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Mineralogical, geospatial, and statistical methods combined to estimate geochemical background of arsenic in soils for an area impacted by legacy mining pollution

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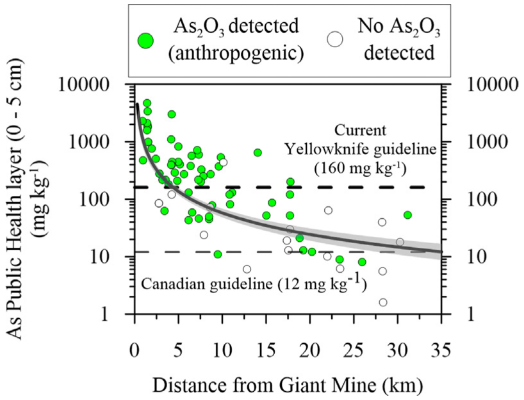
HIGHLIGHTS

- Background soil As assessed for an area impacted by 60 years of mining emissions.
- Statistical, geospatial, and mineralogical tools identified industrially impacted soils.
- Mineralogy of As minerals provided unambiguous evidence of source.
- Arsenic trioxide is predominant As mineral in surface soils within 15 km of mine roasters.

GRAPHICAL ABSTRACT



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ABSTRACT

The estimation of geochemical background is complex in areas impacted by point sources of atmospheric emissions due to unknowns about pollutant dispersion, persistence of pollutants on the landscape, and natural concentrations of elements associated with parent material. This study combined mineralogical analysis with conventional statistical and geospatial methods to separate anthropogenically impacted soils from unimpacted soils in the Yellowknife area, Northwest Territories, Canada, a region that was exposed to 60 years of arsenic (As)-rich atmospheric mining emissions (1938–1999) and that hosts natural enrichments of As. High concentrations of As (up to 4700 mg kg^{-1}) were measured in publicly accessible soils near decommissioned roaster stacks in the region and strong relationships between As and distance from the main emission sources persisted in surface soils and soils at depth in the soil profile more than 60 years after the bulk of mining emissions were released. Mineralogical analysis provided unambiguous evidence regarding the source of As minerals and highlighted that most As in surface soils within 15 km of Yellowknife is hosted as anthropogenic arsenic trioxide (As_2O_3), produced by roaster stack emissions. Statistical protocols for the estimation of geochemical background were applied to an existing database of till geochemistry ($N = 1490$) after removing samples from mining impacted

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areas. Results suggested geochemical background for the region is 0.25–15 mg kg^{-1} As, comparable to global averages, with upper thresholds elevated in volcanic units (30 mg kg^{-1} As) that often host sulfide mineralization in greenstone belts in the region.

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1. Introduction

The identification of geochemical background in soils is often sought during mineral exploration and environmental remediation activities (Reimann and Garrett, 2005). The assumption is that concentrations above (or below) a range of natural background conditions may reflect geochemical anomalies indicative of mineralization or pollution (Reimann et al., 2005). The quantification of background, however, can be ambiguous, because of the confounding effects of natural variability and past anthropogenic activities in a region (Matschullat et al., 2000; Reimann et al., 2005). The identification of background is also difficult because of inconsistency in terminology and methodological approaches (Matschullat et al., 2000; Parsons and Little, 2015; Reimann et al., 2005). Matschullat et al. (2000) aimed to clarify some of these issues and proposed that the term *geochemical background* reflect a relative measure to distinguish natural element concentrations from anthropogenically impacted concentrations. The term *geochemical baseline*, is often used interchangeably, yet is distinct and refers to ambient soil conditions in a region impacted by both geogenic processes and legacy anthropogenic impacts without distinguishing between the two (Parsons and Little, 2015). It is not realistic to consider geochemical background as a single value, since natural processes can lead to large ranges in element concentrations in unimpacted soils. Rather, geochemical background should be considered as a range of analyte concentrations in soils not impacted by anthropogenic activities (Reimann et al., 2005). An upper limit of the range of natural concentrations, defined with statistical reliability, is often sought to help identify soils impacted by anthropogenic pollution and to establish remediation criteria reflecting previously undisturbed conditions. The separation of anthropogenically-impacted soils from unimpacted soils is primarily important where samples with elevated analyte concentrations may present a risk to human or ecological health or lead to a limitation of the usage potential of soils (Matschullat et al., 2000).

Previous reviews have highlighted numerous approaches for the estimation of geochemical background (e.g. Matschullat et al., 2000; Reimann and Filzmoser, 2000; Reimann et al., 2005; Gałuszka, 2007; Dung et al., 2013). Many of these approaches focused on statistical techniques to define a range of values or an upper threshold limit reflecting unimpacted soils. The application of statistical techniques requires careful consideration of the data distribution and since geochemical data are rarely normally or lognormally distributed many parametric methods (e.g. use of the mean and standard deviation) are typically not appropriate (Reimann et al., 2005; Reimann and Filzmoser, 2000; Reimann and Garrett, 2005). Estimates using non-parametric methods are much more robust against the influence of extreme outliers that are often present in geochemical datasets (Reimann and Filzmoser, 2000). For example, Reimann et al. (2005) reviewed several parametric and non-parametric methods for estimating geochemical background and highlight the use of the Tukey boxplot, median ± 2 median absolute deviation (Md ± 2MAD), and empirical cumulative distribution functions as well suited for the estimation of threshold values and ranges of background conditions. While statistical approaches yield thresholds and ranges with statistical reliability based on empirical distributions, it is widely acknowledged that a robust estimation of geochemical background benefits from the application of a variety of tools, including statistical, geospatial, and geochemical techniques (Matschullat et al., 2000; Reimann et al., 2005). Geographical displays allow for the geospatial visualization of datasets and facilitate the identification of hotspots or anomalies (Reimann et al., 2005). Geochemical methods, including mineralogical methods, provide indispensable information on how specific elements are hosted in mineral phases, which can yield important information on whether the mineral originated from an anthropogenic or geogenic source (Bromstad et al., 2017). Realistic risk assessment should include careful study of the mineralogy of samples to determine how elements of concern are hosted and whether or not, and under what conditions, they are bioaccessible (Reimann and Garrett, 2005). The initiation of clean up activities solely because a statistical threshold has been reached may be unnecessary and could in fact worsen the environmental situation, if previously stable minerals are disturbed so that the solubility of minerals is enhanced via alteration of redox or weathering conditions (Reimann and Garrett, 2005). Mineralogical assessment can be time-consuming and expensive, therefore the power of mineralogical techniques is enhanced when used in combination with techniques that can be applied to larger sample populations (i.e. statistical and geospatial techniques). It should be acknowledged that different approaches will likely yield different estimates for geochemical background ranges and upper threshold limits. Undoubtedly, choices need to be made in the calculation of background estimates, therefore expert knowledge and clear articulation of method assumptions are required.

Regions impacted by point sources of pollution, such as smelters and refineries, present a complex environment for the determination of natural background, because of unknowns about the distribution and fate of pollutants in the environment and the natural presence of these elements in local soils and bedrock (Díez et al., 2007; Parsons and Little, 2015; Reimann et al., 2000, 2009). Arsenic (As) is a pollutant of global concern, because of its carcinogenic and toxic effects (Smedley and Kinniburgh, 2002). An important contributor of As to the environment is the waste associated with the production of base metals and gold (e.g. McMartin et al., 1999; Jamieson, 2014). The Yellowknife area in northern Canada presents a complicated environment to explore the concept of geochemical background since there is a 60-year legacy of As pollution in the region related to the mining and roasting of gold-bearing arsenopyrite and limited pre-mining geochemical data from the area (Jamieson, 2014; Walker et al., 2015). The area also hosts natural enrichments of As associated in arsenopyrite-bearing gold ore bodies (Boyle, 1979; Kerr, 2006). Beyond the impact of past mining emissions on soils, the region is relatively pristine as there are few anthropogenic sources of pollution outside of the city proper, making this an opportune area to attempt to separate anthropogenic mining and geogenic sources of As in the soil environment. Previous estimates of geochemical background in soils in the Yellowknife region suggest As concentrations in soils are elevated relative to other jurisdictions due to natural processes associated with mineralization and bedrock enrichment (ESG, 2001; GNWT, 2003). Recent work has highlighted the persistence and widespread dispersion of As from historical mining and roasting emissions and suggests that elevated As in soils and lake sediments may be the result of widespread dispersion of As from past mining emissions rather than natural processes (Bromstad et al., 2017; Galloway et al., 2017; Jamieson et al., 2017; Schuh et al., 2018; Van Den Berghe et al., 2018; Cheney et al., 2020; Palmer et al., 2020; Sivarajah et al., 2020).

In this study we present a novel approach to differentiate between anthropogenic and natural sources of As at a regional scale by combining statistical and geospatial approaches for background estimation with solid-phase speciation analysis of As-hosting minerals in soils. The specific objectives of this study were to: 1) characterize the extent of influence of past mining emissions on soils in the region using data from surface and soil cores; and 2) estimate the range and upper threshold of geochemical background for soils overlying the predominant bedrock lithologies in the region. We explored whether mineralogical analysis would help to distinguish between natural and anthropogenic sources of As in soils close to mining point sources, so that geochemical background could be estimated using soils that were unequivocally representative of natural variability.

2. Background

2.1. Mining history and previous work on soils in the region

The Yellowknife Greenstone Belt was one of the most productive and profitable gold districts in Canadian history. The two largest mines in the region, Giant Mine (1949–2004) and Con Mine (1938–2003), produced more than 13 million ounces of gold over their operating periods (Bullen and Robb, 2006). Gold was hosted in arsenopyrite (FeAsS), that was roasted as part of the processing technique to make the ore more amenable to cyanidation. The roasting of As-bearing ore created emissions of sulfur dioxide (SO_2) and arsenic vapour, that condensed to arsenic trioxide (As_2O_3) dust when released to the atmosphere (Jamieson, 2014; Walker et al., 2015). Roasters were operational in the region for more than 60 years between the Giant (1949–1999) and Con mines (intermittently 1938–1970). During these operations more than 22,000 t of As_2O_3 were released to the surrounding environment (Hocking et al., 1978; Wrye, 2008). Giant Mine was the largest emitter and released an estimated 20,000 t of As_2O_3 over its mine life. The bulk of As_2O_3 emissions from Giant Mine (>86%) were released prior to 1964 (Wrye, 2008). While there were high emissions in the early years of operations (pre-1958) at the two mines, in later years most of the As_2O_3 dust was captured. At Giant, >90% of the dust produced (~2,370,000 t) is currently stored in underground chambers, whereas at Con, the arsenic trioxide was treated on site, integrated with tailings, or sold commercially (Hauser et al., 2006).

The widespread distribution of As_2O_3 resulted in environmental impacts to soils (Hocking et al., 1978; Hutchinson et al., 1982; Jamieson et al., 2017), lake waters (Houben et al., 2016; Palmer et al., 2015), and lake sediments (Galloway et al., 2017; Schuh et al., 2018; Cheney et al., 2020; Palmer et al., 2020) across the region. Several studies since the 1970's have reported concentrations of As and antimony (Sb) (another roaster associated element) in near-surface soils in the Yellowknife region (Bromstad et al., 2017; Hocking et al., 1978; Hutchinson et al., 1982; Jamieson et al., 2017; St. Onge, 2007). A detailed summary of existing soil research in the Yellowknife area is reported in Jamieson et al. (2017). Consistent among these studies spanning almost five decades is a clear inverse relationship between soil As concentrations and distance from the legacy point sources of pollution at Giant and Con Mines. It remains unclear, however, the extent to which geogenic sources of As, associated with sulfide mineralization near gold deposits, influence As concentrations in soils in the vicinity of legacy mining operations.

While previous work in the region has focused on estimating the distribution of total As in surface soils, there has been little attention directed at understanding the mineral form of As in surface soils across the region. Detailed mineralogical analyses of surface soils on the Giant Mine property demonstrated that the most common As hosts were As_2O_3 and roaster-generated iron-oxides (maghemite and hematite), both anthropogenic in origin from stack emissions (Bromstad et al., 2017; Walker et al., 2005). Bromstad et al. (2017) noted that most of the As_2O_3 observed in surface soils on the Giant Mine property was likely deposited prior to 1964. This indicates limited dissolution of As_2O_3 and suggests that legacy As_2O_3 is persisting on the landscape for decades, yet little information exists for soils beyond mine lease boundaries.

Several attempts have been made to estimate geochemical background As concentrations in soils in the Yellowknife region to support remediation and reclamation efforts. The Government of the Northwest Territories used an average natural background of 150 mg kg^{-1} As with a reasonable upper limit (90th percentile of available data) of 300 mg kg^{-1} for setting the site-specific soil quality guidelines for the Yellowknife area for residential (160 mg kg^{-1} As) and industrial (340 mg kg^{-1} As) soils (GNWT, 2003). This estimate of geochemical background was based on soil data from a variety of sources, but all within close proximity to Yellowknife (ESG, 2001). Based on previous work, many of the soils used in this estimation were likely impacted by stack emissions in the region, even 50 cm below the surface, which may be influenced by dissolution and downward mobilization from surface soils (Hocking et al., 1978; Hutchinson et al., 1982; Kerr, 2006; Jamieson et al., 2017). Kerr (2006) recognized the importance in removing sample data close to the historic roaster stacks in developing background As estimates. Data within 5 km of Giant Mine were not included in background estimates for granitoid (5–10 mg kg^{-1}) and volcanic lithologies (10–30 mg kg^{-1}), but no information is included on the methodology used to calculate geochemical background (Kerr, 2006). Recent work has indicated that the impact of stack emissions in soils and lake sediments extends beyond 20 km from Yellowknife (Jamieson et al., 2017; Pelletier et al., 2020) and perhaps as far as 40 km (Cheney et al., 2020). Considering this information, an estimation of geochemical background should acknowledge these regional impacts and likely exclude soils near historical point sources of emissions, unless mineralogical evidence suggests that high As in soils near emissions point sources is associated with natural enrichment.

2.2. Study area

The study area includes much of the Slave Geological Province (172,500 km^2), a late Archean craton extending from the north shore of Great Slave Lake, Northwest Territories to the Coronation Gulf in Nunavut. The treeline transition intersects the Slave craton and separates Taiga Shield, in the south, from Tundra Shield, in the north (Ecosystem Classification Group, 2009). Underlying bedrock is composed of metavolcanic and metasedimentary rocks intruded by granitoid plutons (Helmstaedt, 2009). The Slave craton was glaciated in the late Wisconsinan and covered by the Laurentide Ice sheet until ~13,000 ka BP (Wolfe et al., 2017b). During deglaciation, the southern portion of the Slave craton, close to Great Slave Lake and below 280 MASL, was inundated by Glacial Lake McConnell (13,000 to 9500 ka BP). Consequently, surficial materials in this region are dominated by glaciolacustrine and glacifluvial sediments (Wolfe et al., 2017b). Most of the study area was not covered by Glacial Lake McConnell and surficial materials are dominated by thin veneers of glacial till (Kerr, 2006). Soils in the region are poorly developed because of the cold, dry climate, and relatively recent deglaciation (Wolfe et al., 2017a). In general, the region forms a gently undulating glaciated landscape characterized by thin covers of surficial materials and dominated by exposed bedrock outcrops (Wolfe et al., 2017a).

3. Material and methods

This study relied on previously reported data from several soil and till geochemical surveys conducted in the Slave Geological Province (Supporting information Table S1). Several of the studies employed distinct sampling and analytical techniques, which presented an issue of intercomparability between datasets. Therefore, data were not pooled for statistical analyses, and the two primary datasets (Jamieson et al., 2017; Kerr and Knight, 2005) were used to address distinct and independent questions about: 1) the origin and distribution of As in soils close to emission point sources; and 2) estimating geochemical background of As in surficial materials across the Slave Geological Province.

3.1. Origin and distribution of As in soils near legacy point sources of mining emissions

The first part of this study was focused on understanding the distribution and mineralogy of As-hosting minerals in surface soils within a

30-km radius of Yellowknife (Fig. 1) to elucidate the impact of past mining emissions on local soils. A central question for this part of the study was whether we could determine whether As measured in surface soils was of anthropogenic or geogenic origin. Total As data presented were reported previously in Jamieson et al. (2017). Mineralogical data is from the MSc theses of Oliver (2018) and Maitland (2019), which relied on the same samples as collected in Jamieson et al. (2017), using the same field collection and preparation methods.

3.1.1. Field collection

Four hundred and seventy-nine soil samples were collected during three summers (2015–2017) within a 30-km radius of Yellowknife using aluminum soil core tubes that were pushed or driven into the soil with a sledgehammer. All sampling targeted undisturbed locations free of municipal and industrial disturbance, including the Giant Mine and Con Mine properties. Soils were sampled from four distinct terrain units to assess the influence of terrain type on the variation of soil As across the region, including bedrock outcrop soils, bedrock outcrop soils with tree cover, forested soils, and peatlands. Bedrock outcrop soils were typically thin (<30 cm) organic rich soil pockets within expansive bedrock outcrop areas. Bedrock outcrop soils with tree cover had similar soil conditions to bedrock outcrop soils, but with some trees, primarily jack pine (*Pinus banksiana*). Forested soils had thicker soils than the bedrock classes and were either characterized by: 1) a cover of black spruce (*Picea mariana*) with a thin organic layer overlying poorly developed soils or tills; or 2) a cover of white paper birch (*Betula papyrifera*) overlying thick deposits of fine-grained mineral soils, which are commonly underlain by permafrost in the region (Wolfe and Morse, 2016). Peatlands were thick organic deposits, typically overlying permafrost, with little to no tree cover. Cores were sealed in the aluminum tubes with laboratory wrapping film, frozen and shipped to Queen's University where they were kept frozen until analysis. Prior to analysis, core tubes were cut open with a table saw, separated with a ceramic knife and subsectioned into 5-cm intervals. In this study, samples were not sieved and only gently ground prior to analysis to preserve materials as they would be encountered in the field and to reduce the potential of screening out important As mineral hosts. Analytical efforts were focused on the samples from the upper 5-cm of the soil column ($N = 407$), referred to here as the Public Health layer after Parsons and Little (2015) and consistent with the surface layer of soil that contributes to incidental human exposure. All surface materials were left in place during sampling, including leaf litter, mosses and surface vegetation, but large sticks and woody material were removed if present. Sixty samples were prepared for analysis from the 5-cm interval at the base of the core tube and are referred to as “downcore samples” to assess downward migration of As and the concentration-distance

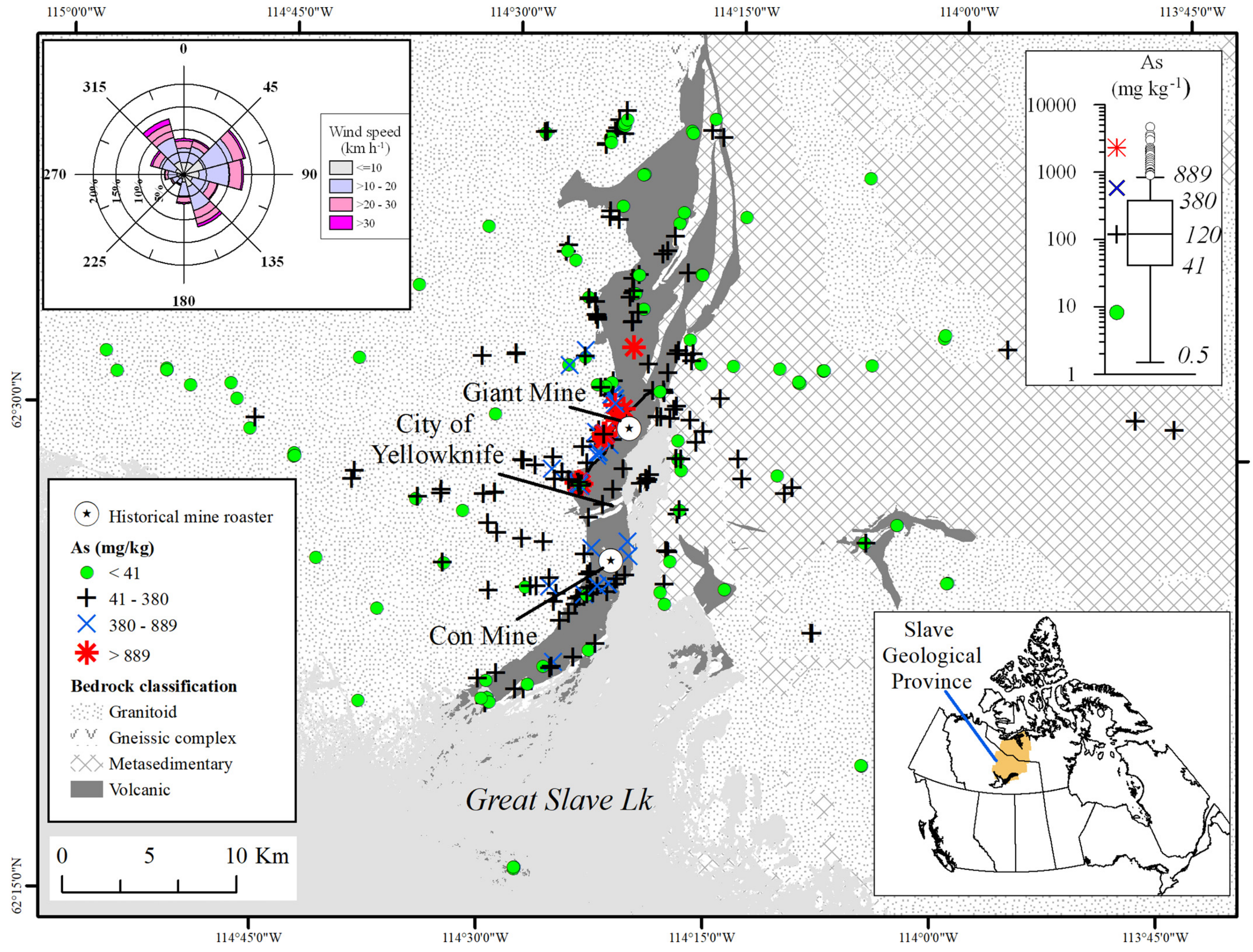

Fig. 1. Arsenic concentrations in Public Health layer samples (0–5 cm) within a 30 km radius of Yellowknife ($N = 407$). Data are symbolized following the Tukey boxplot method (presented in upper right inset): less than 1st quartile (green circles), between 1st and 3rd quartile (black crosses), between 3rd quartile and upper fence (3rd quartile + 1.5*IQR) (blue X), and beyond the upper fence are considered outliers (red asterisk). Inset in upper left of figure shows mean wind speed and frequency for wind directions at Yellowknife (1953–1999) (Environment and Climate Change Canada, 2020).

relationship at depth. The depth of these samples ranges from 10 to 38 cm below the soil surface and typically represents the base of the soil column at sampling locations. At eleven sites, soil cores were sectioned through the soil profile to explore chemical gradients in the soil column. The appendices in Jamieson et al. (2017) include descriptions of the groundcover and soil at each sampling site.

3.1.2. Total metal(loid) analyses

A portion of each subsectioned core was homogenized and submitted for near-total elemental analysis at the Analytical Services Unit (ASU) at Queen's University. Samples were digested using *aqua regia* solution (HCl and HNO_3) and subsequently analyzed for a suite of metal (loid)s via inductively coupled plasma-mass spectrometry (ICP-MS) (for Au and Sb) or inductively coupled plasma – optical emissions spectrometry (ICP-OES) (20 elements). Only the data for As (referred to here as total As) are discussed in this study, however, all analytical data are presented in the appendices of Jamieson et al. (2017). Sample homogeneity and analytical reproducibility were assessed using field duplicates (paired samples collected in close proximity in the field), split samples (samples from same depth interval prior to sample homogenization), and internal laboratory duplicates (samples from same depth interval after sample homogenization). These results are presented in Jamieson et al. (2017) and a summary of these results is presented in the Supporting information.

3.1.3. Mineralogical analysis

A subset ($N = 85$) of the 479 Public Health layer samples were targeted for mineralogical analysis via Scanning Electron Microscopy (SEM) based automated mineralogy at Queen's University. Samples for detailed mineralogical analysis were selected to represent a range of total As concentrations (1.6–4700 mg kg^{-1}) and from spatially distributed locations across the region that integrated the distance gradient from point sources of mining emissions and proximity to ore bodies. Samples were air-dried, gently disaggregated in a mortar, and mounted in epoxy. Graphite powder (<44 μm) was added to minimize agglomeration. The epoxy was allowed to harden at room temperature and the pucks were ground and polished by hand, then carbon-coated. Details of sample puck preparation can be found in Oliver (2018) and Maitland (2019). Automated mineralogy was accomplished using methods similar to those described in Schuh et al. (2018). The method was optimised to find and identify As-bearing phases even in cases where only a few particles were present. Total particle counts ranged from hundreds to hundreds of thousands of grains per slide, and arsenic-hosting minerals comprise anywhere from less than ten grains to thousands of grains per thin section. The distribution of As among multiple As hosts in each samples was calculated based on the area occupied by that mineral and the mass of As present in that mineral (Schuh et al., 2018). Mineral Liberation Analysis - automated mineralogy (MLA-AM) was used to distinguish the number of particles and to calculate the area of each particular As-bearing phase in a thin section. The thickness of the phase in a thin section was assumed 1 μm. For arsenic trioxide, arsenopyrite, realgar, enargite, and scorodite the amount of As in each phase was determined using standard mineral formulae to calculate chemical compositions. For less well-defined minerals containing mixed spectra, approximate As weight % values were established based on previous work completed in the area (Supporting information, Table S2).

3.2. Estimation of natural background in the Slave Geological Province

The second part of this study was directed at developing an estimate of geochemical background for As in soils overlying the main bedrock lithologies of the Slave Geological Province and relied on data from till geochemical surveys conducted across the Slave craton ($N = 1560$) between 1992 and 2001 by the Geological Survey of Canada (Kerr and Knight, 2005). Details on the field and laboratory analytical techniques are presented in the Supporting information (Table S1). In brief, composite till samples were collected from hand dug pits 10–70 cm below the surface and were sieved prior to analysis to include silt and clay sized fractions (<63 μm). Samples were analyzed for total As using instrumental neutron activation analysis (INAA), which is considered a total measurement of elements in a sample (Revel and Ayrault, 2000). The intention of the surveys was to compile geochemical information for mineral exploration, therefore, known areas of sulfide mineralization were often targeted, potentially skewing As measurements upwards. In this study, we provide new interpretation of these data to understand the range of geochemical background in different bedrock lithologies of the Slave Geological Province.

Finally, in order to enhance the geospatial visualization of data across the Slave craton, we included data from two additional till surveys (Kjarsgaard et al., 2013; Normandeau, 2020). Data from the three studies across the Slave craton were symbolized by quartiles using the Tukey boxplot method in figures, therefore differences in field, laboratory, or analytical methodologies were assumed to have little influence on grouping of data.

3.3. Data analysis

3.3.1. Spatial distribution of As and As mineralogy across the Yellowknife area

Spatial patterns in the distribution of As in Public Health layer soils in the Yellowknife area were displayed graphically in maps using boxplot classes, so that symbol classes transferred the data structure into a spatial context (Reimann et al., 2005). We used concentration-distance plots to explore the relationship between soil As and distance from Giant Mine (the main emission source of As in the region). The effect of soil sample location in relation to Giant Mine and the prevailing wind direction axis, on soil As concentration, was also analyzed. Sites were classified according to terrain type and bedrock lithology to explore the influence of these two factors on the regional distribution of As in the region. Detailed sampling ($N = 107$) in two areas west of Giant Mine resulted in an uneven distribution of sampling points across the region, therefore these sampling plots were down sampled and the median concentration of As in each plot was used in subsequent analyses. Bedrock classes were based on the geospatial database of bedrock geological features in the Slave craton (Stubley and Irwin, 2019), and included granitoid, metasedimentary and volcanic lithology units. Direction relative to Giant Mine and the prevailing wind axis was determined by first calculating the angular direction (0–360°) relative to Giant Mine, then aligning the 0°/180° axis to the prevailing wind direction of 80° by subtracting this amount from the original angular direction and transforming to a scale of -1 to $+1$ by taking the cosine of the difference. Values of $+1$ indicate sites directly downwind of Giant Mine and values of -1 indicate sites directly upwind, in relation to the prevailing wind for this region. The influence of terrain type, bedrock lithology, and wind direction (grouped by cardinal direction) on the distribution of Public Health layer As concentrations was assessed using the non-parametric Kruskal Wallis test for significant differences between grouping variables. Post-hoc pairwise Wilcox tests were used to identify between which groups significant differences existed. The influence of distance relative to Giant Mine on soil As was assessed through bivariate linear regression. Log transformation were used where required to meet regression model assumptions.

A general linear model was subsequently formulated with two continuous variables (distance and normalized wind direction) and two factors (terrain type and bedrock lithology) to test for their individual effects on soil As concentrations, and any possible interactions among them. A reverse stepwise approach was used to sequentially remove non-significant independent variables ($p > 0.05$). The relative importance of any independent variable determined to be statistically significant was then calculated using the RELAIMPO package in R (Grömping, 2006). The independent R^2 metric was used to quantify relative importance of regressors. It is calculated by averaging sequential sums of squares over all orderings of regressors in the model. The sum of independent R^2 values yields the unadjusted R^2 for the full model. The independent R^2 for each regressor can be compared to determine its relative importance to observed variance in the dependent variable. In the context of our soil arsenic model, it represents the unique contribution of each independent variable to variance in soil As concentration across the study area. For partially correlated regressors, the independent R^2 is particularly useful because it summarizes only the independent contribution of each to the observed variance in the dependent variable.

We used the identification of As_2O_3 and the proportion of total As (from ICP-OES analysis) as As_2O_3 to fingerprint the extent and magnitude of anthropogenic impact in Public Health layer soils near Yellowknife. Although the minerals arsenolite and claudetite (both As_2O_s) can be found naturally, they are very rare, usually formed as oxidation products directly on arsenic sulfide precursor minerals. This association is not observed in the Yellowknife area and the particles of As_2O_3 in the regional soils, identified as arsenolite by microdiffraction (Bromstad et al., 2017) are discrete and resemble those observed in Giant Mine roaster dust from the underground chambers (Lum et al., 2020). Based on these features, and the known release of 22,000 t of As, dominantly $As_2O_{3,}$ from Giant and Con roasters, we assumed that all As_2O_3 present in the soil samples is anthropogenic. The roaster-derived maghemite and hematite are also anthropogenic, and can usually be distinguished from natural iron oxides by texture (Bromstad et al., 2017), but the difficulty in doing that for thousands of particles resulted in the decision to focus on As_2O_3 in this study. The concentration of As_2O_3 expressed in mg kg^{-1} was determined by multiplying total As (as measured by ICP-OES) for a sample by the proportion of As hosted as As_2O_3 using the SEM-automated mineralogy technique for the subsample slide mount.

3.3.2. Estimating geochemical background for the Slave Geological Province

The concept of estimating background can be problematic over large areas (e.g. continents) because of variability in geology, climate, vegetation, and soil forming processes (Reimann and Garrett, 2005). In this study, we developed an estimate of geochemical background for the four main lithologies of the Slave Geological Province, and justify its usefulness because the size of the study area (~172,500 km^2) is similar to previous studies (Chen et al., 2001; Reimann et al., 2009; Reimann and Garrett, 2005; Salminen and Tarvainen, 1997) and bedrock geology and surficial geomorphology are relatively consistent across the region. Climate and vegetation gradients in the region may influence some soil forming processes, but these differences were not expected to have a major influence on the distribution of As compared to anthropogenic sources or As-bearing mineralization.

Environmental data distributions are rarely normal or lognormal, because the data are spatially dependent and typically influenced by multiple processes that vary across space (Reimann and Filzmoser, 2000). This has consequences for statistical analyses that assume normal or log normal distribution. The quantification of geochemical background for the Slave Geological Province was based on 1564 till samples from Kerr and Knight (2005). Consistent with the graphical display of Public Health layer samples in the Yellowknife area, As in tills from the Slave craton were displayed in maps using boxplot classes. Since there is a strong relationship between the concentration of soil As and distance from point sources of pollution in the region, we removed all data within 20 km of Yellowknife, based on the results from concentration-distance plots and mineralogical analyses. We tested normality of all remaining original and ln-transformed data ($N = 1490$) using histograms, quantile plots, boxplots, and the Shapiro–Wilk test of normality. Since neither the original nor ln-transformed distributions met assumptions of normality, several non-parametric methods were used for estimating the range and upper thresholds of geogenic background. These methods included the use of the median ± 2 median absolute deviations (Md ± 2MAD), Tukey boxplots, and calculation of the 90th, 95th, and 99th percentiles of the data. Outliers were identified as data beyond the third quartile plus 1.5 times the interquartile range ($Q3 + (1.5 \times IQR)$) but were not excluded from the data so that natural geochemical anomalies were included, and because the data had already been screened for anthropogenic influence.

4. Results

4.1. Relationships between soil As and distance from legacy mining emission sources

The concentration of As in Public Health layer soils ranged from <2 to 4700 mg kg^{-1} (median = 120 mg kg^{-1}) within 30 km of Yellowknife (Figs. 1 & 2A). In general, As concentrations were higher closer to Yellowknife and lower with increasing distance from the city and Giant Mine (Figs. 1 & 2A). Within 20 km of Yellowknife, 95% of Public Health layer samples exceeded the CCME guideline for residential soils (12 mg kg^{-1}), whereas only 49% of soils beyond 20 km exceeded this value (Fig. 2A). No samples exceeded the Yellowknife specific guideline for residential soils (160 mg kg^{-1}; GNWT, 2003) beyond 17.5 km from Yellowknife, irrespective of underlying bedrock lithology. Fig. 2A highlights that sampling likely did not extend far enough from Yellowknife to discern a distance at which concentrations no longer decreased since the slope of the relationship does not approach zero by the maximum sampling distance.

An inverse relationship between As concentration and distance from Giant Mine was also evident for samples collected at 10–40 cm depth in the soil profile (Fig. 2B). The relationship was significant ($p < 0.001$), however, the model fit was lower than observed for samples in Public Health layer soils (Fig. 2B). Similar to the distribution of As in Public Health layer soils, there was substantial variation in the concentration of As in downcore samples (Fig. 2B). Variation was higher for samples collected close to Giant Mine, where As ranged from 2.7 to 1200 mg kg^{-1} within 5 km of the legacy roaster, compared to distances beyond 20 km where As ranged between 2 and 63 mg kg^{-1} As. In downcore samples, most of the samples (85%) collected beyond 10 km from Giant Mine were below the CCME guideline for residential soils (12 mg kg^{-1}) (Fig. 2B).

The results from chemical analyses through the soil profile demonstrate dampening of the As gradient in soil profiles with increasing distance from Yellowknife (Fig. 3). Arsenic concentrations were highest in surface soils at all distances from Yellowknife and the chemical gradient was most pronounced in sites closest to Yellowknife, where mean As measured 795 mg kg^{-1} in surficial soils (0–5 cm) and 35 mg kg^{-1} at depth (25–30 cm) (Fig. 3). At sites beyond 15 km from Yellowknife mean As measured 27 mg kg^{-1} and 5 mg kg^{-1} in surficial soils and soils at depths >20 cm from the surface, respectively (Fig. 3). Soils at depth are often considered representative of conditions unimpacted by atmospheric emissions of contaminants (Kerr, 2006) and for sites further than 10 km from Giant Mine, soil As >20 cm below the surface ranged between 2 and 16 mg kg^{-1} (Fig. 3).

4.2. Variability in Public Health layer As by terrain type, wind direction, and underlying bedrock geology

While a significant decreasing trend in Public Health layer As concentrations was observed with increasing distance from Giant Mine, there was substantial variation in Public Health layer As concentrations throughout the region, including at sites proximal to legacy mine roasters (Fig. 2). For example, within 5 km of the historic roaster stack at Giant Mine As concentrations ranged between 8 and 4700 mg kg^{-1} (Fig. 2A). The highest concentrations of As in soils were measured in areas adjacent to the legacy mine roasters at Giant and Con Mine and were highest in thin outcrop soils overlying granitoid bedrock immediately west of Giant Mine, consistent with predominant wind direction in

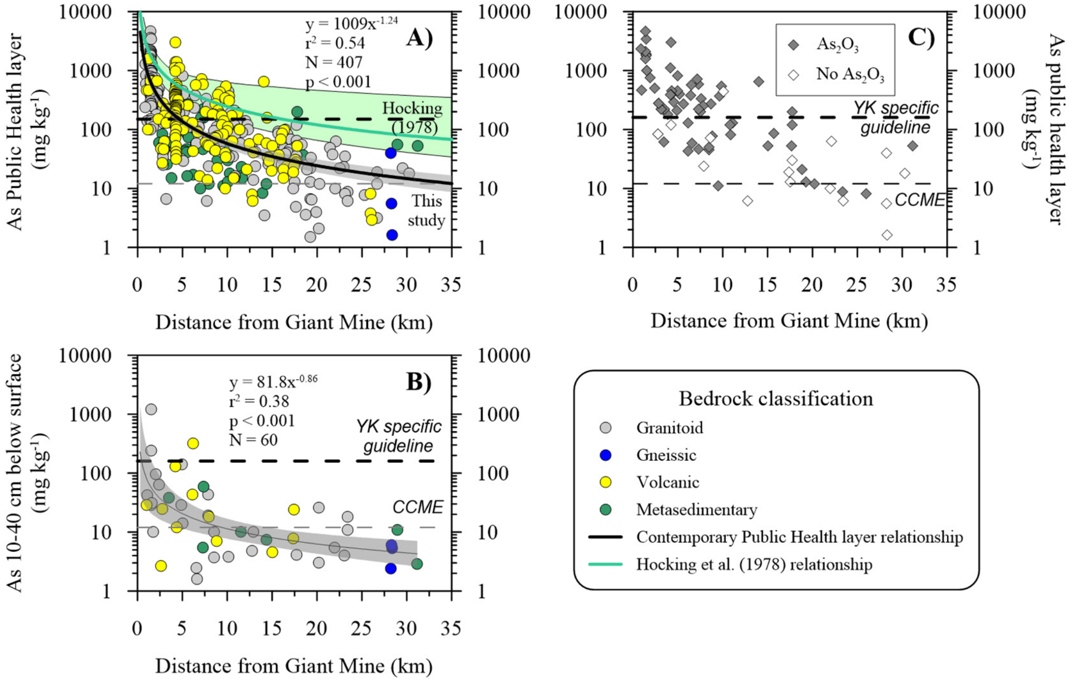

Fig. 2. The concentration of arsenic in soils with distance from the historical Giant Mine roaster colour coded by underlying bedrock classification for: A) the Public Health layer (0–5 cm); and B) soils 10–40 cm below the soil surface. Panel C) The presence and absence of As_2O_3 in a subset of Public Health layer soils ($N = 82$) as determined by SEM. The Canadian Soil Quality Guideline for the Protection of Environmental and Human Health (12 mg kg^{-1}) (CCME, 2007) and a Yellowknife specific remediation guideline for residential soils (160 mg kg^{-1}) (GNWT, 2003) are indicated as dashed lines. The 95% confidence interval of the regression lines in panels A and B are indicated by the shaded areas. The historical relationship between As in the A0 soil horizon and distance from Giant Mine from Hocking et al. (1978) is presented in panel A (95% confidence interval in green shade).

the region from the east and not associated with areas of known sulfide mineralization (Figs. 1 and 2A). We measured significant differences in the distribution of As in Public Health layer soils for samples grouped by terrain unit (Kruskal-Wallis chi-squared = 19.96, df = 3, $p < 0.001$) and cardinal wind direction from the Giant Mine roaster stack (Kruskal-Wallis chi-squared = 19.49, df = 3, $p < 0.001$) (Fig. 4). In the comparison between terrain units, median As concentration was lowest in samples collected from forested areas with thick soils. No significant differences were noted between the distributions of As collected on bedrock outcrops, whether they were tree covered or not, or in peatland terrain (Fig. 4A). Comparison of soil As concentrations grouped by cardinal wind direction revealed significantly higher soil As to the south and west of Giant Mine than in areas to the north and east. Although significant differences in the distribution of As were measured in soils overlying different bedrock units, there was no significant difference between the distribution of As overlying granitoid and volcanic lithologies (Fig. 4C). Soil As was lowest overlying metasedimentary units, which are predominately to the east of Yellowknife (Figs. 1; 4C).

A generalized linear model (GLM) with three statistically significant variables was identified for describing soil arsenic concentrations within 30 km of Yellowknife (adjusted $R^2 = 0.52$, $p < 0.0001$). The regressors included in this model were distance to Giant Mine, direction relative to Giant Mine (normalized to prevailing wind) and terrain type. Bedrock was removed from the model due to lack of significance between the two primary lithologies of interest (granitoid and volcanic). The model results are presented in the Supporting information (Table S3) and show that distance from Giant Mine, wind direction and terrain type had a significant effect on ln-transformed As in the region. The relative importance analysis identified distance to be the single-most important predictor of soil arsenic in the context of the GLM model (independent $R^2 = 0.39$) followed by terrain type (independent $R^2 = 0.08$) and direction (independent $R^2 = 0.06$).

4.3. Solid-phase As speciation in Public Health layer samples

Mineralogical results presented in Figs. 2C and 4 identify the extent to which legacy mining emissions were dispersed and continue to persist in surface soils. Arsenic trioxide was detected in 82% of the 85 Public Health layer samples that were investigated for As mineralogy, including several sites located more than 25 km from Giant Mine (Fig. 2C). While Fig. 2C highlights the presence or absence of As_2O_3 in samples, Fig. 5 shows the relative proportion of As_2O_3 with respect to total As in each sample. In samples where As_2O_3 was detected it was the predominant As-hosting mineral but the relative proportion of total As as As_2O_3 differed along the distance gradient from Yellowknife and Giant Mine (Fig. 5; Supporting information Table S4). Specifically, for sites within 5 km of Giant Mine, As_2O_3 accounted for more than 80% of total As measured in samples and at distances up to 20 km from Giant Mine more than 50% of total As (Fig. 5). Arsenic trioxide was detected in 49 of 50 samples where total As was above the Yellowknife specific remediation guideline of 160 mg kg^{-1} (Fig. 2C).

Several other As-hosting minerals were observed in samples from the region (see Supporting information Table S4), including additional minerals inferred to derive from mining sources. Specifically, scorodite was found in several samples near Con Mine and may be related to processing waste from pressure oxidation that was used later in mine life at Con Mine (Walker et al., 2015) and roaster-generated iron oxides, which were interpreted to be of anthropogenic origin based on texture, were widely observed near Giant Mine (Walker et al., 2005; Bromstad et al., 2017). However, as previously explained, distinction of these roaster-generated iron oxides from natural pedogenic Fe, Mn-oxides was not feasible for all samples. Consequently, the anthropogenic proportion of As in soils in the region was likely underestimated, since these other minerals were not considered in the proportion of total As as anthropogenic species (Fig. 5). Arsenopyrite and As-bearing pyrite were expected to be the predominant As-hosting minerals associated with natural

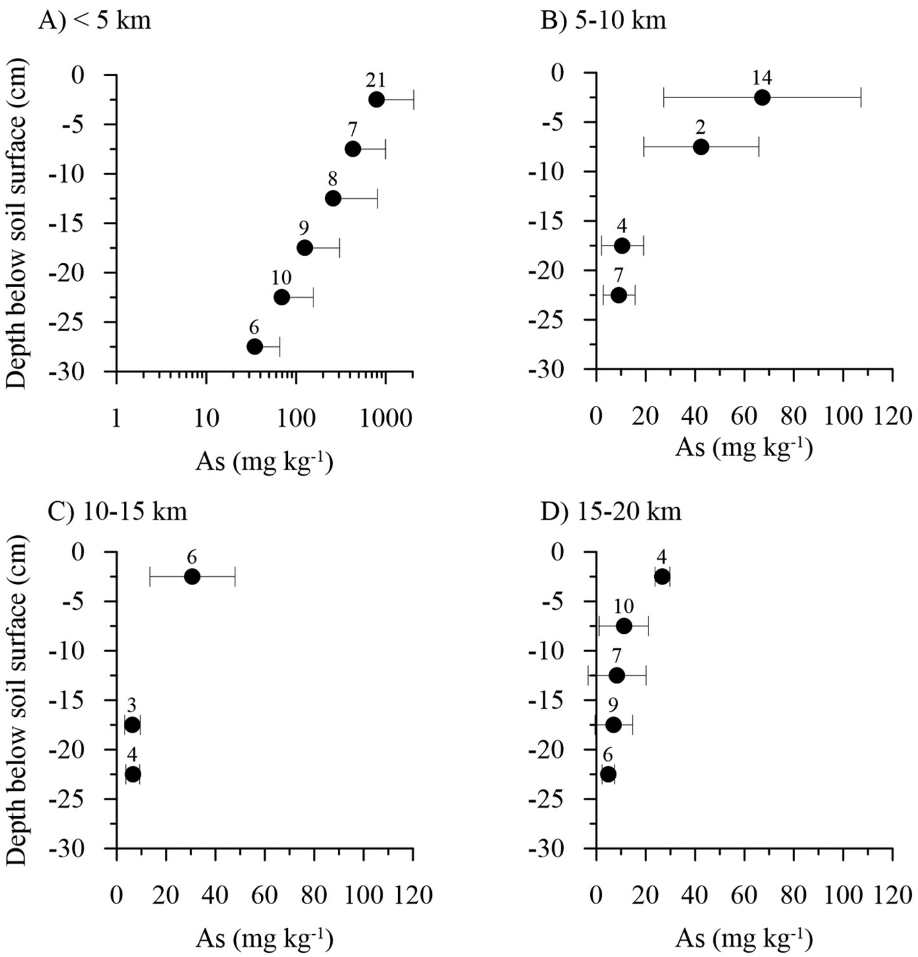

Fig. 3. Soil core As profiles from sites along a distance gradient from Giant Mine in 5 km intervals: A) <5 km; B) 5–10 km; C) 10–15 km; and D) 15–20 km. The black circles represent the mean concentration of As at each sampling interval. The horizontal lines represent the standard deviation of As measurements, and the numbers above the lines indicate the number of measurements included in the calculation of the summary statistics for each depth interval. Note, horizontal axis in panel A) is logarithmic scale and the standard deviation is only noted in the positive direction for clarity.

enrichments of As in the region, as these are the dominant As minerals in bedrock and mineralization. Arsenopyrite was observed in 24% of samples, but typically accounted for <5% of As where it was detected (Supporting information Table S2). Where arsenopyrite measured >10% of total As, total soil concentrations of As were less than the YK specific guideline of 160 mg kg^{-1} (Supporting information, Table S2). Pyrite was observed more frequently than arsenopyrite (75% of samples), but the proportion of As in samples as pyrite was typically low and had a framboidal texture suggesting secondary precipitation.

4.4. Geochemical background in the Slave Geological Province

We used data from a geochemical survey that spans much of the Slave Geological Province, including relatively pristine areas beyond municipal and mining impacts, to better understand natural variability of As in surficial materials in the region and to provide context for soil As concentrations close to point sources of legacy mining emissions. The compilation presented in Fig. 6A demonstrates substantial variation in the concentration of As in tills and soils across the Slave Geological

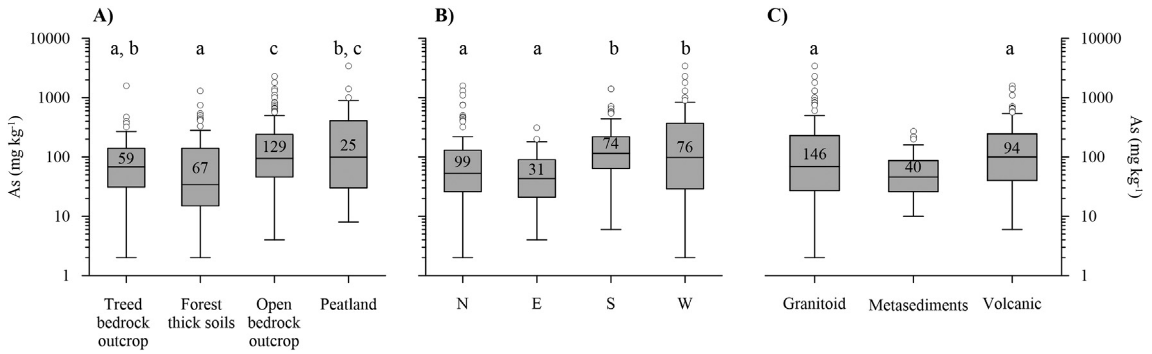

Fig. 4. Arsenic concentrations in Public Health layer samples by terrain unit, wind direction, and bedrock lithology. Numbers within boxes represent the number of samples in each group. Letters above groups indicate between group comparisons with no significant difference using pairwise Wilcoxon rank sum test at $p < 0.05$.

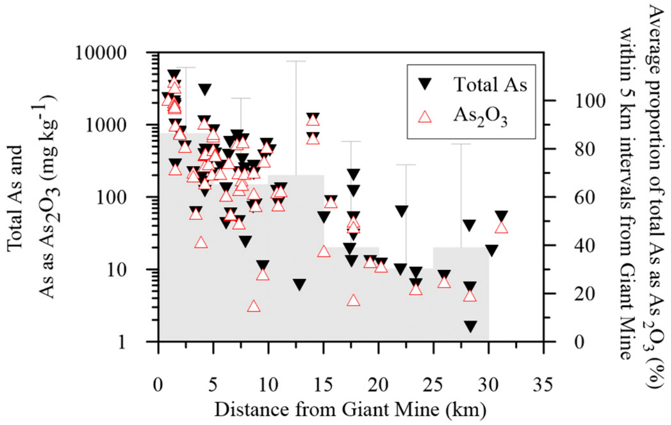

Fig. 5. Total As and As_2O_3 (mg kg^{-1}) in Public Health layer samples (0–5 cm) with distance from the historic Giant Mine roaster. Total As (mg kg^{-1}) was measured by ICP-OES following an *aqua regia* digestion of the soils. The concentration of As_2O_3 (mg kg^{-1}) was determined by multiplying total As by the proportion of As hosted as As_2O_3 in each sample as determined by the SEM-automated mineralogy technique. The shaded bars represent the mean proportion of total As as As_2O_3 in samples from 5 km intervals with increasing distance from Giant Mine.

Province (range: 0.25–1050 mg kg^{-1}). Arsenic concentrations measured <22 mg kg^{-1} in 95% of samples, yet there were distinct areas with clustering of outliers. The most obvious area dominated by outliers was observed near Yellowknife (Fig. 6A & B), but smaller clusters were also observed in the Beaulieu River Belt and along the Northwest Territories – Nunavut border in the Courageous Lake and Indin Lake belts (Fig. 6A) associated with known gold deposits in the region (GNWT, 2016).

Several statistical methods were applied to the till data presented in Kerr and Knight (2005) to estimate the range and upper threshold of geochemical background in the region. The data were screened to exclude samples collected within a 20 km radius of Yellowknife, since these data were expected to have been impacted by atmospheric emissions from legacy roasters in the region based on results from the concentration-distance plots (Fig. 2) and mineralogical evidence (Fig. 5) presented in Sections 4.1 and 4.3. The distribution of the original and ln-transformed data differed significantly from an ideal Gaussian (normal) curve following results from the Shapiro-Wilk test for normality (Original data: $W = 0.08$, $p < 0.001$; ln-transformed data: $W = 0.95$, $p < 0.001$) (Supporting information Fig. S2). Multiple inflection points in the cumulative frequency diagram for the original data indicated the presence of several subpopulations in the data and suggest the influence of multiple processes on the data distribution (Supporting information Fig. S2). The data were not screened further as we were interested in exploring subpopulations driven by differences in bedrock lithology and areas of mineralization. Since neither the original or ln-transformed data followed a normal distribution we excluded the use of parametric tools for the estimation of the range of geochemical background and focused on non-parametric methods, including the metrics provided by the Tukey boxplot. The lower and upper fences of the screened Kerr and Knight (2005) data suggest a geochemical background range in the Slave Geological Province between 0.25 and 15 mg kg^{-1} As (Fig. 6, Table 1). Several other statistical approaches were applied to the data to estimate the upper threshold of background As in tills in the region, since the definition of upper threshold is often the focus of efforts in environmental remediation work and the selection of which metric to use is often a point for discussion by decision-makers (Table 1). The Md ± 2MAD approach was the most conservative technique resulting in an upper threshold of 11 mg kg^{-1}. The use of the upper fence and the 90th percentile yielded slightly higher results of 15 and 14 mg kg^{-1}, respectively. The use of the 95th and 99th percentiles of the data distribution resulted in much higher estimates for the upper threshold of background and were within the portion of the data distribution identified as data outliers by the boxplot method ($>Q3 + 1.5 \times IQR$) (Fig. 6, Table 1).

The large number of samples across bedrock lithologies in the Slave Province ($N = 1490$) allowed for the estimation of background As by bedrock unit and comparisons between units. Significant differences in the distribution of As in tills were noted between underlying bedrock types (Kruskal-Wallis test of differences: chi-squared = 58.66, df = 3, $p < 0.001$). The upper threshold of geochemical background As was highest in tills overlying volcanic bedrock units, but varied substantially depending on the metric used to define the upper threshold (Fig. 7; Table 1). In tills overlying volcanic bedrock, upper thresholds of geochemical background ranged between 15 and 282 mg kg^{-1} for the Md ± 2MAD and 99th percentile approaches, respectively (Table 1). Upper thresholds for background As concentrations varied less between techniques in tills overlying lithologies other than volcanic bedrock (Table 1). Significant differences in the distribution of As in tills were noted between all bedrock lithology units except the volcanic and metasedimentary units (Fig. 7).

5. Discussion

5.1. Impacts from legacy mining emissions persist in soils near Yellowknife

Impacts from mining emissions have been documented in Yellowknife area soils since Hocking et al. (1978). The data presented in this study demonstrate that soil As remains elevated in the Yellowknife region more than 60 years since the bulk of As_2O_3 was released from mining operations and more than 20 years since mining emissions ceased in the region. Strong relationships between the distance from the main emission point source (Giant Mine) and the concentration of As in Public Health layer soils and soils at depth persist in the region (Fig. 2A & B). A comparison of the best fit lines for contemporary and historical relationships between soil As and distance from Giant Mine suggests that concentrations of soil As have decreased in the region since reported by Hocking et al. (1978) (Fig. 2A). The comparison between the two datasets should be interpreted with caution, as the Hocking et al. (1978) data represent far fewer samples ($N = 17$) than reported in this study, were concentrated within 10 km of the historical roasters at Giant and Con mines, and employed different field and analytical methods. However, the distinct difference between the best fit lines, even within 10 km of Giant Mine, suggests the gradual recovery of soils in the region over the last 40 years.

The combination of statistical, geochemical and mineralogical methods applied in this study represents a novel approach to distinguishing between natural and anthropogenic enrichment of As in soils for areas impacted by legacy mining emissions. Multiple lines of evidence support the supposition that concentrations of As in Yellowknife area soils are elevated relative to other areas in Canada and the world because of the atmospheric deposition of As from legacy mining activities and not associated with natural enrichment from sulfide mineralization. First, the clear concentration-distance relationship between soil As and distance from contaminant point sources (Fig. 2) are consistent with other regions that have been impacted by point sources of pollution (e.g. McMartin et al., 1999; Reimann et al., 2000) and suggest widespread As contamination of soils in the region, irrespective of proximity to sulfide mineralization. Second, sampling through the soil profile shows that As concentrations decrease substantially with sampling depth (Fig. 3), consistent with an atmospheric source of As (Ukonmaanaho et al., 2004; Yang et al., 2014). The dampening of the As gradient in the soil profile with increasing distance from the contaminant point sources shows the far greater magnitude of impact in soils close to the legacy mine roasters. As such, As concentrations at depth, which are often used to represent atmospherically unimpacted conditions, should be interpreted with caution, as the continued dissolution and downward migration of As may result in reprecipitation of As minerals at depth that are ultimately derived from mining sources. Finally,

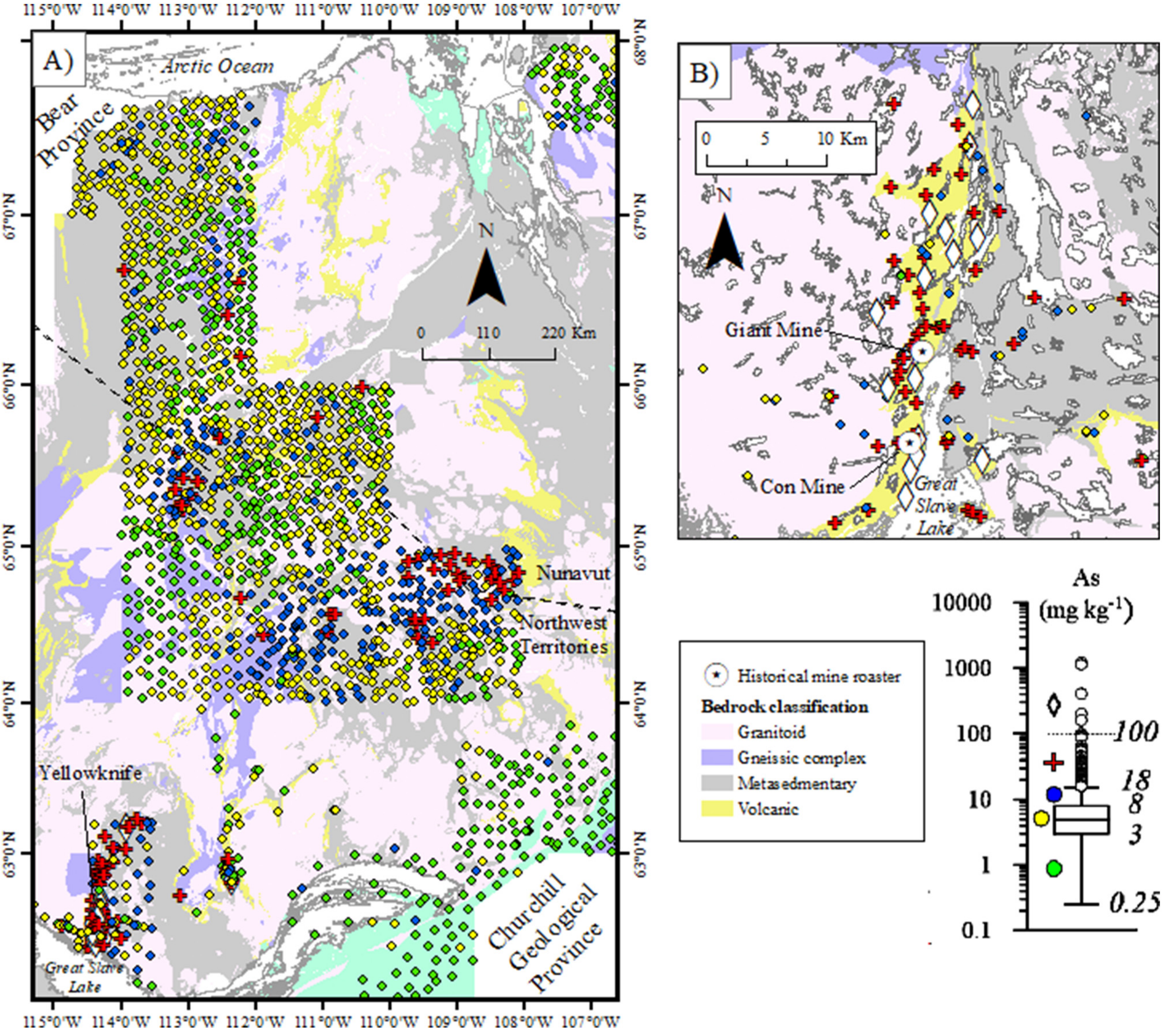

Fig. 6. Distribution of As in soils and till in: A) the Slave Geological Province; and B) the Yellowknife area. All samples collected between 10 and 70 cm below the soil surface. Data presented in these maps represent a compilation of 4 geochemical soil surveys conducted between 1999 and 2016. See Methods for field and analytical methods for each of the studies in the compilation. Data are symbolized following the Tukey boxplot method, where data are presented as: less than 1st quartile (green circles), between 1st and 3rd quartile (yellow circles), between 3rd quartile and upper fence (3rd quartile + 1.5*IQR) (blue circles), and beyond the upper fence are considered outliers (red crosses) and far outliers (open diamonds).

mineralogical assessment of soil samples from the region provides unambiguous information on whether As found in soils is derived from anthropogenic or natural processes. The mineralogical evidence shows that As in Public Health layer soils is overwhelming associated with As_2O_3 in the region, as As_2O_3 accounts for more than 80% of total As for samples collected within 5 km of Giant Mine and more than 50% of total As at sites up to 20 km (Fig. 5). Further, it should be acknowledged that while the remaining As identified in samples is not associated with

Table 1
Summary statistics for till As concentrations (mg kg^{-1}) from Kerr and Knight (2005) excluding samples within 20 km of Yellowknife, representing natural background in the region. Upper fence is calculated as the 3rd quartile + 1.5 × IQR (interquartile range).

	N	Max	Min[a]	Median	MAD	Upper threshold estimates				
						Median + 2MAD	Upper fence	Percentile		
								90th	95th	99th
All samples	1490	1190	0.25	4.8	3.1	11	15	14	22	46
Volcanic	161	1190	0.25	5.6	4.7	15	30	39	65	282
Granitoid	570	36	0.25	4.5	3.1	11	15	12	14	27
Metasedimentary	613	1150	0.25	5.2	3.0	11	15	16	21	44
Gneissic complexes	146	26	0.25	3.4	3.1	9.6	13	9.8	11	19

[a] Note, minimum detection limit for As in Kerr and Knight (2005) data was 0.25 mg kg^{-1}, therefore data reported at this level may represent values below the minimum detection limit of the instrument.

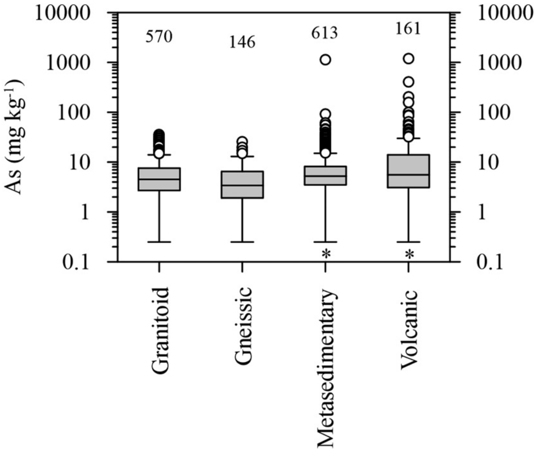

Fig. 7. Tukey boxplots for As in silt and clay fraction of till (data >20 km from YK) from the Kerr and Knight (2005) dataset. The horizontal line represents the median, the box limits represent the 1st and 3rd quartiles. Whisker limits indicate the upper (Q3 + 1.5*IQR) and lower (Q1 − 1.5*IQR) fences of the data distribution. Outliers represent values beyond the upper fences and are indicated by open circles. Numbers above the plots represent the number of samples for each bedrock type. Kruskal-Wallis test for differences between groups indicates that there are significant differences in the distributions between groups (chi-squared = 58.658, df = 3, $p < 0.001$). Letters below groups indicate As distributions that are not significantly different ($p > 0.05$) (Pairwise comparison between groups using Wilcoxon rank sum test). Note, the two highest As values in the volcanic group are associated with gossans near Discovery Mine (Kerr and Knight, 2005).

As_2O_3, in many cases it may ultimately be derived from it, as secondary As-bearing minerals forming in-situ following the dissolution of As_2O_3.

The abundance of As_2O_3 identified in Public Health layer soils was a surprising observation, since As_2O_3 is expected to be highly soluble under field conditions (Riveros et al., 2000). Typically, studies on the environmental fate of As_2O_3 have stressed the importance of understanding environmental conditions controlling the formation and stability of secondary As minerals, rather than assessing the factors that control As_2O_3 dissolution (Qi and Donahoe, 2008; Yang and Donahoe, 2007). Previous work in the Yellowknife region highlighted the persistence of As_2O_3 in soils on the mine property near the roaster at Giant Mine (Bromstad et al., 2017). Several reasons for the limited mobility of As_2O_3 in surface soils on site have been proposed, including the cold and dry climate of the Yellowknife area, slow dissolution kinetics, and the incorporation of Sb in the As_2O_3 structure, which may limit solubility (Bromstad et al., 2017; Dutrizac et al., 2000). This study builds on this previous work and shows that As_2O_3 is persisting in weathering environments throughout the region. Table S2 in the Supporting information highlights that mineral phases that are likely geogenic in origin (arsenopyrite, pyrite, some of the Fe-oxides that formed as weathering products of those sulfide minerals) account for a small proportion of As-hosting minerals in the majority of samples in this study indicating that most of the As measured in surface soils in the region is attributable to legacy mining sources rather than natural enrichment associated with gold-bearing mineralization.

The extent of environmental impact from point sources of pollution is often sought for environmental management and remediation purposes. In this study, As concentration-distance relationships for Public Health layer soils (Fig. 2A) and soils at depth (Fig. 2B) suggest that impacts were relatively minor beyond 20 km from Giant Mine compared to areas close to Giant Mine. Surface enrichments of As (Fig. 3) and the identification of As_2O_3 (Fig. 5) beyond 20 km indicates that while impacts are substantially less than in areas close to Yellowknife, soils beyond 20 km can be impacted by legacy mining emissions. This shows the important contribution of mineralogical analysis in regional background assessments for areas with legacy anthropogenic impacts. In general, the concentration-distance relationships, soil profile sampling and mineralogical assessment of samples indicated that sampling Public Health layer soils within a 30-km range was not far enough from Yellowknife to confidently determine a robust zone of influence from past mining emissions in soils in the region. Evidence from recent studies in lake sediments also suggests a wider impact from legacy pollution sources than previously reported and likely extend beyond 40 km from emission point sources (Cheney et al., 2020). Studies from Flin Flon, MB and Sudbury, ON estimate maximum impacts of As pollution up to 104 km from pollution sources (McMartin et al., 1999). We would expect the zone of influence to be smaller in the Yellowknife region, since the stacks for the roasters at Giant Mine were substantially shorter (max height approx. 70 m) (Silke, 2013) than at smelting facilities in Flin Flon and Sudbury (max height approx. 380 m) (Hutchinson and Whitby, 1977), which would reduce the atmospheric dispersion of pollutants. While we show that sampling of Public Health layer soils in this study did not extend to adequate distance from legacy mining emission sources, it is clear that soil As declines steeply with increasing distance from historical As emission sources so that As concentrations in most soils beyond 20 km are below Canadian guidelines for agricultural and residential soils (12 mg kg^{-1}) (Fig. 2A & B).

5.2. Variability in Yellowknife area soil As driven by regional and local factors

The substantial variation in Public Health layer soil As in the Yellowknife area (Fig. 1) highlights the importance of several regional and local factors beyond proximity to point sources of As emissions in controlling the distribution of As in soils in the region. The influence of dispersal of atmospheric pollutants along predominant wind axes is well established (Fritsch et al., 2010; McMartin et al., 1999; Reimann et al., 2009) and the data presented in this study show that soil As was significantly elevated at sites downwind to the west of Giant Mine irrespective of distance from the roaster (Fig. 1; Table 1). Soil As was also elevated to the south of the Giant Mine roaster, that corresponds with the secondary wind axis in the region, but may be confounded by high As concentrations derived from emissions at Con Mine, that is located south of Giant Mine. The lowest concentrations of soil As were measured at sites east of Giant Mine and correspond with relatively rare westerly winds in the region (Fig. 1). The distribution of soil As to the east of Giant Mine and Con Mine is also influenced by the lack of sampling within 2.5 km of the former roaster stacks because of the presence of Yellowknife Bay (Fig. 1).

In smelter affected soils from temperate regions, soils from forested areas typically have higher metal(loid) burdens than in open areas, such as grasslands and crop fields, due to greater canopy interception and retention of atmospheric particles (Douay et al., 2009; Ettler et al., 2005). In this study we observe the inverse, where soil As was highest in open areas of bedrock outcrops. Much of the shield landscape is dominated by expansive bedrock outcrops with pockets of thin soils. Bromstad et al. (2017) highlight that these soil pockets act as sinks on the landscape, as atmospheric pollutants deposited on exposed bedrock areas are washed downslope and accumulate. In the relatively cold and dry climate there is little opportunity for these metal(loid)s in soils to be remobilized except during snowmelt or periods of high rainfall. At the local scale, the distribution of As_2O_3 particles in individual samples may be an important factor driving As variability within localized areas, since As_2O_3 is extremely As-rich (76 wt% As). Consequently, bulk As concentration is highly dependant on the number of As_2O_3 particles found in a sample.

5.3. Estimation of geochemical background for the Slave Geological Province

The estimation of geochemical background in this study draws on a large number of till samples ($N = 1490$) collected over a wide area with consistent parent material that includes much of the Slave Geological

Province. Our estimates for the upper threshold of geochemical background in the region were well below previous estimates for the area, including the estimate from ESG (2001) that was used to derive current residential (160 mg kg^{-1}) and industrial (340 mg kg^{-1}) environmental remediation guidelines in the region (GNWT, 2003) and were comparable to the Canadian Soil Quality Guideline for the Protection of Environmental and Human Health (12 mg kg^{-1}, CCME (2007)). The upper threshold limits estimated in this study (Table 1) were also in line with geochemical background estimates from other locations around the world. Reimann and Garrett (2005) summarized median As concentrations in soils from 14 studies across the world and highlighted As concentrations in undisturbed soils were typically <30 mg kg^{-1} As. The exception was soils in the Saualpe region in Austria where geochemical background As in soils was 101–115 mg kg^{-1} and was attributed to natural As enrichment in parent material from the region.

We acknowledge that tills do not solely represent material weathered in situ, and may be derived from the erosion and entrainment of material from substantial distances up-ice. However, soil development in the Slave craton is limited, due to the cold dry climate, prevalence of exposed bedrock, and relatively recent deglaciation and recession of Glacial Lake McConnell and ancestral Great Slave Lake. Consequently, tills represent the most common terrestrial unconsolidated material in the region and an appropriate medium to represent geochemical background in soils.

The estimation of upper thresholds of till As by underlying bedrock lithology suggests that underlying geology did have an effect on till As across the Slave Geological Province. The distribution of As was highest in tills overlying volcanic bedrock units (Fig. 7). These are the units that typically host gold-bearing mineralization in greenstone belts throughout the region (Boyle, 1979; GNWT, 2016) and the world (Smedley and Kinniburgh, 2002; Tanaka, 1988). Boyle and Jonasson (1973), Tanaka (1988) and Smedley and Kinniburgh (2002) provide detailed summaries of As concentrations in various bedrock lithologies and soils from previous studies, including from the Yellowknife area. In general, concentrations of As in igneous source rocks are low (0.1–12 mg kg^{-1} As, $N = 411$) and less than in sedimentary units (0.1–188 mg kg^{-1} As, $N = 674$) because the adsorption and/or co-precipitation of As with Fe minerals during sedimentation processes can enrich As in sedimentary units. That being said, Boyle and Jonasson (1973) and Tanaka (1988) present a clear picture of substantial As enrichment in bedrock and soils near mineralized shear zones, which can host high concentrations of As associated with sulfide deposits. These As enrichments are typically localized and may only extend a few meters to a few hundred meters (Boyle and Jonasson, 1973; Smedley and Kinniburgh, 2002; Tanaka, 1988). For example, in a mineralized shear zone in a greenstone belt near Motapa Mine, Rhodesia (now Zimbabwe) very high concentrations (>1000 mg kg^{-1} As) of As were measured in host rock and subsequently decreased to ~1 mg kg^{-1} As within 100 m of the shear zone (Tanaka, 1988). In this study, clear As anomalies are noted in several areas across the Slave Province beyond Yellowknife, and these enrichments are highly localized and correspond with areas of known mineralization. We note that the highest concentrations of till As were measured overlying volcanics near the Discovery gold deposit (Fig. 6A) and were associated with sites where gossans, typical of weathered sulfide deposits, were identified by Kerr and Knight (2005). Regardless of high till As measured in some localized areas (As >100 mg kg^{-1}), the bulk of till data, as defined by the 95th percentile, was below 22 mg kg^{-1} As (Table 1).

6. Concluding remarks

Continued investigation and monitoring of soils are essential to the understanding of ecosystem recovery in areas that have been impacted by mining emissions. This study provides new information on the concentration and solid-phase speciation of As in soils in the Yellowknife region and presents a novel strategy for identifying and delineating anthropogenic impacts in soils. Mineralogical tools were critical in identifying the main mineral hosts of As in soils and allowed for the unambiguous attribution of most of the As in soils close to point sources of mining emissions to anthropogenic sources rather than natural As enrichment. The coupling of mineralogical results with broad geochemical surveys facilitated the delineation of impacted areas and estimation of the range of geochemical background. The large number of till samples collected across much of the Slave Geological Province as part of Geological Survey of Canada efforts (Kerr and Knight, 2005) was an immense resource and permitted the estimation of geochemical background conditions by underlying bedrock lithology, which showed that the upper threshold of geochemical background is likely slightly elevated in soils overlying volcanic bedrock units compared with other lithology units. Using more than a thousand soil measurements it can be concluded that natural arsenic enrichment may occur in areas of sulfide mineralization, but the influence is highly localized and cannot account for the broad enrichment of arsenic in soils by mining emissions in the Yellowknife area, which are substantially elevated compared to geochemical background in the Slave Geological Province.

The fact that As was overwhelmingly associated with legacy mining emissions close to Yellowknife does not necessarily imply a risk to human or ecological health in interacting with these soils. Human health and ecological risk assessments have been conducted in the region (e.g. Canada North Environmental Services, 2018; Cheung et al., 2020) and as new information is released these assessments should be revisited to ensure findings are up to date. The information from this study should be used to acknowledge that widespread As contamination persists in the region and will need to be considered in future land use management decisions. Ultimately, this study demonstrates the strength of using multiple methods in the estimation of geochemical background and will be useful for resource managers required to untangle anthropogenically impacted soils from those that may be naturally enriched in metal(loid)s.

CRediT authorship contribution statement

MJP: Study design, methodology, data analysis and interpretation, manuscript preparation; **HEJ:** Study design, methodology, data analysis and interpretation, manuscript review and preparation; **ABR:** Data analysis, manuscript review; **KM:** Methodology, data collection, data analysis, manuscript review; **JO:** Methodology, data collection, data analysis, manuscript review; **HF:** Data interpretation, manuscript review; **MR:** Statistical analyses, data interpretation, manuscript review.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.145926.

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