Map of the area of tree-core sampling with nearby stillwaters, monitoring wells and contours of TCE plumes in groundwater collected in Summer 2005 and September-October 2006 (FEI, 2006; AMEC, 2009), showing the distribution of the concentrations of PCE in tree cores; the numbers represent tree-core samples. Note the cluster of PCE detection in the north. *(Figure prepared by Daniel Frawley).*

Limited groundwater subsurface data (groundwater and soils) are available for the tree-core sampling site. Besides in August 2009 (AMEC, 2011), analysis of soil and groundwater samples indicated no detectable PCE and TCE contamination in the vicinity of stillwater #2 and few sampled trees. However, the cluster of positive results for PCE may nonetheless be attributable to contamination sources in the former landfill site.

5.3. Elemental compositions of tree rings

Among the 63 elements analyzed, the concentrations of the following elements were below the detection limits and are not discussed further: As, Au, B, Be, Bi, Dy, Er, Eu,Ga, Gd, Ge, Hf, Hg, Ho, In, La, Li, Lu, Na, Pr, Pd, Pt, Re, Sc, Se, Sn, Ta, Tb, Te, Th, Tl, Tm, V, W and Yb. On the other hand, the elements detected in tree rings included essential elements for all plants (Ca, K and Mg) and additional trace elements (Ag, Ba, Cd, Ce, Co, Cr, Cs, Cu, Fe, Mn Mo, Nb, Nd, Ni, Pb, Rb, Sb, Sm, Sr, Ti, U, Y, Zn and Zr). The concentrations obtained for the essential elements are higher than those for the trace elements. The essential elements are nutrients and therefore, are beneficial for the plant growth, reproduction and/or metabolism, whereas trace elements (or non-essential elements) are generally absorbed in small amounts by plants during the uptake of essential elements and are not known to be of any use to plants (Kabata-Pendias, 2001; 2004; Dunn, 2007). However, most plants are able to absorb and tolerate higher concentrations of trace elements in their environment, especially in case of metal pollution. Because of their toxicity, trace elements are often associated with human health and environmental problems and therefore, they are of particular importance. The detected trace elements display erratic concentration patterns in the selected annual growth rings. Therefore, chemical changes in the tree growing environment, as the result of contamination due to unsound solid waste disposal practices until 1990 at the former landfill site, could not be inferred from the obtained trace element concentrations.

6. CONCLUSIONS

The following conclusions are drawn from this research:

1. Tree-core sampling is restrained by the presence and distribution of mature trees and further by the extensive marshes and stillwater bodies at the landfill site.
2. The detection of BTEX compounds and PCE in tree-core samples collected at the landfill site suggests contamination of shallow groundwater (~2.5 m deep) by waste disposal at the landfill site.

3. An anomalous zone of high sum BTEX concentrations and PCE content has been identified at the landfill site to guide the drilling of boreholes and wells for further investigations of the site.

4. While negative results for MTBE, 1,1-DCE, *cis*-DCE and *trans*-DCE were obtained and TCE was detected in only few tree-core samples, continued site monitoring for these compounds is recommended until the clean-up process is completed.

5. Although the tree-core method indicated feasibility for the detection of trace elements in the subsurface environment, more research on the application of dendrochemistry for trace elements in Canada north environment is needed.

6. Tree-core analysis is potentially an excellent field-screening tool to locate potential areas of major contamination ('hot spots') during preliminary site assessments and continuous monitoring. This method can provide first-hand data to assist solid waste management and pollution control authorities in minimizing or preventing possible environmental damages.

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APPENDIX: FIELD PICTURES

Figure A1: One of the several open solid waste dump areas of the former landfill covered with loose sand: Top of the escarpment *(top)* and bottom of the escarpment *(bottom)*.

Figure A2: Surface metallic debris are still visible at the former landfill site

Figure A3: Discarded containers of lubricant oil *(top)* and pesticide DDT *(middle)*, and fuel drums *(bottom)* still observed at the former landfill site.

Figure A4: The presence of extensive wetland areas hampers drilling of boreholes and monitoring wells and therefore, effective site assessments with the traditional soils and groundwater sampling.

Figure A5: Daniel Frawley is getting ready to collect a core sample from a white birch tree.

Figure A6: Sean Murphy screwing the tree corer in a black spruce tree to collect a core sample.

Figure A7: Sean Murphy is on his way to the next tree to sample carrying an iced cooler containing sampled tree cores for the analysis of volatile organic compounds (VOCs).

Figure A8: A day in the field with Morgon Mills, program coordinator at the Labrador Institute, Memorial University. Morgon graciously assisted with the collection of core samples, while getting the fieldwork experience. Note in the background, the orange rust colored stillwater.

Figure A9: Dr. Merline Fonkwe taking the last core sample of the field campaign from a trembling aspen tree.

Figure A10: Dr. Merline Fonkwe in the field well protected against mosquitos and biting flies!