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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

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Abstract

This research examines the feasibility of analyzing tree cores to detect BTEX compounds and MTBE in groundwater in eastern Canada subarctic environments, using a former landfill site in the remote community of Happy Valley-Goose Bay, Labrador. Petroleum hydrocarbon contamination at the landfill site is the result of environmentally unsound pre-1990's disposal of households and industrial solid wastes. Tree cores were taken from trembling aspen, black spruce and white birch and analyzed by headspace-gas chromatography-mass spectrometry. BTEX compounds were detected in tree cores, corroborating known groundwater contamination. A zone of anomalously high concentrations of total BTEX constituents was identified and recommended for monitoring by groundwater wells. Tree cores collected outside the landfill site at a local control area suggest the migration of contaminants off-site. Tree species exhibit different concentrations of BTEX constituents, indicating selective uptake and accumulation. Meanwhile, MTBE was not found in the tree cores and is considered to be absent in the groundwater. The results demonstrate that tree-core analysis can be useful for detecting anomalous concentrations of petroleum hydrocarbons, such as BTEX compounds, in subarctic sites with shallow unconfined aquifers and permeable soils. This method can therefore aid in the proper management of contamination during landfill operations and after site closures.

Keywords: Labrador; solid waste disposal; organic pollutants; phytoscreening; BTEX compounds; MTBE; preliminary site assessments; remote location

1. Introduction

Landfilling remains the most prevalent method of organized solid waste disposal in remote communities of the eastern Canadian subarctic (Ryan 2010; Zagozewski et al. 2011). There has been and continues to be substantial environmental controversy surrounding landfilling practices (El-Fadel et al. 1997; Rowe et al. 1997), though solid waste disposal facilities have evolved from uncovered and unlined landfills or open dumps to modern engineered landfills (e.g. Barrett and Lawler 1995; Slack et al. 2005; Eggen et al. 2010). However, subsurface pollution may occur at any time during landfills' active and post-closure phases (Allen 2001; Sawhney and Kozloski 2004). This represents a human health and environmental hazard, which requires control measures by solid waste management and pollution control authorities (Christensen et al. 2001; Fatta et al. 1999; Kjeldsen et al. 2002; Manfredi et al. 2009). In order to better evaluate the pollution risks posed by leachate emissions from landfills into the underlying soil and groundwater, and to inform corrective or remedial actions, such sites must be characterized and monitored long-term (Cifrian et al. 2013; El-Fadel et al. 2001; Laner et al. 2011). The traditional technique of sampling (soil via boreholes and groundwater via monitoring wells) is extremely costly, technically difficult, and time-consuming to implement, particularly at remote subarctic sites. Therefore, attention is increasingly being given to tree-core analysis, as a simple and cost-effective field-screening approach that can successfully identify and vector borehole and well drilling towards possible zones of subsurface contamination (Algreen et al. 2015; Burken et al. 2011; Vroblesky et al. 1999).

Tree-core analysis (also referred as to phytoscreening) has been used in environmental science to detect and monitor subsurface contamination by a variety of volatile organic compounds (VOCs) since the pioneering research by Vroblesky et al. (1999). Trees take up compounds through their roots, bark, or leaves and can incorporate the compounds into their cells; therefore, the chemistry of soil, groundwater and atmosphere can be inferred via the analysis of tree tissues (Cutter and Guyette

1993; Padilla and Anderson 2002). To date, compared to the attention paid to chlorinated ethenes, few studies have analyzed tree cores to assess soil and groundwater contamination by petroleum hydrocarbon constituents, like benzene, toluene, ethylbenzene and m, p, o-xylenes (collectively referred to as BTEX) or methyl tertiary-butyl ether (MTBE) or both (Algreen 2015; Algreen et al. 2015; Holm 2011; Landmeyer et al. 2000; Rein and Trapp 2009; Sorek et al. 2008; Trapp et al. 2005; Weishaar et al. 2009). The studies undertaken were all located in temperate, subtropical, or mediterranean regions, and they have met with some success in providing the semi-quantitative data needed for preliminary site evaluations, especially for BTEX compounds. Besides the practical and financial convenience, another crucial advantage of tree-core analysis is that because of its root system, a single tree can take up compounds from a much larger area (many cubic meters of soil and groundwater) than a single traditional soil or groundwater sample (Dunn 2007). Nonetheless, the applicability of tree-core analysis must be evaluated site by site, because compound uptakes by trees depend on site-specific conditions, the physiological characteristics of the tree species used, and the properties of the contaminants in question (Cutter and Guyette 1993; Trapp 2007).

The feasibility of using tree-core analysis to detect subsurface contamination by VOCs has not been studied in the eastern Canadian subarctic. This study therefore aimed to determine whether the analysis of tree cores could be useful in this context, using the most common deciduous and coniferous tree species to assess concentrations of subsurface BTEX compounds and MTBE at a former landfill site in the remote, subarctic community of Happy Valley-Goose Bay in Labrador. If substantiated as a valuable approach, tree-core analysis could be integrated into preliminary site evaluations of possible subsurface contamination at other old or still operational landfills and other facilities in efforts to minimize negative impacts on the environment and public health. In addition, this paper compiles and describes the data available in open literature to provide, in conjunction with the present study, a foundation for the application of tree-core analysis to track subsurface pollution by petroleum hydrocarbons.

2. Materials and methods

2.1. 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. 1). It covers an area of 306 km2 and has a population of 7552 (Government of Canada's 2011 census). 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 (https://weather.gc.ca/canada_e.html). 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. 1). 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; Fig.1).

2.2. Landfill site: physiography and hydrogeology

The landfill site covers approximately 6 km2 of low-lying land at an average elevation of 10 m (a.s.l.). 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 from approximately 1941 to 1990 (Figs. 1 and 2; JWEL 1992; BFA 1996). The refuse was covered at different points of time with sand (JWEL 1992); however, surface metallic debris is still visible (Fig. 3). 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 named stillwater (AMEC 2009; Fig. 2). Groundwater is unconfined and flows south to southeast towards the Churchill River, following low topography (see Fig. 2). 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). Horizontal hydraulic gradients across the Landfill site averaged to 0.001 m/m. Vertical hydraulic gradients at the well nest locations ranged from 0.009 m/m to 0.136 m/m (AMEC, 2009).

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. Two separate plumes of BTEX compounds have been identified cross-cutting stillwater #4 (AMEC 2009; FEI 2006; Fig. 2). 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).

2.3. Field sampling

Tree-core samples were taken in the eastern portion of the landfill site (Fig. 2). This area is of concern because initial site investigations found VOCs (including BTEX compounds), PAHs, heavy metals, and pesticides in both groundwater (from test pits; locations not shown) and surface water (including samples from the stillwaters); 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).

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.1), to assess the possibility of the landfill site contributing to off-site contaminant levels nearby.

2.4. 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), Holm et al.

(2011) and Vroblesky (2008). 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. 2). In addition, tree-core samples were taken from 3 trembling aspens and 4 black spruces at the local control site. Core samples 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 tree-corer (Haglöf®). Tree cores 8 cm in length were taken at a height of about 1 m above the ground surface, the bark was discarded and the wood quickly broken into several smaller pieces, then placed into 20 mL glass screw-top vials sealed with PTFE-lined septum caps (Gerstel®). 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 (Fig. 1) for analysis. Further details are given in the Supplementary Material.

2.5. Tree-core analysis

Concentrations of BTEX compounds and MTBE in tree-core samples were determined 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 (see Supplementary Material). 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). To generate calibration curves, standard solutions were prepared in concentration ranges of 0.4 – 10 µg/L for MTBE and all the BTEX constituents, along with 10 – 400 µg/L for toluene from a certified reference material (CRM47505 Supelco®) diluted in deionized

181 water (see Supplementary Material). The vials were heated at 70˚C in an incubator for 30 minutes
182 under gentle shaking and 200 µL volume of headspace was extracted from each vial using a heated
183 gas-tight syringe and immediately injected into the GC instrument for analysis. The m-and p-
184 xylenes could not be resolved and were measured together. The calibration curves (peak areas of
185 quantification ions vs. concentration of standards in aqueous phase) were linear ($R^2 > 0.996$).
186 Results for the core samples containing the compounds of interest at a concentration below 0.4 µg/L
187 (lower end of the calibration interval) were reported as such (< 0.4 µg/L) if the signal to noise ratio
188 was higher than 3; in this case 0.4 µg/L represents the quantification limit (QL). If the signal to
189 noise ratio was lower than 3, the results were reported as below the detection limit (< DL). The
190 recovery efficiency of MTBE and BTEX compounds was tested by spiking four core samples from
191 white birch trees with 1 mL of the prepared standard solution at a concentration of 4.0 µg/L.
192 Recoveries ranged from 29% to 77% and were related to the octanol-water partition coefficients of
193 the compounds (see Supplementary Material for details). No correction for recovery was performed
194 since semi-quantitative data from tree-core analyses are in themselves sufficient for field screening
195 of groundwater contamination by VOCs (e.g. Algreen et al. 2015; Vrobesky 2008). Contaminant
196 concentrations in core samples are reported in units of micrograms per liter of headspace**.** 10 ug/L
197 corresponds to about 0.288 mg/kg in dry wood**.** Any resulting values below the QL were assigned to
198 half QL for representation purpose (see Table 1, 2 and 3).

199 *2.6. Data quality assessment*

200 The quality of sampling, sample handling and analytical data was monitored by collecting travel
201 blanks, field trip blanks, air blanks and field duplicates (details in Supplementary Material). Trace
202 amounts (almost all values < QL) of toluene, ethylbenzene and xylenes were detected in travel
203 blanks; BTEX components were also detected in field trip blanks with values also lower than the
204 laboratory QL. This suggests that the core samples may have been contaminated by the Styrofoam

containers used for shipping the core samples (details in Supplementary Material). However, this was found to have no significant effect on the analytical results of the tree-core samples and therefore, blanks corrections were not applied. Air samples at the vicinity of the trees contained trace amounts (all values < QL) of BTEX components with limited presence of benzene. Obtained results for field duplicate pairs, collected approximately 1 cm vertically apart at selected trees, show good repeatability with relative standard deviation (RSD**)** up to 5% for 5 of the 6 field duplicate pairs (see Table 1 and 2).

3. Results and Discussion

3.1 Concentrations of the BTEX compounds in tree cores

BTEX compounds were identified, in general, in tree-core samples at both the landfill site and the local control site. At the landfill site (Table 1), benzene concentrations were generally low (0.20 µg/L) with only two core samples having higher values, of 1.1 µg/L and 2.3 µg/L respectively. In contrast, toluene content is much higher with the concentrations in the majority of the samples (40) in the range 0.40 µg/L to 137 µg/L; the remaining samples (16) have a toluene concentration of 0.20 µg/L. Ethylbenzene was identified in small amounts with the majority of the core samples having a concentration of 0.2 µg/L; only one sample yielded a concentration of 0.93 µg/L. When detected, the content of m- and p-xylene was 0.40 µg/L in most of the samples (31), with only one sample having a concentration of 1.13 µg/L. In comparison with other BTEX constituents, the occurrence of o-xylene was less frequent and restricted to fewer samples (10) at a concentration of 0.20 µg/L.

At the local control site (Table 2), on the other hand, the concentrations were low but similar to those obtained at the landfill site for benzene (0.20 µg/L) and ethylbenzene (0.20 µg/L), and for m- and p-xylene (0.40 µg/L), which were detected only in some core samples. As for toluene, it was found at the highest concentration when compared with the other BTEX constituents. Toluene

content in most of the samples ranged between 1.1 µg/L to 40.2 µg/L, whereas low toluene concentrations of 0.20 µg/L were also measured in aspen core samples.

At the landfill site, all tree species contained detectable concentrations of all or selected BTEX compounds in varied proportions. This is supported by the measurement tests of groundwater and surface water in the sampling area (Serco 2001; AMEC 2011). In October 2000, elevated BTEX with maximum concentration of 1180 µg/L for benzene and 13 µg/L for Ethylbenzene, was observed in the groundwater from test pits (locations not shown) at the head of stillwater #1, encompassing trees nos. 3, 5, 13, 4, 30 and 31 (Serco 2001; see Figs. 2 and 4). Further sampling program in February 2010, indicated BTEX contamination in groundwater samples in the area around stillwater #2, enclosing trees nos. 15, 8, 1, 9 and 7; measured groundwater samples indicated concentration ranges of 0.5 – 14.0 µg/L for benzene, 0.3 – 31.0 µg/L for toluene, 0.6 – 5.4 µg/L for ethylbenzene and 0.26 – 37.0 µg/L for total xylenes (AMEC 2011). Moreover, although low, the concentrations of BTEX in tree-core samples were corroborate groundwater results in the vicinity of the sampling area (Fig. 2: 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 (Dunn 2007). This suggests that groundwater BTEX concentration is the primary factor governing the concentrations obtained from tree-core samples at this site. As for the local control area, the BTEX compounds in tree-core samples indicate 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), who have urge 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.

252 (2008), who used core samples from eucalyptus (Eucalyptus camaldulensis) and rosewood
253 (Dalbergia sisso), and willow (Salix sp.) and aspen (Populus tremula), respectively. The low content
254 of BTEX in the tree cores might be due to BTEX degradation (Sorek et al. 2008). Studies on
255 phytoremediation of petroleum products confirm a relatively rapid break-down of petroleum
256 hydrocarbons, including BTEX, in the root zones of tree stands and soil profiles under natural
257 aerobic conditions (Nichols et al. 2014; Wilson et al. 2013).

258 *3.2 Spatial distribution of the sum BTEX in tree cores*

259 The normal quantile – quantile (Q – Q) plot was used to identify the background threshold
260 value (and anomalous values) of the sum BTEX concentrations in tree-core samples (e.g. Reimann
261 et al. 2005; Papastergios et al. 2011). Two different populations were identified using changes
262 (breaks) in the slope of a probability plot of sum BTEX concentrations, interpreted as indicating
263 background (lower) and anomalous (higher) values (Fig. 3). The first bend of the slope on the Q – Q
264 plot curve occurs at sum BTEX concentrations of 1.7 µg/L; values less than 1.7 µg/L represent
265 background values, while values above 1.7 µg/L are anomalous. The anomalous values are mostly
266 dominated by high levels of toluene, with two values dominated by benzene (Fig. 3). To delineate
267 anomalous zones, core samples from each tree species representing the two populations are shown
268 with different symbols and colors on a separate sample collection map (Fig. 4). The clustering of
269 anomalous values of sum BTEX compounds in tree-core samples is observed between stillwater #2
270 and #3 and at the vicinity of stillwater #4. These delineated zones of elevated sum BTEX
271 concentrations are optimal for the installation of groundwater monitoring wells for further
272 investigations of the site.

273 *3.3 Comparison of BTEX compounds uptake between tree species*

274 From Table 1 it can be seen that toluene concentrations are clearly higher in black spruce (mean
275 42.5 µg/L) than in aspen (mean 0.91 µg/L) or birch (mean 0.8 µg/L). Pine trees have been observed

to emit elevated levels of toluene under stress (Heiden et al. 1999) and contribute to atmospheric levels of toluene (White at al. 2009), so an endogenous, natural source in black spruce cannot be excluded beforehand. However, some arguments support the possibility that measured concentrations more likely originate from external sources, i.e. groundwater. First, the wide range of values (5.4 to 146 µg/L) does not indicate production of toluene by black spruce. Second, more 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. 4). Moreover, the next samples in this direction (nos. 28 and 29) have the highest levels of benzene measured in aspen wood (Fig. 4). Thus, contamination is the most likely explanation for the elevated levels found in the trees. Although tree uptake of VOCs depends on species-specific physiology, toluene is most likely to be absorbed and accumulated in larger amounts than other BTEX constituents, or perhaps more stable, as observed in this study and in previous research (Algreen 2015; Algreen et al. 2015; Sorek et al. 2008); this finding is independent of climatic environments and other specific site conditions.

3.4 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). When compared with BTEX compounds, MTBE is more resistant to biodegradation, has a lower log Kow, a greater tendency to move rapidly through soil and groundwater, and is readily available for tree uptake and translocation (Briggs et al.

1982; Borden et al. 1997; Squillace et al. 1997; Vroblesky 2008). The latter characteristic has been demonstrated in both laboratory and field conditions, using trees from different species. 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). Conversely, a more recent investigation has found no MTBE in tree-cores from mature (stem diameter > 10 cm) willow and aspen trees at a site with known jet fuel-contaminated subsoil and shallow (2-3 m deep) groundwater (Algreen et al. 2015). Therefore, the absence of MTBE in core samples is an indication of the absence of groundwater MTBE contamination at this site. Given that buried drums are still buried 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.

4 Compilation and description of available data from open literature: The flops and tops in BTEX compounds detection using tree-core analysis

Among the studies using tree-core analysis to detect subsurface contamination by VOCs, many have successfully investigated chlorinated ethenes, such as tetrachloroethylene (PCE) and trichloroethylene (TCE) (e.g. Vroblesky et al. 2004, 1999; Larsen et al. 2008; Limmer et al. 2011; Limmer and Burken 2015).Schumacher et al., 2004; Sorek et al. 2008; Wittlingerova et al. 2013). In contrast, reports of successful applications for tracking soil and groundwater contamination by petroleum hydrocarbons, including BTEX compounds, are rare, even though BTEX compounds are also frequent subsurface pollutants and are similarly soluble in water. It may be that tree-core analyses for assessing BTEX compounds have encountered some limitations, which in some cases, lead to less successful applications, most of which remain unpublished. The studies described in this

section are summarized together with the present study for comparison in Table 3. The data are from a number of contaminated sites in a range of ecosystems with tree-core samples from 15 different tree species and measurement of BTEX compounds performed mostly by headspace extraction, or in one case study, by headspace solid-phase microextraction followed by gas chromatography-mass spectrometry.

Rein and Trapp (2009) carried out tree-core analysis at a former hydrogenation plant near Zeitz (Germany), in an area of known very high benzene groundwater contamination (100 to > 1000 mg/L). In May 2009, 14 tree-core samples were taken across the plume. Toluene could not be detected in any of the tree cores, and benzene was only found in one tree in the source zone at a rather low concentration of 6.4 µg/kg wood dry weight (dw). Sixteen additional core samples were taken in July 2009 and no BTEX compounds were detected, except in two trees from the benzene source zone, with benzene concentrations of 5.5 and 4.2 µg/kg wood dw.

At the Hradčany site, a former Soviet military airport in the Czech Republic, a free-phase layer of jet fuel covered the groundwater at 8 m below ground surface (bgs). Levels of petroleum hydrocarbons in soil ranged from 10 to 18000 mg/kg soil dw (Machackova et al. 2008). About 20 tree-core samples were collected and BTEX compounds were detected only in those trees growing on the gas plume of the ventilation outlets of the soil venting system (Trapp et al. 2005).

At the former gas works site in Søllerød (Denmark), BTEX compounds are still present in groundwater at 4 to 5 m bgs (25 to 23000 µg/L; benzene <0.2 to 950 µg/L) and in soil (sum BTEX 100 mg/kg, 1 sample). The corresponding levels in tree-core samples obtained by Algreen (2015) were maximum 0.1 µg/kg benzene and 0.05 µg/kg xylene (recalculated from µg/L for a wood density of 1 kg/L), and detects were limited to three samples (benzene) and one sample (xylene) respectively, out of 52. Toluene and ethylbenzene were not detected in any sample. Moreover, the anomalous tree-core samples were not near the location of highest groundwater concentrations. At another Danish site near Gentofte, concentrations of benzene in groundwater were about 1600 µg/L

at 4 to 5 m bgs, with sum BTEX up to 13600 µg/L. Tree-core samples (21) were taken and analyzed, but among the BTEX compounds only xylene was found in a few samples (3 samples, with maximum 0.3 µg/kg) and the spatial correlation to BTEX compounds in groundwater was weak (Algreen 2015). In the studies of Algreen (2015), toluene was the most frequently detected compound (found in 59% of the samples), xylenes and ethylbenzene were measurable in 19% and 16% of the samples and benzene was measured in only 7% of all samples.

In the more successful applications of tree-core analysis, the levels of BTEX compounds detected in tree-core samples, although reflecting the distribution in groundwater, were comparatively low, corroborating with the findings of this study. At the Szprotawa former military airport in Poland, concentrations of BTEX compounds of > 1400 µg/L (sum of BTEX approximately 20:20:500:900 µg/L B:T:E:X, varying with sample) in groundwater (1.5 to 2.2 m depth) and of 100 to 240 mg/kg soil (dry weight sum of BTEX approximately 2:10:75:150 mg/kg B:T:E:X, varying with sample) were determined around the abandoned fuel station (Algreen, 2015; Algreen et al. 2015). Because of the absence of trees growing on the hot spot, cores of nearby trees were sampled and contained a maximum of 27 µg/kg (sum of BTEX, recalculated from µg/L for a wood density of 1 kg/L; 4:12:5:6 µg/kg B:T:E:X) (Algreen, 2015; Algreen et al. 2015).

Landmeyer et al. (2000) found MTBE, BTEX and trimethylbenzene in tree cores from trees growing above a gasoline-contaminated shallow aquifer at a gasoline station near Beaufort, South Carolina (USA). Concentrations of benzene ranged from below detection limit to 7.2 µg/L and were 508 µg/L in an adjacent groundwater well. Toluene had a better tree uptake, with the highest levels of 26.2 µg/L and 674 µg/L in the tree core and groundwater, respectively. Similarly at a gas station in Tel Aviv (Israel), Sorek et al. (2008) detected relatively low concentrations of the BTEX compounds (< 100 µg/kg) in tree cores from trees growing directly above a lens of petroleum hydrocarbons floating on the groundwater table at 8 m bgs, whereas the concentrations in the nearby groundwater well were higher: 1100 µg/L for benzene, 2400 µg/L toluene, and 860 µg/L for xylene.

Holm (2011) reported the opposite outcome in tree-core samples taken at a former military base in Potsdam-Krampnitz near Berlin, Germany. Benzene and other BTEX compounds were present in most samples and in large amounts, but there was an insignificant correlation with groundwater BTEX concentrations. It is likely that the core samples, measured by HS-SPME, were contaminated by background benzene in the air or during handling or transportation.

All these study sites with non-detectable or low levels of BTEX compounds in tree-core samples have in common a characteristic, which distinguishes them from the present study: either they have a high depth to groundwater of ≥ 8 m bgs (Zeitz, Hradcany and Tel Aviv sites; Table 3) or the aquifer is constrained by aquitards such as horizontal clay layers, which act as barriers to the contact between tree roots and vapour phase of BTEX compounds or the capillary fringe (Zeitz, Gentofte and Søllerød sites; Table 3). By contrast, successful detections of BTEX compounds have been reported from contaminated sites with shallow groundwater at 2.5 m bgs or less (Szprotawa and this study; Table 3). This leads to the conclusion that tree-core analysis can reliably detect petroleum hydrocarbons such as BTEX compounds only at field sites with shallow unconfined aquifers and permeable soils. Moreover, there is a risk of sample contamination because benzene or toluene is widespread used.

5. 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 in tree-core samples collected at the landfill site and local control area indicates contamination of shallow groundwater (~2.5 m deep) by waste disposal at the landfill site, whereas the local control area is influenced by the migration of contaminant off-landfill site.

3. Uptake and accumulation of BTEX constituents vary between tree species: higher concentrations of toluene dominate in black spruce, whereas concentrations of benzene, ethylbenzene, m- and p xylenes, and o-xylene fall within similar range in all the examined tree species.
4. An anomalous zone of high sum BTEX concentrations has been identified at the landfill site to guide the drilling of boreholes and wells for further investigations of the site.
5. While negative results for MTBE in tree-core samples were obtained, suggesting the absence of MTBE in groundwater, continued site monitoring is recommended.
6. A shallow unconfined aquifer and permeable soils are important field site characteristics for the successful application of tree-core analysis for petroleum hydrocarbons, such as BTEX compounds.
7. Tree-core analysis is potentially an excellent field-screening tool during preliminary site assessments for petroleum hydrocarbon-contaminated groundwater in remote subarctic regions. 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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Fig. 1 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 and the city of St. John's where the core samples were freighted for analysis.

Fig. 2 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, monitoring wells, and contours of BTEX plumes in groundwater collected in summer 2005 and Sept.-Oct. 2006 (AMEC 2009; FEI 2006), in the vicinity of the sampling area are also shown. The direction of groundwater flow is indicated.

Fig. 3 Normal quantile - quantile (Q–Q) plot showing the first bend of the slope curve at sum BTEX concentration of 1.7 µg/L, which separates the sum BTEX concentrations into two populations: (1) background (lower) values, represented by grey squares; and (2) anomalous (higher) values, represented by orange circles for core samples containing higher levels of toluene and yellow circles for core samples containing higher levels of benzene.

Fig. 4 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.

Table 1 Location, tree characteristics, and concentrations in micrograms per liter (µg/L) of the petroleum hydrocarbon constituents benzene, toluene, ethylbenzene, m-and p-xylene, and o-xylene in the headspace of vials containing tree cores collected at landfill site in Happy Valley-Goose Bay, August-September 2014.

Notes: MTBE was not found in tree cores. Resulting values below the QLs of 0.4 µg/L for benzene, toluene, ethylbenzene and o-xylene, and of 0.8 µg/L for m- and p- xylene were set to half QL values 0.2 µg/L and 0.8 µg/L, respectively for representation. Dup = duplicate sample; a.s.l = above sea level; <DL = below detection limit; "–" = co-elution, ratios of quantification and confirmatory ions do not conform to those obtained from a standard.

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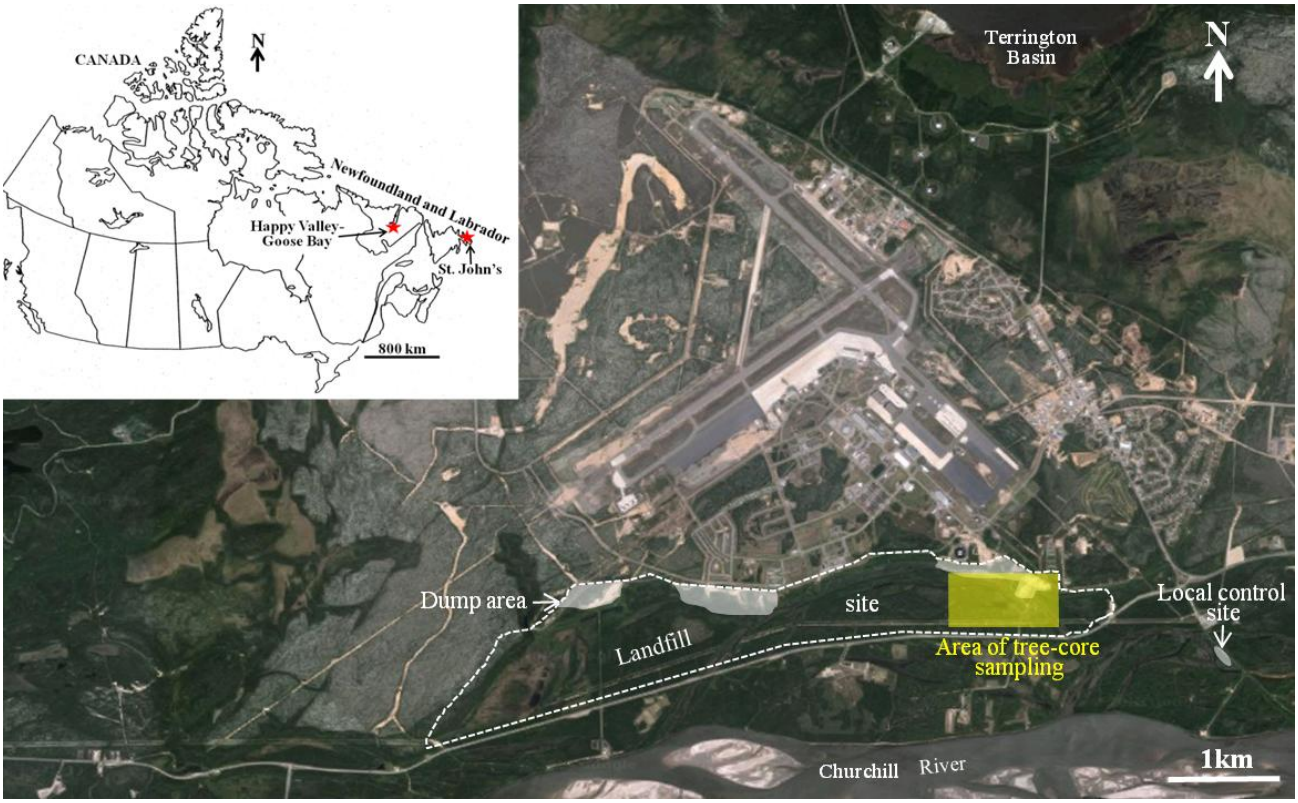
Table 3 Overview of field site characteristics and measurement methods of petroleum hydrocarbons (especially BTEX compounds) in tree-core samples from reports found in open literature and the present study.

Note: HS-GC-MS = headspace-gas chromatography-mass spectrometry; HS-SPME-GC-MS = headspace solid-phase microextraction-gas chromatography-mass spectrometry; GW =groundwater.



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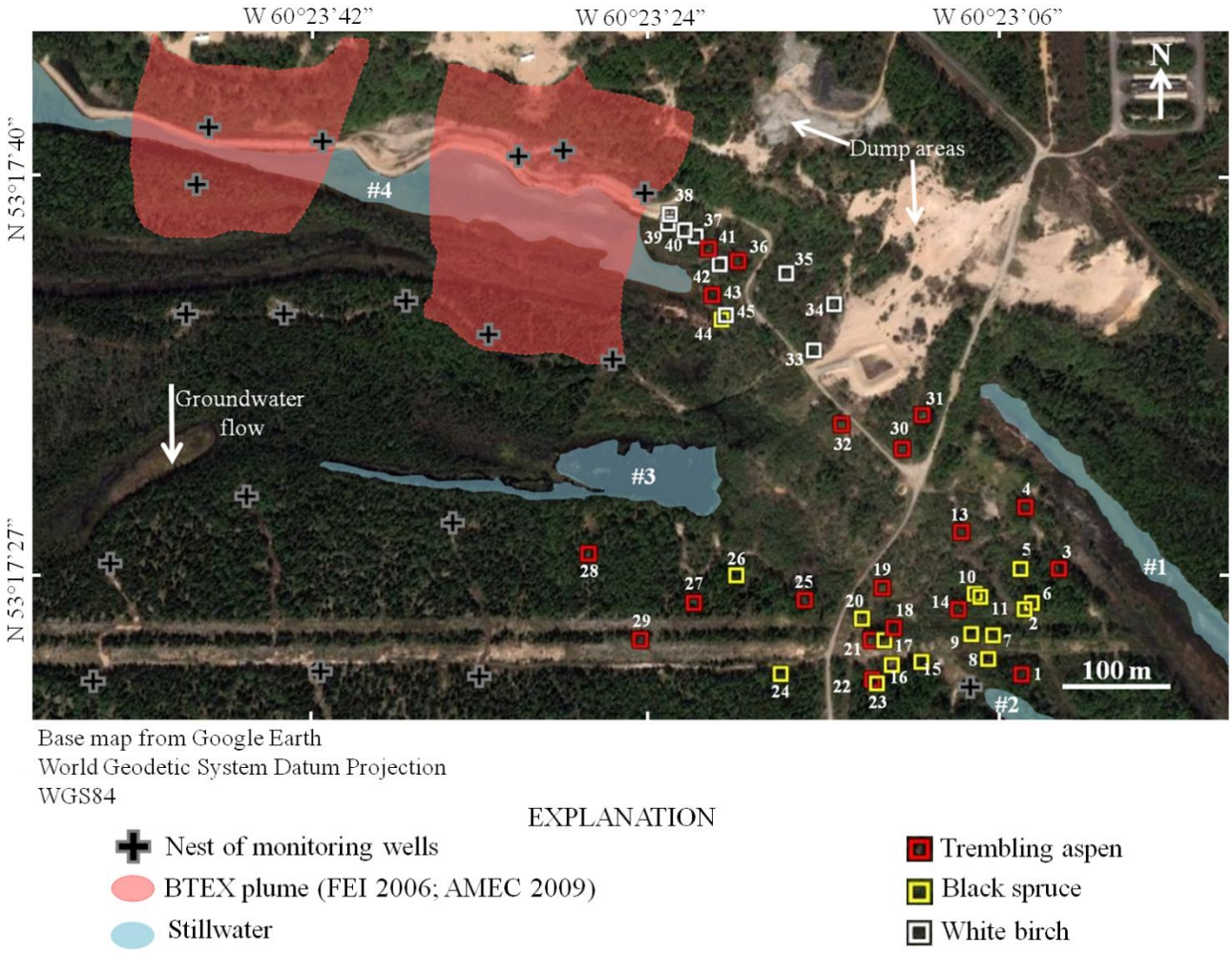

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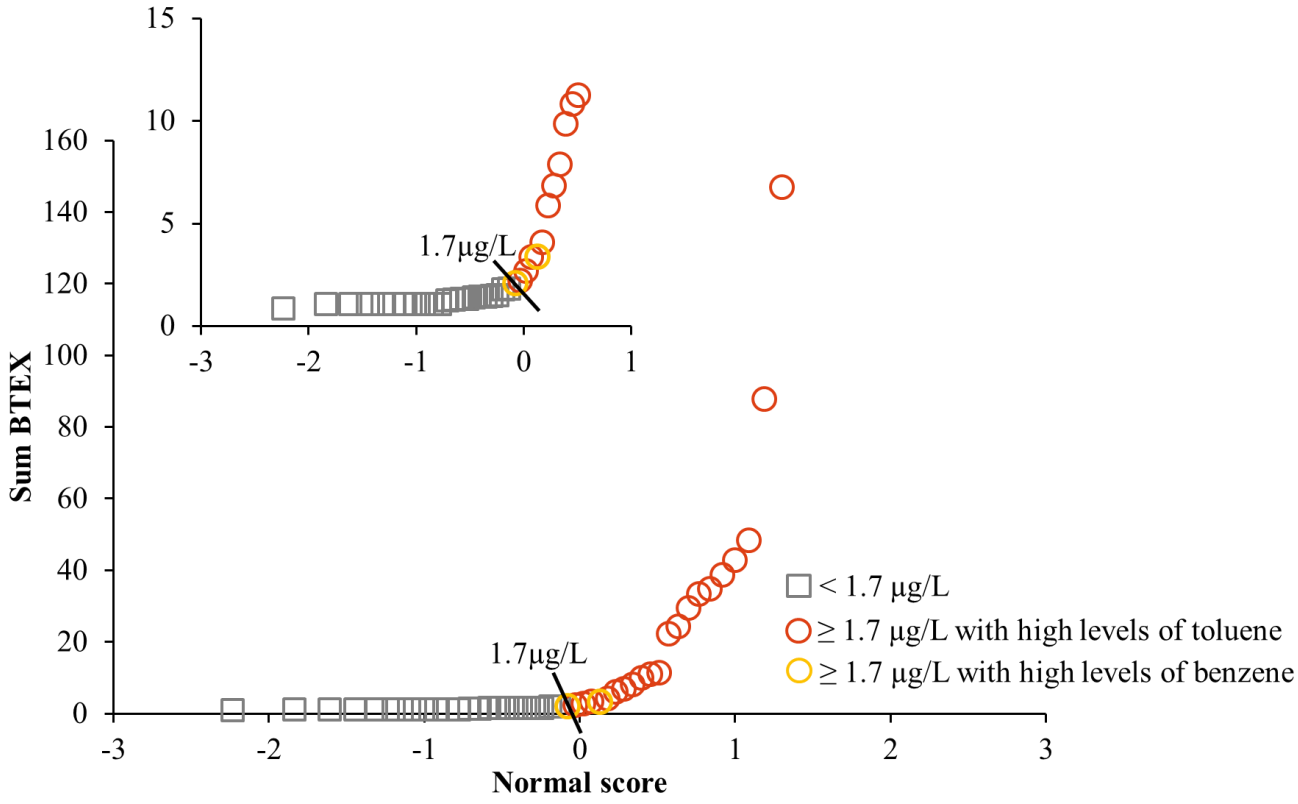

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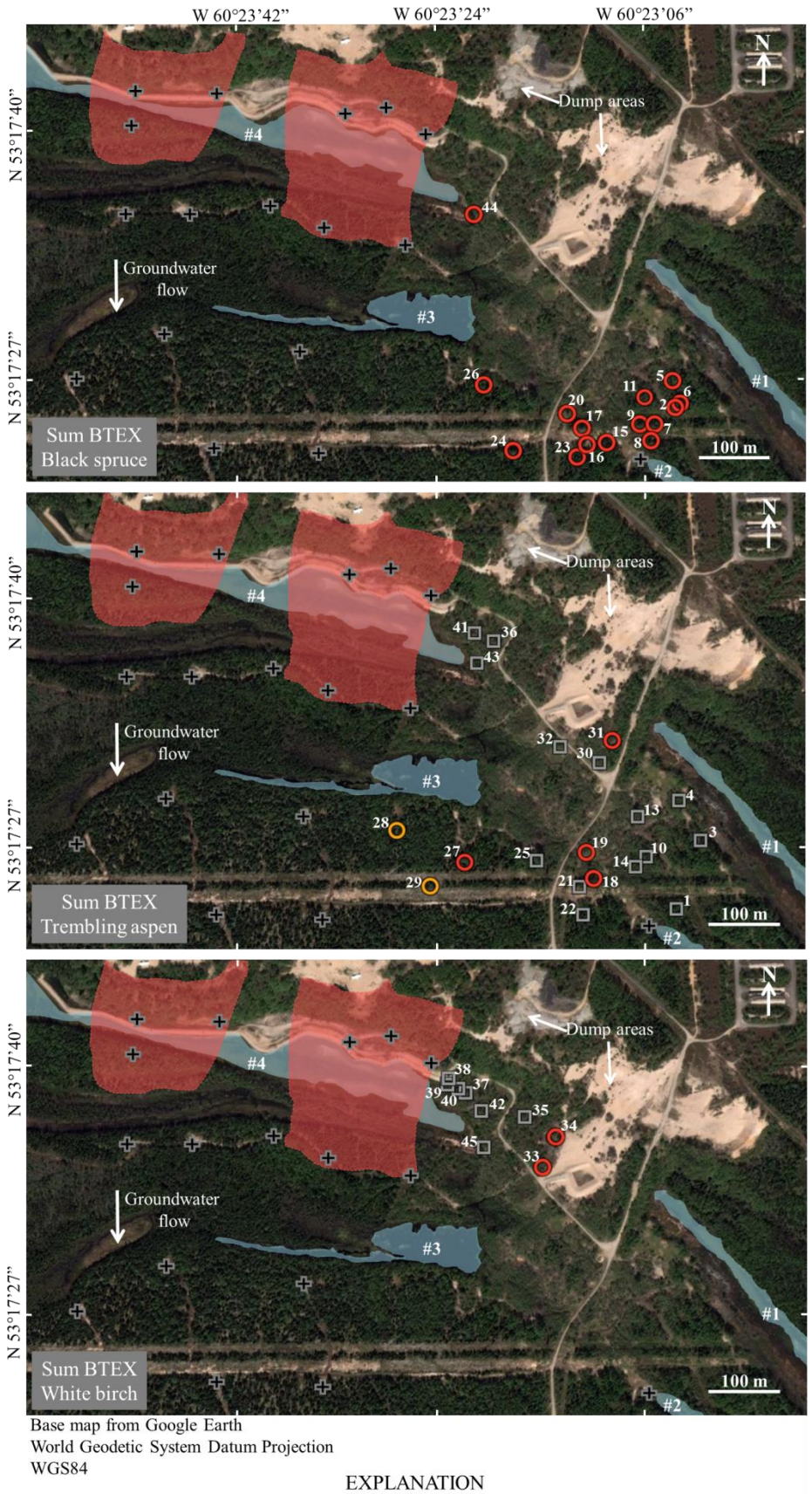
W 60°23'42"
W 60°23'24"
W 60°23'06"
N 53°17'40"
N 53°17'27"
N
Dump areas
Groundwater flow
#1
#2
#3
#4
100 m
Sum BTEX Black spruce
Sum BTEX Trembling aspen
Sum BTEX White birch
Base map from Google Earth
World Geodetic System Datum Projection
WGS84
EXPLANATION
Nest of monitoring wells
BTEX plume (FEI 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

670

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Tree Identifier (Fig. 2 and 3)	Latitude	Longitude	Elevation of tree location a.s.l. (m)	Tree species	Tree diameter (cm)	Concentrations (µg/L)					Sum BTEX
						Benzene	Toluene	Ethyl-benzene	m- and p-xylene	o-xylene	
1	53°17'23.60"	60°23'03.90"	8	Trembling aspen	33	0.20	0.44	0.20	0.40	–	1.2
2	53°17'25.70"	60°23'03.70"	9	Black spruce	31	0.20	7.4	0.20	–	–	7.8
3	53°17'27.00"	60°23'01.80"	10	Trembling aspen	39	0.20	0.63	0.20	0.40	–	1.4
4	53°17'29.00"	60°23'03.60"	11	Trembling aspen	23	0.20	0.2	0.20	0.40	–	1.0
5	53°17'27.00"	60°23'03.90"	12	Black spruce	23	0.20	38.2	0.20	–	–	38.6
6	53°17'25.90"	60°23'03.30"	11	Black spruce	26	0.20	29.0	0.20	–	–	29.4
7	53°17'24.90"	60°23'05.40"	11	Black spruce	21	0.20	10.8	0.20	–	–	11.2
8	53°17'24.10"	60°23'05.70"	11	Black spruce	25	0.20	10.4	0.20	–	–	10.8
9	53°17'24.90"	60°23'06.60"	11	Black spruce	19	0.20	5.4	0.20	–	–	5.8
10	53°17'26.20"	60°23'06.40"	10	Trembling aspen	28	0.20	0.20	0.20	0.40	–	1.0
10Dup	53°17'26.20"	60°23'06.40"	10	Trembling aspen	28	0.20	0.20	0.20	0.40	–	1.0
11	53°17'26.20"	60°23'06.20"	11	Black spruce	27	0.20	87.3	0.20	–	–	87.7
13	53°17'28.20"	60°23'07.10"	11	Trembling aspen	21	0.20	0.55	0.20	0.40	–	1.4
14	53°17'25.70"	60°23'07.30"	11	Trembling aspen	24	0.20	0.47	0.20	0.40	–	1.3
15	53°17'24.00"	60°23'09.30"	9	Black spruce	18	0.20	21.8	0.20	–	–	22.2
16	53°17'23.90"	60°23'10.90"	11	Black spruce	18	0.20	23.7	0.20	–	–	24.1
17	53°17'24.70"	60°23'11.30"	10	Black spruce	18	0.20	32.8	0.20	–	–	33.2
18	53°17'25.10"	60°23'10.80"	1	Trembling aspen	30	0.20	1.4	0.20	0.40	–	2.2
19	53°17'26.40"	60°23'11.40"	5	Trembling aspen	18	0.20	2.5	0.20	1.13	–	4.0
20	53°17'25.40"	60°23'12.50"	4	Black spruce	33	0.20	6.4	0.20	–	–	6.8
21	53°17'24.70"	60°23'12.00"	6	Trembling aspen	25	0.20	0.20	0.20	0.40	–	1.0
22	53°17'23.30"	60°23'11.70"	6	Trembling aspen	23	0.20	0.20	0.20	0.40	–	1.0

685 **Table 1** (continued)

Tree Identifier (Fig. 2 and 3)	Latitude	Longitude	Elevation of tree location a.s.l. (m)	Tree species	Tree diameter (cm)	Concentrations (µg/L)					Sum BTEX
						Benzene	Toluene	Ethyl-benzene	m- and p-xylene	o-xylene	
23	53°17'23.30"	60°23'11.70"	6	Black spruce	31	0.20	47.7	0.20	–	–	48.1
24	53°17'23.60"	60°23'16.90"	6	Black spruce	27	0.20	34.2	0.20	–	–	34.6
25	53°17'26.00"	60°23'15.60"	5	Trembling aspen	29	0.20	0.20	0.20	0.40	–	1.0
25Dup	53°17'26.00"	60°23'15.60"	5	Trembling aspen	29	0.20	0.80	0.20	0.40	–	1.6
26	53°17'26.80"	60°23'19.30"	4	Black spruce	27	0.20	146	0.20	–	–	147
26Dup	53°17'26.80"	60°23'19.30"	4	Black spruce	27	0.20	137	0.20	–	–	137
27	53°17'25.90"	60°23'21.60"	6	Trembling aspen	26	0.20	9.0	0.20	0.40	–	9.8
28	53°17'27.50"	60°23'27.30"	8	Trembling aspen	25	1.1	0.43	0.20	0.40	–	2.1
29	53°17'24.70"	60°23'24.50"	7	Trembling aspen	23	1.5	0.59	0.93	0.40	–	3.4
30	53°17'30.90"	60°23'10.30"	14	Trembling aspen	24	0.20	0.60	0.20	0.40	–	1.4
31	53°17'32.00"	60°23'09.20"	15	Trembling aspen	18	0.20	0.94	0.20	0.40	–	1.7
32	53°17'31.70"	60°23'13.60"	12	Trembling aspen	19	0.20	0.20	0.20	0.40	–	1.0
33	53°17'34.10"	60°23'15.10"	13	White birch	22	0.20	0.91	0.20	0.40	0.20	1.7
34	53°17'35.60"	60°23'14.00"	14	White birch	24	0.20	1.8	0.20	0.40	0.20	2.6
35	53°17'36.60"	60°23'16.60"	13	White birch	32	0.20	0.40	0.20	0.40	0.20	1.2
35Dup	53°17'36.60"	60°23'16.60"	13	White birch	32	0.20	0.44	0.20	0.40	0.20	1.2
36	53°17'37.00"	60°23'19.20"	10	Trembling aspen	25	0.20	0.53	0.20	0.40	–	1.3
37	53°17'37.80"	60°23'21.50"	8	White birch	34	0.20	2.5	0.20	0.40	0.20	3.3
38	53°17'38.50"	60°23'22.90"	9	White birch	26	<DL	0.20	0.20	0.40	0.20	0.80
39	53°17'38.20"	60°23'23.00"	7	White birch	28	0.20	0.20	0.20	0.40	0.20	1.0
40	53°17'38.00"	60°23'22.10"	6	White birch	25	0.20	0.20	0.20	0.40	0.20	1.0
41	53°17'37.40"	60°23'20.80"	6	Trembling aspen	30	0.20	0.20	0.20	0.40	–	1.0
42	53°17'36.90"	60°23'20.20"	8	White birch	26	0.20	0.58	0.20	0.40	0.20	1.4
43	53°17'35.90"	60°23'20.60"	8	Trembling aspen	34	0.20	0.20	0.20	0.40	–	1.0
43Dup	53°17'35.90"	60°23'20.60"	8	Trembling aspen	34	0.20	0.20	0.20	0.40	–	1.0
44	53°17'35.10"	60°23'20.10"	6	Black spruce	34	0.20	42.3	0.20	–	–	42.7
45	53°17'35.10"	60°23'20.00"	6	White birch	34	0.20	0.47	0.20	0.40	0.20	1.3

686

687 **Table 2** Location, tree characteristics and tree-core concentrations in micrograms per liter (µg/L) of the petroleum hydrocarbon constituents
688 benzene, toluene, ethylbenzene, m-and p-xylene, and o-xylene in the headspace of vials containing tree cores collected at the local control
689 site in Happy Valley-Goose Bay, August-September 2014.

690 Notes: MTBE was not found in tree cores. Resulting values below the QLs of 0.4 µg/L for benzene, toluene, ethylbenzene and o-xylene, and of 0.8 µg/L
691 for m- and p- xylene were set to half QL values 0.2 µg/L and 0.8 µg/L, respectively for representation. Dup = duplicate sample; a.s.l = above sea level;
692 <DL = below detection limit; "–" = co-elution, ratios of quantification and confirmatory ions do not conform to those obtained from a standard.

Tree identifier	Latitude	Longitude	Elevation of tree location a.s.l. (m)	Tree species	Tree diameter (cm)	Concentrations (µg/L)					Sum BTEX
						Benzene	Toluene	Ethyl-benzene	m- and p-xylene	o-xylene	
BK-2	53°17'18.60"	60°21'32.70"	0	Black spruce	20	0.20	6.6	0.20	–	–	7.0
BK-3	53°17'16.40"	60°21'30.90"	3	Black spruce	30	0.20	40.2	0.20	–	–	40.6
BK-5	53°17'13.50"	60°21'29.70"	5	Black spruce	21	0.20	38.0	0.20	–	–	38.4
BK-6	53°17'18.60"	60°21'32.70"	10	Trembling aspen	27	0.20	1.1	0.20	0.40	–	1.9
BK-7	53°17'14.30"	60°21'27.00"	9	Trembling aspen	31	0.20	0.20	0.20	0.40	–	1.0
BK-7Dup	53°17'14.30"	60°21'27.00"	9	Trembling aspen	31	0.20	0.20	0.20	0.40	–	1.0

693

694 **Table 3** Overview of field site characteristics and measurement methods of petroleum hydrocarbons (especially BTEX compounds) in tree-
695 core samples from reports found in open literature and the present study.
696 Note: HS-GC-MS = headspace-gas chromatography-mass spectrometry; HS-SPME-GC-MS = headspace solid-phase microextraction-gas
697 chromatography-mass spectrometry; GW = groundwater.

Study area	Regional climate	Depth to groundwater table (m)	Groundwater aquifer	Compounds measurement method	Tree species	Was tree-core analysis successful?	Sources
Gasoline station near Beaufort, South Carolina, USA	Humid subtropical	0.6 – 3.9	Well-sorted sand	HS-GC-MS	Oak	yes	Landmeyer et al. 2000
Hradčany site, former Soviet military airport, Czech Republic	Continental, warm dry summers	8	Sand and gravel (0 – 3m), fine grained sandstone	HS-GC-MS	Conifers (spruce and pine), birch	no	Trapp et al. 2005
Gas station in Tel Aviv, Israel	Mediterranean	8	Sand and gravel	HS-GC-MS	Rosewood, Eucalyptus	yes (in low concentrations)	Sorek et al. 2008
Former military base Potsdam-Krampnitz near Berlin, Germany	Atlantic to continental	1.3 – 7, and > 9	Fine to medium sized sands intermixed with silt layers	HS-SPME-GC-MS	Birch, willow, poplar, locust, maple, linden	no (due to cross contamination)	Holm 2011
Former hydrogenation plant near Zeitz, Germany	Humid continental with mild summer	8 – 9.4	Silty sand and gravel, with top layer of silt	HS-GC-MS	Sycamore maple, poplar, oak	erratic (detected in 1-2 trees only)	Rein and Trapp 2009
Former gas works site in Søllerød, Denmark	Humid continental with mild summer	4	Varying layers of silt, clay and clay till	HS-GC-MS	Poplar	no (no correlation to GW)	Algreen 2015
Gentofte site, Denmark	Humid continental with mild summer	5	Silt, clay and sand	HS-GC-MS	Willow, poplar	no (no correlation to GW)	Algreen 2015
Szprotawa former military airport, Poland	Continental, warm dry summers	1.5 – 2.2 (0.9 to 3.5)	Thin layer of silt underlain with sand and gravel	HS-GC-MS	mostly willow and poplar	yes	Algreen et al. 2015
Former landfill site at the Canada Force Base 5 Wing Goose Bay in Happy Valley-Goose Bay, Labrador, Canada	Subarctic with cool summer	0 – 2.5	Loose fine to medium-grained sands with scare interbedded clayey silt	HS-GC-MS	Black spruce, trembling aspen, white birch	yes	This study

698