Suitability of surficial media for Ni–Cu–PGE exploration in an established mining camp: a case study from the South Range of the Sudbury Igneous Complex, Canada

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Abstract: A geochemical study over the southwestern part of the South Range of the Sudbury Igneous Complex was completed to assess the suitability of surficial media (humus, B-horizon soil and C-horizon soil) for delineating geochemical anomalies associated with Ni–Cu–PGE (platinum group element) mineralization. Another objective was to test whether Na pyrophosphate can eliminate the effects of anthropogenic contamination in humus. Results of this study suggest that the natural geochemical signature of humus is strongly overprinted by anthropogenic contamination. Despite no indication of underlying or nearby mineralization, metal concentrations in humus samples by aqua regia collected downwind from smelting operations are higher compared to background, including up to 13 times higher for Pt, 12 times higher for Cu and nine times higher for Ni. The high anthropogenic background masks the geogenic signal such that it is only apparent in humus samples collected in the vicinity of known Ni–Cu–PGE deposits. Results of this study also demonstrate that anthropogenically derived atmospheric fallout also influences the upper B-horizon soil; however, lower B-horizon soil (at >20 cm depth) and C-horizon soil (both developed in till) are not affected. Glacial dispersal from Ni–Cu–PGE mineralization is apparent in C-horizon till samples analysed in this study. Compared to the background concentrations, the unaffected C-horizon till samples collected immediately down-ice of the low-sulfide, high precious metal Vermilion Cu–Ni–PGE deposit are enriched over 20 times in Pt (203 ppb), Au (81 ppm) and Cu (963 ppm), and over 30 times in Ni (1283 ppm).

Keywords: surficial geochemistry; humus sampling; surficial contamination; till sampling

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 Soil is the chemically differentiated upper layer of overburden (also known as regolith); the most common soil type in glaciated terrain is podzol (Kauranne 1992). Podzolic soils make up 14.3% of the surface of glacial sediments, and over time, the oxidation, disintegration, and decay of these organic compounds form humus (i.e. humification) (Kauranne 1992). Humus has been known to reflect the presence of heavy metal anomalies associated with mineralization in the surrounding bedrock as well as in the overburden (Dunn et al. 1989; Hoffman and Woods 1991; Rogers and Dunn 1993; Hattori et al. 2009; van Geffen et al. 2012; Schmidt et al. 2017). Trees and plants can take up and translocate trace elements from deeper soil or underlying bedrock via roots (Rogers and Dunn 1993). Metals taken up by the tree roots, therefore, may be present in the overlying humus and can provide an indication of the geochemical signature of the underlying soil and bedrock. Humus has been used successfully in delineating dispersion from occurrences of commodities including Au, Pb–Zn, Ni–Cu–PGE (platinum group element), W and U (Table 1). Humus has also been successfully used to locate deeply buried mineralization (>100 m) as in the case of the Restigouche volcanogenic massive sulfide (VMS) Zn–Pb–Cu deposit in north-central New Brunswick (Hall et al. 2003).

Huminus is underlain by an Ae-horizon that consists of weathered minerals that are leached of elements (e.g. Al, Fe and Mn), followed by a B-horizon that is enriched in precipitated Fe, and Al- and Mn-oxides (Kauranne 1992). The B-horizon can be divided into an uppermost Bt-horizon that consists of clay minerals such as kaolinite that bind the downward transported and leached Fe from the Ae-horizon, a middle Bt-horizon and the lowermost Bt-horizon (Kauranne 1992). Conventionally, B-horizon soil (developed on till and from here referred to as B-horizon till) sampling has been used in mineral exploration surveys (Fuchs and Rose 1974; Rose et al. 1979) and has been successful in delineating dispersion from commodities such as Au, Ni–Cu, and PGEs (Coker et al. 1991; Hall et al. 2003). Results of this study suggest that the humus has been strongly influenced by anthropogenic contamination. Despite no indication of underlying or nearby mineralization, metal concentrations in humus samples by aqua regia collected downwind from smelting operations are higher compared to background, including up to 13 times higher for Pt, 12 times higher for Cu and nine times higher for Ni. The high anthropogenic background masks the geogenic signal such that it is only apparent in humus samples collected in the vicinity of known Ni–Cu–PGE deposits. Results of this study also demonstrate that anthropogenically derived atmospheric fallout also influences the upper B-horizon soil; however, lower B-horizon soil (at >20 cm depth) and C-horizon soil (both developed in till) are not affected. Glacial dispersal from Ni–Cu–PGE mineralization is apparent in C-horizon till samples analysed in this study. Compared to the background concentrations, the unaffected C-horizon till samples collected immediately down-ice of the low-sulfide, high precious metal Vermilion Cu–Ni–PGE deposit are enriched over 20 times in Pt (203 ppb), Au (81 ppm) and Cu (963 ppm), and over 30 times in Ni (1283 ppm).

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Table 1 Summary table of regional geochemical sampling programs that have tested the suitability of humus as a viable sampling medium for mineral exploration targeting Au, PGEs and base metals

| Commodity | Sample medium | Region | Location | Minerals/Mineralization | Element content in humus | Reference |
|-----------|---------------|--------|----------|-------------------------|-------------------------|-----------|
| Au        | Humus         | Thunder Bay district, northern Ontario | Williams property, Hemlo area | Au-bearing pyrite | Elevated As (up to 89 ppm), Au (up to 75 ppb), Br (20 ppm), Hg (up to 230 ppb), Mo (26 ppm), Pb (210 ppm), Sb (53 ppm) in humus samples collected in the vicinity of mineralization | Fortescue (1985) |
| Au        | Humus         | Northeastern Ontario | Timmins-Kaminiskota area | Sulfide minerals associated with Cu–Zn–Au–Ag deposits in the area | Elevated Cu, As, Sb, Au, Pb, Zn, Ag, Cd, Bi and Se associated with Au mineralization; Samples around Kidd Creek metallurgical site and at least 22 km downwind are contaminated with smelter-related metals such as Cu, Zn, Pb, Cd, Ag, Bi, Mo and Se. This contamination does not affect the C-horizon till samples | McClenaghan et al. (1998) |
| Au        | Humus         | Colorado, USA | Front Range mineral belt, Empire District of Colorado | Au in pyrite, chalcopyrite | Greater than 0.6 ppm Au in humus samples collected in the vicinity of Au mineralization | Curtin et al. (1968) |
| Cu–Co–Au | Humus         | Finland | Southern Finland | Chalcopyrite, arsenopyrite, bornite, malachite | Cu (up to 429 ppm), Co (up to 70 ppm), As (up to 758 ppm), Mo (up to 356 ppm) and Zn (up to 396 ppm) | Peuranieni (1991) |
| Mo        | Humus         | Finland | Aittojarvi (northwestern Finland) | Molybdenite with some chalcopyrite and pyrite | Mo (up to 1732 ppm), Cu (up to 347 ppm), Zn (up to 1520 ppm) and Co (up to 579 ppm) | Kauranne (1976) |
| Ni–Cu–Pb–Zn | Humus | Finland | Petolahti, Taluspera (western Finland), Kolima, Kotanen (central Finland), Ritomaki (northern Finland) | Petolahti (Ni–Cu ore in pentlandite and chalcopyrite, 0.7% Cu and 0.65% Ni); Kotanen (arsenopyrite with low Cu; Ritomaki (sphalerite bearing boulders, Zn ore); Taluspera (gabbros with high Cu content) | Pb, Zn, Cu anomalies in humus accompanied by metal anomalies in the surrounding till | Kauranne (1967), Kauranne (1976) |
| Ni–Cu–PGE | Humus         | Northern Ontario | Lac des Iles PGE deposit (Roby Zone) | PGM, chalcopyrite, pentlandite | Elevated Cu (up to 88 ppm), Au (up to 31 ppb), Ni (up to 121 ppm), Pd (up to 340 ppb) and to a lesser extent W (up to 5 ppm) | Fortescue et al. (1988) |
| Ni–Cu–PGE | Humus         | Northeastern Ontario | Sudbury Igneous Complex | Nipissing gabbro (local averages: 0.50% Ni, 1.10% Cu, 700 ppb Pt, 4.5 ppm Pd and 500 ppb Au) | Humus (ashed) samples overlying mineralization contain up to 79 ppb Au, 114 ppb Pt, 1410 ppb Pd, 1855 ppb Ni, 4470 ppm Cu and 36 ppm As | Coker et al. (1991) |
| Ni–Cu–PGE | Humus         | Southeastern Manitoba | Mayville Igneous Complex | Pyrrhotite, chalcopyrite, pyrite (Grab samples returned a maximum concentration of 520 ppb Pt and 400 ppb Pd) | Pd (up to 1.8 ppb), Au (up to 5 ppb) | Teyer (2006) |
| W         | Humus         | Central and northern Sweden | Allebouda Mountain, northern Sweden | Molybdenite, scheelite, wolframite, casseriterite | Elevated W (up to 128 ppm), Sn (up to 73 ppm), Mo (up to 349 ppm); anomalies in humus coincide with anomalies in till geochemistry | Toverud (1979) |
| W         | Humus         | Central and northern Sweden | Hogsfors, central Sweden | Scheelite, fluorite | Elevated W (up to 108 ppm); anomalies in humus coincide with anomalies in till geochemistry | Toverud (1979) |
| W         | Humus         | Central and northern Sweden | Yxsjon, central Sweden | Scheelite | Elevated W (up to 993 ppm); wind blown dust from the Yxsjoberg W Mine may have contaminated the humus in the area | Toverud (1979) |
| U         | Humus         | Labrador, Canada | Jacque’s Lake, Central Mineral Belt | U and Th mineralization | 0.05–885 ppm U in samples collected across significant radiometric anomalies. Humus is also enriched in Ba, Cr, Fe, Mo, Pb, Cs, and Sc. | Nyade et al. (2013) |
Surficial exploration in the SIC

et al. 2003; Cameron and Hattori 2005). The B-horizon is underlain by the C-horizon, which is the parent material (Kauranne 1992). Sampling of C-horizon soil (developed on till and from here referred to as C-horizon till) is the recommended practice for soil sampling geared towards heavy mineral collection and drift prospecting in glaciated terrain (Spirito et al. 2011; McClenaghan et al. 2020). Till is the first derivative of bedrock and reflects the geochemical, mineralogical, and lithological signature of bedrock up-ice from deposition. Commodities of which C-horizon till sampling has delineated dispersion from mineralization include Au, Pb–Zn, Cu, diamonds, and U (McClannagh and Kjarsgaard 2001; McMartin and McClannagh 2001; Hashmi et al. 2015; McClannagh and Peter 2016; Plouffe et al. 2016; McClannagh et al. 2018, 2019).

The efficacy of humus for geochemical sampling has also been tested near past and/or active mining operations; however, most attempts have been unsuccessful in distinguishing the geogenic geochemical signature from anthropogenic overprints (Henderson et al. 1995; Henderson and McMartin 1998; Schmidt et al. 2017). Assessment of the effects of smelting in the Flin Flon–Snow Lake area by Henderson and McMartin (1995); Henderson et al. (1998), and McMartin et al. (1999) demonstrated that humus geochemistry is influenced by both natural and anthropogenic processes. Similarly, van Geffen et al. (2012) concluded that humus was not a suitable sample medium to delineate the natural geochemical signature of the Talbot VMS Cu–Zn prospect due to the atmospheric fallout from the Flin Flon smelter, 160 km to the NW. Furthermore, unlike the study by Fortescue et al. (1988) near the Lac des Iles PGE deposit, where the authors concluded that humus was suitable for sampling (Table 1), a later study by Barnett (2007) concluded that humus was contaminated by anthropogenic (mining) activity and therefore was not suitable for sampling.

For this study, the South Range of the Sudbury Igneous Complex (SIC) was chosen to test the efficacy of humus geochemistry for detecting mineralization in an established mining camp (Fig. 1). Nickel–Cu–PGE mineralization was first discovered in the SIC in the 1880s (Ames and Farrow 2007), and mining and smelting commenced in the region in 1885; initially in open-air roasting pits (1885–1928), and later in smelters (Freedman and Hutchinson 1980). Three smelters (now decommissioned) were active in the region: the Copper Cliff smelter, 5 km SW of Sudbury, the Coniston Smelter c. 15 km east of Sudbury, and the Falconbridge smelter, c. 20 km NE of Sudbury. Nickel and Cu emissions in the 1970s from smelting operations were estimated to have released 1100 tonnes of Ni and Cu particulates into the atmosphere every year (Dudka et al. 1996; Dudka and Adriano 1997). The effects of smelting on vegetation have been studied extensively in the SIC (Supplementary data 1) (Hutchinson and Whitby 1974, 1977; Freedman and Hutchinson 1980; Adamo et al. 1996; Dudka et al. 1996; Dudka and Adriano 1997; Hutchinson and Gunderman 1998; Sucharová and Suchara 2004; Tropea et al. 2010; Babin-Fenske and Anand 2011; Lanteigne et al. 2014; Schmidt et al. 2017). Mining and smelting of Ni–Cu ores in the SIC has resulted in the contamination of local soils with Cd, Co, Cu, Cr, Fe, Mn, Ni, S, Pb and Zn (Hutchinson and Whitby 1977; Dudka et al. 1996). Accumulation of anthropogenic Cu and Ni in peat and water has also been reported, showing that the effects of smelting on vegetation are severe within 2 km of the smelter but minimal (but detectable) at 30 km (Gignac and Beckett 1986). Similarly, Hutchinson and Whitby (1974, 1977) and Freedman and Hutchinson (1980) noted a decrease in the Ag, Cd, Co, Cu, Fe, K, Mn and Ni content in soils (upper 0–10 cm) with increasing distance from the smelters. However, these latter authors also suggested that elevated levels of key elements associated with Ni–Cu–PGE mineralization in the SIC may be due to both the natural geochemical signatures and smelter particulate fallout.

Most of the studies on soil and humus geochemistry in the SIC have been completed with the aim of assessing the impact of anthropogenic contamination on the ecosystem. Only rare studies have assessed the suitability of soil as sample medium for mineral exploration in the SIC (Table 1). However, none of these studies has

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**Fig. 1.** The Denison and Drury townships (`the study area`) are in the SW corner of the Sudbury Igneous Complex, c. 30 km SW of the city of Sudbury. The location of decommissioned smelter operations is also indicated. The closest smelter, Copper Cliff is c. 20 km NE of the study area.
characterized in detail the geochemical profile of the O-, B- and C-horizons derived from barren and mineralization-derived till. One potential way to quantify the anthropogenic overprint on the geochemical signature in vegetation is to use partial extractions (Hall et al. 1996, 2003; Hall and Pelchat 1997; Bajc and Hall 2000a). Partial extractions are based on the premise that elements held in secondary phases such as chelates, and humic and fulvic acids in organic matter (Kauranne 1992), clay minerals and Fe–Mn oxyhydroxide minerals are labile (Hattori et al. 2009). Partial extractions can attack different organic and mineral phases in the humus and this preferential dissolution allows for the release of labile elements that are bound to the phase being targeted by the leach, leaving other phases largely unaffected (Hall et al. 1996, 2003). The efficiency of a Na pyrophosphate solution in extracting metals bound to humic and fulvic complexes in soil has been extensively studied since the late 1940s (Bremner and Lees 1949; Schnitzer and Desjardins 1966; Papp et al. 1991; Michaelson and Ping 1997) and has been shown to effectively extract organic-bound Fe, Al, Zn, Mn and to a lesser extent Cu (Hall and Pelchat 1997).

This study has three objectives: (a) characterize the geochemical signature of surficial media (i.e. the soil horizons: humus, and B-horizon and C-horizon till) in the study area; (b) determine whether the use of Na pyrophosphate can minimize the anthropogenic signal in humus; and (c) compare the geochemical signature of humus, and B-horizon and C-horizon tills to determine whether both can detect and delineate geochemical anomalies associated with mineralization. The findings of this research could then be applied to mineral exploration in other parts of the SIC and in mining-impacted regions in glaciated terrain.

Location and physiography

The study area is c. 30 km SW of the city of Sudbury and comprises Drury and Denison townships (Fig. 1). The area has low relief, and the topography is influenced by the bedrock geology. Generally, highly resistant intrusive rocks of the SIC form steeply sloping uplands in the north, NE and NW and less resistant metasedimentary and metavolcanic rocks of the Huronian Supergroup make up flat to undulating topography in the southeastern, southwestern, and south-central parts of the study area. Vegetation consists of coniferous (white pine and jack pine) and deciduous (red maple and red oak) trees (Hutchinson and Whitby 1977). The prevailing wind direction is to the SW (Environment and Climate Change Canada 2021) and the nearest Ni-Cu smelter is at Copper Cliff (Inco superstack), c. 20 km to the NE; thus, the study area is directly downwind of the Inco superstack.

Geology

Bedrock geology

The bedrock geology and mineralization described here are summarized from the compilation by Ames et al. (2005) and more recent detailed mapping (Fig. 2) (Gordon et al. 2015, 2018a; Bajc et al. 2016; Simard et al. 2016; Généreux et al. 2017; Gordon and Généreux 2017; Gordon 2018). The ENÉ-oriented Sudbury structure (Lightfoot 2016) lies at the boundary between the Archean granitic and gneissic rocks of the Superior Province in the north and pre-SIC Paleoproterozoic metasedimentary and metavolcanic rocks of the Southern Province in the south (Fig. 1). The Sudbury Structure comprises: (1) the main mass consisting of a lower sublayer (norite and gabbro) and an upper granophyre; (2) radial and concentric quartz diorite offset dikes; (3) brecciated and shock-metamorphosed footwall rocks, known as the Sudbury Breccia; (4) crater-fill breccias overlain by sedimentary rocks of the Whitewater Group.

The oldest rocks in the study area are granodiorite and granite in the NW corner of the study area. These Neoarchean granodiorites and granites were intruded by the Paleoproterozoic Matachewan diabase swarm in the NW part of Drury Township. Gabbro, gabbronorite and anorthosite are present in east-central Drury Township and interpreted to belong to the East Bull Lake Intrusive Suite. The southern half of the study area is dominated by metasedimentary rocks of the Hough Lake Group and metasedimentary and metavolcanic rocks of the Elliot Lake Group, all part of the Paleoproterozoic Huronian Supergroup. The metasedimentary and metavolcanic rocks of the Huronian Supergroup were intruded by mafic rocks of the Nipissing Intrusive Suite. Quartz monzonite and granite of the Paleoproterozoic Creighton Pluton are present in the northeastern corner of Denison Township. Granophyre, quartz gabbro, norite, quartz diorite and breccia units of the SIC occur in the north-central and northeastern part of the study area. All rocks in the study area that are older than the SIC also contain variable amounts of Sudbury breccia, which formed during the meteorite impact event that created the SIC (Rousell et al. 2003). East-trending Mesoproterozoic to Paleoproterozoic, quartz diabase ‘trap dykes’ and Mesoproterozoic olivine diabase dykes of the Sudbury Dyke Swarm are the youngest rocks in the study area (Krog et al. 1984; Bleeker et al. 2015).

Mineralization

The three main styles of Ni–Cu–PGE mineralization in the study area associated with the SIC are ‘contact’-, ‘footwall’-, and ‘offset’-style (Ames and Farrow 2007). The Crean Hill deposit in Denison Township contains both footwall- and contact-style mineralization (White 2012). Massive sulfide, footwall- and contact-type mineralization is Ni-rich (pentlandite and Ni-pyrrhotite dominant), whereas low-sulfide high precious metal (LSHPM), footwall-type mineralization is Cu-rich (chalcopyrite dominant) (Ames et al. 2005; Ames and Farrow 2007). At Crean Hill, massive sulfide ore contains c. 5 wt% Ni, 5 wt% Cu and 5–10 g/t Pd + Pt, whereas LSHPM footwall ores average 30 wt% Cu, 5 wt% Ni and 30 g/t Pd + Pt (White 2012).

Offset-style mineralization is present in west-central Denison Township and the southeastern corner of Drury Township. It includes the 8.5 km long, SW-trending Worthington Offset Dyke (Fig. 2) (Farrow and Lightfoot 2002; Ames and Farrow 2007) as well as quartz diorite mapped NE of the Worthington Offset. The Worthington Offset hosts the Totten Mine, where the PGEs occur in metagabbro of the Paleoproterozoic metavolcanic rocks (Lightfoot 2002). In 2002, the Totten Mine had reserves of 8.4 Mt at 1.42% Ni, 1.90% Cu and 4.7 g/t (Pt + Pd + Au) (Farrow and Lightfoot 2002). The Vermilion deposit, which contains LSHPM Cu–Ni–PGE–Au mineralization, is also associated with offset-style mineralization (White 2012). Deformed, granophytic biotite–quartz diorite and foliated Sudbury breccia are the host rocks to mineralization (Szentpeteri et al. 2003). Approximately 4000 tonnes of ore grading 11.2% Cu, 11.6% Ni, 54 g/t Pd, 21 g/t Pt, 5.8 g/t Au and 7.4 g/t Ag were mined from the deposit in 1910 (Farrow and Lightfoot 2002). Nickel–Cu–PGE–Au mineralization is also hosted in metagabbro of the Nipissing Intrusive Suite (Gordon 2018). Mineralization consists of disseminated pyrrhotite and chalcopyrite and up to 940 ppm Cu, 470 ppm Ni, 21 ppb Au, 26 ppb Pd and 22.4 ppb Pt have been reported from rock samples collected in the Drury Township (Gordon et al. 2018a).

Surficial geology

The local surficial geology is summarized from Hashmi (2016). Surficial deposits in the Sudbury region are the product of the advance and retreat of the Laurentide Ice Sheet during the Late
Wisconsinan glaciation (23,000–10,500 years BP) (Barnett 1992). Till is the oldest surficial sediment, deposited either as a thick continuous blanket (>1 m) or as a discontinuous veneer (<1 m) on steeply sloping bedrock. The local basal till is a massive, moderately consolidated, dark grey to brown, grey diamicton, with a silty sand matrix. Basal till has a variable clast content (15 to 45%), and the local bedrock units are the source for a high proportion of the clasts (Hashmi 2018). The till is locally overlain by glaciolacustrine deposits (associated with deglaciation) that consist of massive to laminated, sand, silt and clay ranging from a few centimetres to several metres in thickness. The glaciolacustrine sediments are the most extensive surficial unit that overlies both till and bedrock. Also associated with deglaciation are glaciofluvial sand and gravel deposits in the north-central, northwestern and southwestern parts of the study area. Other minor surficial sediments in the study area include aeolian sand associated with paraglacial activity, fluvial sand and silt along major streams in the southeastern part of the study area, and organic material in low-lying poorly drained areas.

Methods

Field work

During the 2015 and 2016 field seasons, 113 humus, 96 B-horizon and 118 C-horizon till samples were collected for geochemical analyses. Soil samples were collected from a depth ranging from a few centimetres for humus, tens of centimetres for B-horizon till and as deep as possible for relatively unweathered C-horizon till (>50 cm to up to 2 m). At each sampling site, where possible, 500 ml of humus, and 2–3 kg each of B- and C-horizon till were collected. The inability to collect all three soil horizon types at each site was due either to a lack of humus development, or a lack of till at the site. In addition to the regional sample grid of c. 1 sample per 2 km², higher-density soil sampling was completed over and down-ice of known Ni–Cu–PGE mineralization, to characterize potential clastic dispersal as well as geochemical dispersion from it. Humus sample depth was highly dependent on its maturity and thickness.
Humus samples were preferably collected near outcrop to ensure that its geochemistry either reflected the till or bedrock composition but not glaciolacustrine sediments. After collection, each humus sample was sieved onsite through a 5 mm mesh stainless steel sieve to remove coarse roots, wood fragments and mineral matter, and the presence of charcoal within or overlying the humus was noted where present at each site. The B-horizon and C-horizon tills were collected using the sampling procedures outlined by Spirito et al. (2011) and McClennagh et al. (2020). Because glaciolacustrine sediment overlies till locally, care was also taken to ensure that, in the case of B-horizon samples, only B-horizon soil developed on till was collected.

Analyses

The humus samples were dried in a Hotpack® oven at 35°C for 24 hours and subsequently sieved through a 177 μm stainless steel screen using a RO-TAP® sieve shaker for seven minutes. The sieves were cleaned in three stages after every sample. The dust and other particles were brushed out of the inverted sieve, back-flushed with compressed air away from personnel and in the 'blow out' dust hood area to avoid dispersing dust towards personnel or samples, and then wiped out using a methanol swab (J. Pallot, pers. comm., 2021). Chemical analyses of the <177 μm fraction consisted of the following.

1. Loss on ignition (LOI) to estimate the proportion of organic and mineral matter in the sample. A 2 g aliquot was heated progressively to 105, 500 and 1000°C. Heating the sample in N2 to 105°C removes water (Geoscience Laboratories 2020). Subsequent heating in O2 to 500°C removes C from carbonate minerals and organic matter. Lastly, heating the sample to 1000°C in O2 removes all volatiles as well as structural H2O.

2. A modified aqua regia digestion (3:4 nitric acid to hydrochloric acid) on a 2 g aliquot followed by analysis by inductively coupled plasma mass spectrometry (ICP-MS) and inductively couple plasma atomic emission spectrometry (ICP-AES) to determine minor and trace element content. This partial digestion can liberate metals present in organic matter, sulfide minerals, carbonate minerals and oxide minerals; however, it cannot dissolve silicate minerals (Geoscience Laboratories 2020). Following dissolution, metals are loaded onto a C18 SAX cation exchange resin and eluted in 18 ml of 6% HNO3. This dilute solution is then concentrated to 25 ml with 25 ml of Na pyrophosphate and mixed for an hour at room temperature. The solution is subsequently isolated, followed by analysis by ICP-MS.

3. A Na pyrophosphate digestion with ICP-MS analysis to determine minor and trace elements. Here, a 1 g sample is mixed with 25 ml of Na pyrophosphate and mixed for an hour at room temperature. The solution is subsequently isolated, followed by analysis by ICP-MS.

4. Nickel sulfide fire assay (NiS FA) on a 15 g aliquot with ICP-MS analysis was used to determine Au and PGEs (Pt, Pd, Rh, Ru and Ir). This method is the optimal approach for the recovery of low levels of Au and PGEs (Geoscience Laboratories 2020).

5. A modified aqua regia digestion on a 2 g aliquot followed by ICP-MS and ICP-AES analyses to determine minor and trace element content.

The LOI, aqua regia ICP-MS and ICP-AES, PSA, and NiS FA ICP-MS analyses were completed at GeoLabs and Na pyrophosphate ICP-MS was completed at ALS Geochemistry in North Vancouver, British Columbia.

Quality assurance and quality control

Quality assurance procedures for till sampling followed in the field are outlined in Spirito et al. (2011) and McClennagh et al. (2020) and include cleaning of sampling equipment before and after the collection of each sample to minimize cross-contamination and using clearly labelled sample bags to document the sample site. Field duplicates were also collected for each sample medium (six field duplicates for humus and B-horizon till and 10 field duplicates for C-horizon till) to test site variability. Quality control measures consisted of calculation of analytical precision using laboratory duplicates. The accuracy of B- and C-horizon till samples was monitored using certified reference material TILL-1 (CANMET 1995) and in-house standards at the OGS.

Because the number of lab duplicate pairs for humus and till samples was <20, precision was determined as the relative standard deviation calculated at a 95% confidence interval (Piercey 2014). The precision was calculated using nine laboratory duplicate pairs for humus and 10 laboratory duplicate pairs for each of the B- and C-horizon tills (Supplementary data 2). Some elements (Au, Se, Te, Ru) had at least one or both samples of a duplicate pair below detection limit, in which case the duplicate pair was removed from the calculation. The precision for As (except in C-horizon till), Bi (except in C-horizon till), Cd (except in C-horizon till), Co, Cr, Cu, Hg (except in humus by Na pyrophosphate, B- and C-horizon tills), Mo, Ni (except in C-horizon till), Pb, Sb (except in humus by aqua regia and C-horizon till) and Zn is < ± 15%. The precision for Se, Te, Hg and PGEs in B- and C-horizon tills is poor (> ± 20%) because at least one of the duplicate pairs is either below detection limit or both values are below the limit of quantification (three times the limit of detection; Piercey 2014). The precision for Au is poor in all sample media because most Au concentrations are close to the analytical detection limit as well as the nugget effect. We consider these results acceptable for interpretation.

Data treatment and presentation

For plotting purposes, analyses below detection limits were assigned half the lower detection limit value (Clarke 1998). Data above the upper reporting limit were assigned the upper reporting limit plus 0.1. Spatially referenced, coloured and proportional dot plots were created in ArcGIS Pro™. For the proportional dot plots, the geochemical data were split into four categories comprising ‘background’, ‘elevated’, ‘anomalous’ and ‘highly anomalous’ using Jenks’ Optimization or the goodness-of-variance fit (Dent 1999). Statistics including Pearson moment correlation matrix of log-normalized data were generated in LoGASTM.

Results

Soil development

Humus in the study area varies from poorly to moderately to well developed. Poorly developed humus consists of partly decomposed
| Elements | Method          | Min. value | Max. value | Mean  | Standard Deviation | 75th %ile | 90th %ile | 99th %ile |
|----------|----------------|------------|------------|-------|-------------------|-----------|-----------|-----------|
| Ag (ppm) | Na P ICP-MS    | 0.010      | 0.072      | 0.026 | 0.012             | 0.034     | 0.041     | 0.072     |
|          | AR ICP-MS      | 0.09       | 1.38       | 0.039 | 0.021             | 0.051     | 0.070     | 1.32      |
| Al (ppm) | Na P ICP-MS    | 1.53       | 4250       | 1.174 | 0.839             | 1605      | 2239      | 4216      |
|          | AR ICP-AES     | 7.19       | 14750      | 4582  | 3360              | 6308      | 9757      | 14682     |
| As (ppm) | Na P ICP-MS    | 0.18       | 11.05      | 2.68  | 2.26              | 3.50      | 6.73      | 10.91     |
|          | AR ICP-MS      | 1.6        | 28.5       | 8.8   | 5.3               | 11.2      | 17.8      | 27.9      |
| Au (ppb) | Na P ICP-MS    | <1         | 5          | 1     | 1                 | 1         | 2         | 5         |
|          | AR ICP-MS      | <2         | 294        | 10    | 28                | 10        | 15        | 272       |
| Ba (ppm) | Na P ICP-MS    | 10.85      | 150.00     | 50.02 | 29.33             | 68.10     | 95.38     | 147.36    |
|          | AR ICP-MS      | 25.5       | 472.6      | 139.6 | 91.0              | 185.3     | 256.6     | 464.1     |
| Bi (ppm) | Na P ICP-MS    | 0.009      | 1.590      | 0.226 | 0.241             | 0.290     | 0.450     | 1.541     |
|          | AR ICP-MS      | 0.33       | 5.24       | 1.65  | 0.92              | 2.19      | 2.79      | 5.13      |
| Ca (ppm) | Na P ICP-MS    | 290        | 5590       | 2445  | 1605              | 3150      | 3839      | 5581      |
|          | AR ICP-AES     | 833        | 29880      | 5741  | 4275              | 7039      | 11102     | 28699     |
| Co (ppm) | Na P ICP-MS    | 0.353      | 7.550      | 1.517 | 1.168             | 1.766     | 3.090     | 7.259     |
|          | AR ICP-MS      | 2.64       | 25.77      | 8.68  | 4.81              | 9.86      | 14.44     | 26.61     |
| Cr (ppm) | Na P ICP-MS    | 0.21       | 6.16       | 1.76  | 1.29              | 2.44      | 3.52      | 6.14      |
|          | AR ICP-MS      | 3          | 52         | 12    | 8                 | 16        | 24        | 50        |
| Cu (ppm) | Na P ICP-MS    | 4.93       | 237.00     | 45.99 | 30.90             | 58.55     | 126.80    | 235.79    |
|          | AR ICP-MS      | 31.3       | 432.9      | 121.2 | 88.1              | 168.2     | 259.5     | 430.8     |
| Fe (ppm) | Na P ICP-MS    | 60         | 6170       | 1881  | 1401              | 2778      | 3950      | 6160      |
|          | AR ICP-AES     | 981        | 38778      | 10381 | 7070              | 13595     | 20299     | 38326     |
| Hg (ppm) | Na P ICP-MS    | 0.01       | 0.15       | 0.04  | 0.02              | 0.05      | 0.07      | 0.15      |
|          | AR ICP-MS      | 0.05       | 0.46       | 0.24  | 0.09              | 0.30      | 0.34      | 0.45      |
| In (ppm) | Na P ICP-MS    | 0.003      | 0.085      | 0.023 | 0.016             | 0.031     | 0.044     | 0.083     |
|          | AR ICP-MS      | 0.008      | 0.107      | 0.041 | 0.021             | 0.053     | 0.070     | 0.107     |
| K (ppm)  | Na P ICP-MS    | 126        | 4120       | 734   | 581               | 950       | 1160      | 4014      |
|          | AR ICP-AES     | 379        | 2850       | 1082  | 507               | 1311      | 1625      | 2850      |
| LOI (%)  | Thermal decomposition | 11.17     | 94.85     | 62.36 | 23.16             | 81.55     | 88.35     | 94.57     |
| Mg (ppm) | Na P ICP-MS    | 108.5      | 2000.0     | 433.5 | 277.8             | 543.8     | 698.5     | 1962.1    |
|          | AR ICP-AES     | 336        | 6993       | 1486  | 1144              | 1981      | 3338      | 6743      |
| Mn (ppm) | Na P ICP-MS    | 22.40      | 2380.00    | 358.18| 436.28            | 402.25    | 1069.50   | 2363.50   |
|          | AR ICP-AES     | 68         | 3700       | 763   | 966               | 1000      | 1909      | 3700      |
| Mo (ppm) | Na P ICP-MS    | 0.042      | 0.781      | 0.293 | 0.136             | 0.355     | 0.459     | 0.778     |
|          | AR ICP-MS      | 0.44       | 2.42       | 1.16  | 0.41              | 1.36      | 1.79      | 2.41      |
| Na (ppm) | Na P ICP-MS    | 22         | 133        | 51    | 22                | 58        | 76        | 133       |
|          | AR ICP-AES     | 2.75       | 75.40      | 15.09 | 13.45             | 18.76     | 33.53     | 74.72     |
| Ni (ppm) | Na P ICP-MS    | 29.3       | 569.0      | 163.9 | 102.9             | 222.8     | 307.6     | 558.0     |
| Pb (ppm) | Na P ICP-MS    | 3.850      | 134.000    | 37.911| 26.125            | 50.500    | 76.740    | 131.470   |
|          | AR ICP-MS      | 14.8       | >150       | 68.2  | 34.5              | 86.0      | 130.5     | 150.1     |
| Pt (ppm) | AR ICP-MS      | 0.003      | 0.053      | 0.011 | 0.008             | 0.013     | 0.022     | 0.053     |
Table 2 (Continued)

| Elements | Method | Min. value | Max. value | Mean | Standard Deviation | 75th %ile | 90th %ile | 99th %ile |
|----------|--------|------------|------------|------|-------------------|----------|----------|----------|
| S (ppm)  | AR ICP-AES | 0.0087 | 0.0916 | 0.1156 | 0.1262 | 0.162 | 0.2163 | 0.2141 | 0.2552 |
| Sb (ppm) | AR ICP-MS | 0.0365 | 0.0671 | 0.0838 | 0.0651 | 0.0987 | 0.1296 | 0.1457 | 0.2210 |
| Se (ppm) | AR ICP-MS | 0.0611 | 0.6720 | 0.1502 | 0.1054 | 0.1296 | 0.2043 | 0.2094 |
| Sn (ppm) | AR ICP-MS | 0.0671 | 0.1950 | 0.0872 | 0.0355 | 0.0937 | 0.1342 | 0.1457 | 0.2094 |
| Te (ppm) | AR ICP-MS | <0.005 | 0.0087 | 0.0120 | 0.0101 | 0.0163 | 0.0315 | 0.0385 | 0.057 |
| Ti (ppm) | AR ICP-MS | 2.48 | 602.00 | 54.88 | 39.69 | 72.60 | 91.23 | 93.08 | 121.52 |
| Tl (ppm) | AR ICP-MS | 0.006 | 0.155 | 0.027 | 0.021 | 0.039 | 0.147 | 0.148 |
| V (ppm)  | AR ICP-MS | 0.09 | 5.50 | 1.00 | 1.00 | 2.00 | 5.46 | 5.09 | 586.38 |
| W (ppm)  | AR ICP-MS | 0.004 | 0.19 | 0.027 | 0.018 | 0.044 | 0.144 | 0.147 |

Geochemistry of the surficial media

Humus geochemistry

A summary of univariate statistics calculated for humus geochemical data is presented (Table 2) and Hashmi (2018) reported the complete data set. Spatially, sample sites with low LOI values (i.e., <50%) are predominantly located near past and present mining and forestry operations. Regardless of the organic content, humus samples collected in the northeastern part of the study area (i.e. downwind, and closest to the Copper Cliff smelter) and analysed by aqua regia ICP-MS, have higher concentrations of metals such as Ni, Pt, As, Hg and Se compared to the southwestern part of the study area. For example, metal concentrations for 2015-HS-1167 (closest sample site to Copper Cliff and not overlying mineralization) v. 2015-HS-1094 (farthest site from Copper Cliff and not overlying mineralization; Fig. 3a) are up to 13 times higher for Pt (53 ppb v. 4 ppb), 12 times higher for Cu (433 ppm v. 36 ppm), nine times higher for Ni (417 ppm v. 44 ppm), 10 times higher for As (23 ppm v. 2.4 ppm), two times higher for Hg (0.4 ppm v. 0.2 ppm), five times higher for Pb (104 ppm v. 20 ppm), and four times higher for Se (7 ppm v. 2 ppm). This spatial relationship is also observed for the same elements analysed by Na pyrophosphate ICP-MS.

A Pearson product moment correlation matrix of log-normalized data shows that, for humus samples, aqua regia and Na pyrophosphate have a strong positive correlation with each other for all trace elements except Au (Table 3). Ore elements Au, Cu, Ni and Pt have a statistically significant, positive correlation ($r^2 > 0.5$, $n = 107, \rho < 0.01$) with As, Au, Bi, Co, Cu, Hg, In, Mo, Ni, Pb, Pt,
There is also a positive correlation between LOI and Se (0.68), Hg (0.82), Bi (0.51), and Cd (0.51), and a strong negative correlation between V (−0.73), Cr (−0.73), Th (−0.64), U (−0.63) and rare-earth elements (REEs) (−0.54 to −0.80), with LOI in humus samples analysed by aqua regia ICP-MS (Supplementary data 3). Furthermore, some humus samples with high LOI also contained high concentrations of Ni and Cu by both aqua regia ICP-MS and Na pyrophosphate. For example, sample 2015-HS-1162 contained Ni up to 400 and 34 ppm by aqua regia ICP-MS and Na pyrophosphate, respectively and an estimated 89% LOI content: and Cu up to 327 and 165 ppm by aqua regia ICP-MS and Na pyrophosphate, respectively (Supplementary Figure 2).

B-horizon and C-horizon till geochemistry

A summary of univariate statistics calculated for B-horizon and C-horizon geochemistry is presented (Tables 4 and 5), and the complete data set has been reported by the OGS (see Hashmi 2018b). There is a statistically significant, positive correlation ($r^2 > 0.5, n = 71, p = <0.01$) between trace elements in the B-horizon and C-horizon till (except Se). Generally, the B-horizon till contains lower element concentrations and has higher LOI values compared to the C-horizon. Proportional dot plots show that some of the highest ore element contents in both B- and C-horizon till samples are present in till collected over and immediately down-ice (SW) of mineralization (including the Worthington Offset and the Nipissing Intrusive Suite) in central Denison Township. These samples also contain 53–80% organic matter. The highest ore element concentrations are: up to 53 ppb Pt over (barren) metavolcanic rocks of the Elliot Lake Group in the NE corner of Denison Township (2015-HS-1167; Fig. 3a); up to 294 ppb Au by aqua regia ICP-MS (2015-HS-1046; Fig. 3b) over the East Bull Lake Igneous Suite in east-central Drury Township (Au was below detection limit by Na pyrophosphate); up to 569 ppm Ni by aqua regia ICP-MS (2015-HS-1149; Fig. 4a), also overlying the Elliot Lake Group. The highest Ni (75 ppm) by Na pyrophosphate ICP-MS is in a sample (2015-HS-1123) immediately down-ice of the northern tip of the Worthington Offset (Figs 2 and 4a); 433 ppm Cu over metavolcanic rocks of the Elliot Lake Group (2015-HS-1167; Fig. 4b) and this sample also contains the highest Cu, 237 ppm, by Na pyrophosphate.
are in C-horizon till samples collected over the Vermilion deposit (Fig. 5a). Furthermore, compared to the background concentrations, the C-horizon till samples collected immediately down-ice of the Vermilion deposit are enriched over 20 times in Au, Cu and Pt, and over 30 times in Ni. Elevated to anomalous ore element contents also occur in till samples overlying and immediately down-ice of offset mineralization, with up to 12 ppb Au on the northern tip of the Worthington Offset (2015-HS-3123; Fig. 5b), 62 ppm Ni (2015-HS-3155B) and 139 ppm Cu (2015-HS-3155B; Fig. 6b).

Although there is a strong, positive correlation between humus samples analysed by Na pyrophosphate ICP-MS and aqua regia ICP-MS, there appears to be no correlation between humus and B-horizon till, Humus (Na pyrophosphate ICP-MS) and B-horizon till, both analysed by aqua regia ICP-MS and NiS FA. ‘N’ is the number of samples used for the matrix. Positive correlations greater than 0.5 are in bold.

### Discussion

#### Sources of contamination

The main sources of anthropogenic contamination in the region could be derived from: (1) wind-transported, smelter-derived silt particles from nearby smelting operations such as Copper Cliff; (2) wind-transported silt from inactive and active tailings sites in and around the study area; (3) wind-transported particles from transportation corridors for ore and associated products (i.e. haul roads and rail roads); (4) contamination from past and current infrastructure development (Freedman and Hutchinson 1980; Hoffman and Kairua 1984; Gignac and Beckett 1986; Adamo et al. 1996; Hutchinson and Gunderman 1998; Bajc and Hall 2000b; Lanteigne et al. 2014; Schindler 2014; Hashmi 2018a).

Smelting of ores has been carried out in the Sudbury Mining Camp for more than 100 years and has had a strong impact on the surficial environment, especially vegetation in the surrounding regions (Hutchinson and Whitby 1974; Hoffman and Kairua 1984; Gignac and Beckett 1986; Schmidt 2014). Mining and smelting of Ni–Cu ores in the SIC has also resulted in the contamination of humic matter and/or non-decomposing anthropogenically...
derived atmospheric fallout, regardless of location, vegetation decomposition or depth of the sample (Supplementary Figure 1). Humus samples collected in the northeastern part of the study area, closer down-wind to the Copper Cliff smelter (as well as active transportation corridor for mining operations such as Lockerby Mine and Ellen pit) have higher ‘smelter metal’ concentrations than the humus samples collected in the southwestern part of the study area, farther downwind from the smelter. Therefore, it is highly likely that the majority of the ‘smelter metals’ present in humus are derived from fallout from smelter emissions. For example, highly anomalous Cu, Ni and Pt (sample 2019-HS-1167; Figs 3 and 4) and anomalous Au contents are present in a humus sample collected in the northeastern part of the study area, i.e. location close to the Copper Cliff smelter. This sample also contained elevated to anomalous concentrations of ‘smelter metals’, including Cu (433 ppm), Ni (417 ppm), As (23 ppm), Cd (1 ppm), Cr (19 ppm), Co (14 ppm), Fe (18552), Mn (197 ppm), Pb (104 ppm), Se (7 ppm) and Zn (51 ppm). Furthermore, Lanteigne et al. (2014) concluded that particulate matter in smelter emissions identified in the Sudbury area include sulfide minerals (Ni–Cu–Fe–Co), oxide minerals (Ni–Cu–Fe–Co), metallic phases and alloys (Ni–Cu–Fe–Co) as well as slag particles (Lanteigne et al. 2014). Slag, a by-product of smelting has also been recovered from heavy mineral concentrates of C-horizon till samples in the study areas (Hashmi 2018a, 2018b). The sulfide mineral particulates consist of sulfide mineral inclusions that are surrounded by a Fe-oxide and Fe-silicate mineral rim and enriched in smelter-metals such as Cu, Pb, Zn, As, Se, which may be released into the surficial environment via oxidation (Lanteigne et al. 2014); however, the rate of release is dependent on the nature of the metal-bearing phase. Therefore, some of the non-decomposing matter present in humus may be oxidation resistant slag and/or surficial alteration resistant smelter dust, also noted in soils near the Horne smelter in Rouyn-Noranda (Supplementary Data 1)(Knight and Henderson 2006).

Anthropogenic impacts on soil geochemistry

Profile plots (Fig. 7) show that anomalous concentrations of ore and associated elements are present in humus, but the same elements are present in background levels in B-horizon and C-horizon till. This finding suggests that elevated concentrations of metals such as As, Cd, Pb and Se in humus are primarily due to anthropogenic fallout. In the Sudbury Mining Camp, the highest metal and metalloid (such as Ni, Cu, Zn, Co, As, Pb and Se) concentrations are noted in the top 0–10 cm (B-horizon till) profile and decrease with depth with limited translocation to lower horizons and that this contamination is restricted to the top 20 cm (Figs 7 and 8). This because humus can act as a sponge, retaining the anthropogenic fallout (primarily from smelter emissions) and preventing vertical transport of smelter particles to the underlying soil horizons (Wren et al. 2012). Similarly, Bajc and Hall (2000a, 2000b) studied the humus, B-horizon, and C-horizon till geochemical response in the North and

![Fig. 4](http://geea.lyellcollection.org/Downloaded from http://geea.lyellcollection.org/)
Table 4: Summary of statistics for B-horizon till samples analysed by aqua regia ICP-MS (AR ICP-MS), aqua regia ICP-AES (AR ICP-AES) and nickel sulfide fire assay (NiS FA)

| Elements | Method | Min. value | Max. value | Mean | Standard Deviation | 75th %ile | 90th %ile | 99th %ile |
|----------|--------|------------|------------|------|--------------------|-----------|-----------|-----------|
| Ag (ppm) | AR ICP-MS | <0.01 | 12.33 | 0.32 | 1.41 | 0.17 | 0.32 | 11.91 |
| Al (ppm) | AR ICP-AES | 7581 | >38 000 | 21 406 | 5791 | 24 495 | 29 282 | 37 484 |
| As (ppm) | AR ICP-MS | 1.9 | 27.1 | 7.9 | 4.7 | 9.6 | 14.3 | 26.9 |
| Au (ppb) | NiS FA | <0.4 | 80.2 | 3.6 | 10.0 | 2.8 | 4.7 | 78.3 |
| Ba (ppm) | AR ICP-MS | 18.4 | 236.6 | 64.1 | 33.1 | 76.6 | 107.4 | 225.6 |
| Bi (ppm) | AR ICP-MS | 0.05 | 4.69 | 0.23 | 0.55 | 0.19 | 0.24 | 4.57 |
| Ca (ppm) | AR ICP-AES | 386 | 4060 | 1947 | 759 | 2382 | 3021 | 4049 |
| Cd (ppm) | AR ICP-MS | 0.04 | 0.52 | 0.18 | 0.10 | 0.22 | 0.34 | 0.52 |
| Co (ppm) | AR ICP-MS | 4.19 | 41.42 | 12.31 | 5.43 | 15.26 | 19.86 | 38.95 |
| Cr (ppm) | AR ICP-MS | 16 | >120 | 64.1 | 33.1 | 76.6 | 107.4 | 225.6 |
| Cu (ppm) | AR ICP-MS | 0.05 | 4.69 | 0.23 | 0.55 | 0.19 | 0.24 | 4.57 |
| Fe (ppm) | AR ICP-AES | 17 609 | >50 000 | 29 543 | 7495 | 33 160 | 38 990 | 50 000 |
| Hg (ppm) | AR ICP-MS | 0.01 | 0.19 | 0.06 | 0.03 | 0.08 | 0.11 | 0.18 |
| In (ppm) | AR ICP-MS | 0.009 | 1.363 | 0.042 | 0.153 | 0.024 | 0.029 | 1.309 |
| Ir (ppb) | NiS FA | 0.03 | 1.03 | 0.09 | 0.11 | 0.09 | 0.14 | 0.96 |
| K (ppm) | AR ICP-AES | 296 | >2850 | 994 | 602 | 1170 | 1947 | 2850 |
| LOI (%) | Thermal decomposition | 1.33 | 7.44 | 7.44 | 3.30 | 9.22 | 11.63 | 17.83 |
| Mg (ppm) | AR ICP-AES | 2202 | >14 000 | 5713 | 2127 | 7033 | 8715 | 13 578 |
| Mn (ppm) | AR ICP-AES | 122 | 1675 | 290 | 172 | 369 | 431 | 1537 |
| Mo (ppm) | AR ICP-MS | 0.31 | 2.90 | 0.95 | 0.37 | 1.13 | 1.41 | 2.76 |
| Na (ppm) | AR ICP-AES | 40 | 499 | 89 | 51 | 100 | 119 | 468 |
| Ni (ppm) | AR ICP-AES | 14.4 | 340.5 | 45.1 | 38.4 | 48.2 | 66.7 | 320.7 |
| P (ppm) | AR ICP-AES | 202 | >1700 | 676 | 297 | 810 | 1049 | 1687 |
| Pb (ppm) | AR ICP-MS | 4.6 | >150 | 15.7 | 19.4 | 16.3 | 22.4 | 149.4 |
| Pd (ppb) | NiS FA | 0.2 | >4800 | 87.2 | 638.3 | 1.7 | 3.8 | 4800.1 |
| Pt (ppm) | NiS FA | 0.23 | 354.00 | 5.72 | 35.12 | 1.60 | 3.16 | 323.71 |
| Rb (ppm) | AR ICP-MS | 3 | 45 | 17 | 8 | 22 | 28 | 44 |
| Rh (ppb) | NiS FA | <0.08 | 27.60 | 0.54 | 3.18 | 0.13 | 0.20 | 26.80 |
| Ru (ppb) | NiS FA | <0.08 | 3.39 | 0.25 | 0.48 | 0.22 | 0.35 | 3.39 |
| S (ppm) | AR ICP-AES | 73 | 11 222 | 362 | 1220 | 243 | 316 | 11 222 |
| Sb (ppm) | AR ICP-MS | 0.06 | 1.24 | 0.27 | 0.22 | 0.34 | 0.53 | 1.22 |
| Se (ppm) | AR ICP-MS | <0.4 | 11.6 | 1.0 | 1.3 | 1.0 | 1.3 | 11.6 |
| Sn (ppm) | AR ICP-MS | 0.26 | 4.38 | 0.60 | 0.51 | 0.63 | 0.74 | 4.34 |
| Sr (ppm) | AR ICP-MS | 5.07 | 27.21 | 13.19 | 4.29 | 15.14 | 19.65 | 26.88 |
| Te (ppm) | AR ICP-MS | <0.01 | 9.39 | 0.15 | 0.92 | 0.06 | 0.07 | 8.67 |
| Ti (ppm) | AR ICP-MS | 293.9 | 2004.6 | 978.1 | 321.2 | 1154.9 | 1417.4 | 2001.1 |
| Tl (ppm) | AR ICP-MS | 0.049 | 0.966 | 0.147 | 0.104 | 0.159 | 0.235 | 0.919 |
| V (ppm) | AR ICP-MS | 28 | >80 | 45 | 11 | 53 | 61 | 80 |
| W (ppm) | AR ICP-MS | 0.1 | 1.5 | 0.3 | 0.2 | 0.3 | 0.5 | 1.4 |
| Zn (ppm) | AR ICP-MS | 20.49 | 249.90 | 81.59 | 39.79 | 101.55 | 126.21 | 245.19 |
| Elements | Method | Min. value | Max. value | Mean | Standard Deviation | 75th %ile | 90th %ile | 99th %ile |
|----------|--------|------------|------------|------|--------------------|-----------|-----------|-----------|
| Ag (ppm) | AR ICP-MS | <0.01 | 5.27 | 0.22 | 0.72 | 0.11 | 0.27 | 5.27 |
| Al (ppm) | AR ICP-AES | 10709 | 38000 | 18738 | 4823 | 20685 | 25416 | 36810 |
| As (ppm) | AR ICP-MS | 2.2 | 41.1 | 9.7 | 6.1 | 11.8 | 17.3 | 40.0 |
| Au (ppb) | NIS FA | <0.4 | 80.7 | 5.7 | 11.1 | 4.5 | 12.4 | 77.5 |
| Ba (ppm) | AR ICP-MS | 18.7 | 192.2 | 69.4 | 26.6 | 83.2 | 95.1 | 189.2 |
| Bi (ppm) | AR ICP-MS | 0.04 | 3.74 | 0.34 | 0.70 | 0.23 | 0.40 | 3.68 |
| Ca (ppm) | AR ICP-AES | 377 | 5707 | 2615 | 880 | 3127 | 3659 | 5552 |
| Cd (ppm) | AR ICP-MS | 0.1 | 1.1 | 0.2 | 0.2 | 0.3 | 0.4 | 1.0 |
| Ce (ppm) | AR ICP-MS | 10.2 | 70.1 | 61.2 | 13.3 | 70.1 | 70.1 | 70.1 |
| Co (ppm) | AR ICP-MS | 5.41 | 34.29 | 13.99 | 5.38 | 16.76 | 21.57 | 33.42 |
| Cr (ppm) | AR ICP-MS | 10 | >120 | 40 | 18 | 46 | 52 | 120 |
| Cu (ppm) | AR ICP-MS | 8.4 | >500 | 102.4 | 137.2 | 84.1 | 501.0 | 501.0 |
| Fe (ppm) | AR ICP-AES | 16610 | 50000 | 29702 | 6720 | 32787 | 38400 | 50000 |
| Hg (ppm) | AR ICP-MS | 0.01 | 0.38 | 0.08 | 0.05 | 0.09 | 0.14 | 0.37 |
| In (ppm) | AR ICP-MS | 0.013 | 0.894 | 0.039 | 0.106 | 0.025 | 0.048 | 0.872 |
| Ir (ppb) | NIS FA | 0.02 | 1.27 | 0.14 | 0.22 | 0.10 | 0.25 | 1.25 |
| K (ppm) | AR ICP-MS | 385 | 2850 | 1313 | 608 | 1667 | 2125 | 2850 |
| LOI (%) | Thermal decomposition | 1.3 | 18.4 | 4.3 | 2.3 | 5.2 | 6.6 | 17.4 |
| Mg (ppm) | AR ICP-AES | 3.69 | >14000 | 7111 | 2008 | 8315 | 9950 | 14000 |
| Mn (ppm) | AR ICP-AES | 138 | 994 | 361 | 140 | 444 | 517 | 974 |
| Mo (ppm) | AR ICP-MS | 0.25 | 4.95 | 1.05 | 0.73 | 1.22 | 1.60 | 4.81 |
| Na (ppm) | AR ICP-MS | 46 | 534 | 108 | 63 | 118 | 145 | 511 |
| Ni (ppm) | AR ICP-MS | 17.9 | 1282.9 | 87.4 | 160.5 | 57.4 | 237.9 | 1140.7 |
| P (ppm) | AR ICP-MS | 182 | 1189 | 579 | 167 | 704 | 777 | 1154 |
| Pb (ppm) | AR ICP-MS | 4.9 | 150.1 | 19.9 | 21.2 | 22.6 | 34.6 | 150.1 |
| Pd (ppb) | NIS FA | 0.20 | >4800 | 216.75 | 831.42 | 2.98 | 16.10 | 4800.10 |
| Pt (ppb) | NIS FA | 3.83 | 203.0 | 8.5 | 26.4 | 2.5 | 13.7 | 187.4 |
| Rb (ppm) | AR ICP-MS | 3.83 | 46.63 | 17.25 | 7.90 | 21.26 | 28.78 | 45.27 |
| Rh (ppb) | NIS FA | <0.04 | 20.60 | 1.02 | 3.04 | 0.22 | 2.72 | 20.21 |
| Ru (ppb) | NIS FA | <0.08 | 2.20 | 0.26 | 0.35 | 0.26 | 0.67 | 2.20 |
| Sb (ppm) | AR ICP-AES | <0.4 | 4.3 | 0.9 | 0.6 | 1.0 | 1.4 | 4.3 |
| Se (ppm) | AR ICP-MS | 0.24 | 3.32 | 0.61 | 0.42 | 0.61 | 0.84 | 3.25 |
| Sr (ppm) | AR ICP-MS | 8.7 | 43.8 | 17.1 | 5.7 | 20.4 | 23.0 | 42.5 |
| Tc (ppm) | AR ICP-MS | 0.01 | 1.37 | 0.12 | 0.28 | 0.07 | 0.16 | 1.37 |
| Te (ppm) | AR ICP-MS | 659.7 | 1799.8 | 1090.2 | 242.6 | 1219.9 | 1470.9 | 1785.7 |
| Tl (ppm) | AR ICP-MS | 0.059 | 0.616 | 0.168 | 0.076 | 0.198 | 0.259 | 0.571 |
| V (ppm) | AR ICP-MS | 26.00 | 77.00 | 45.91 | 9.88 | 50.00 | 61.00 | 76.40 |
| W (ppm) | AR ICP-MS | 0.10 | 1.80 | 0.32 | 0.32 | 0.30 | 0.60 | 1.80 |
| Zn (ppm) | AR ICP-MS | 25 | 383 | 74 | 47 | 83 | 116 | 360 |
East Ranges of the SIC and concluded that the anthropogenic contamination from smelter emissions is restricted primarily to humus (<10 cm). Conversely, profile sampling at 5 cm intervals through the B-horizon completed at the Vermilion deposit (sample 2016-HS-003; Fig. 8a) shows that some of the highest contents for metals such as As, Cd, Co, Hg, Pb and Sb are present in the upper Bf-horizon and decrease with increasing depth. The changing geochemical composition through the B-horizon indicates that the upper levels of the Bh-horizon may also be partially contaminated by anthropogenic atmospheric fall-out. Elevated As, Cd, Cu, Hg, Pb and Zn in the organic layer of forest soils have also been noted in the vicinity of the Flin Flon smelter (Henderson and McMartin 1995; Henderson et al. 1998). Similarly to our study, they concluded that the total smelter-derived metal concentrations decreased in humus with increasing distance from the smelter and that contamination was concentrated mainly in the organic-rich horizon, but at highly contaminated sites, smelter metals (especially Zn) had migrated down to B-horizon to 45 cm depth. Similarly, metal contamination in soil around the base metal smelter (Horne smelter) in Rouyn-Noranda is restricted to organic rich and upper B-horizons (Daggupaty et al. 2006; Zdanowicz et al. 2006; Dixit et al. 2007; Johnson and Hale 2008; Caplette et al. 2015; Leverington and Schindler 2018; Dinis et al. 2021). Another reason for high metal concentrations in the upper Bf-horizon in our study may be that the metals leached out of the Ae horizon were reprecipitated in the upper Bh-horizon, resulting in higher element content in the upper Bh-horizon that decreases with depth. Lastly, the profile plots in our study also show that Hg content in humus is enriched up to five times relative to the underlying till (Figs 7 and 8). Although atmospheric fallout is a major contributor to Hg enrichment in humus in our study area, there are also geogenic factors responsible for the enrichment. Humus can adsorb metal cations and form complexes and has a higher cation exchange capacity relative to clay minerals (FitzPatrick 1986); therefore, humus has a higher cation holding capacity relative to soil. The strong binding between Hg and humus (Zhu and Zhong 2015) means that Hg contents may remain within humus and accumulate over time. Up to 400 ppb (250 times the regional background) Hg in humus has also been documented by Henderson and McMartin (1995) in the immediate vicinity of the Flin Flon smelter. Overall, there is no correlation between humus and till geochemistry. Based on the ore and associated element content distribution in soil profiles, there is no evidence to suggest the presence of anthropogenic material in the fine fraction (<63 µm) of lower Bh-horizon till samples collected below a depth of 20 cm. Despite the strong anthropogenic imprint in humus and upper Bh-horizon soils (<20 cm) in the Sudbury Mining Camp, fine fraction geochemistry of less weathered, C-horizon till is well-suited to surficial geochemical surveys.
Effectiveness of Na pyrophosphate in eliminating the anthropogenic signal in humus

Log-normalized Pearson product moment correlations show that, except for Au, each element shows a strong positive correlation with itself, between analyses by aqua regia ICP-MS and Na pyrophosphate ICP-MS. Furthermore, element concentrations determined by Na pyrophosphate ICP-MS are much lower compared to those determined by aqua regia ICP-MS/ICP-AES. The Na pyrophosphate digestion targets elements bound to humic and fulvic acid complexes such as Cd, Cu, Pb and Zn, which are held primarily in an easily leachable (labile) form leaving the inorganic fraction relatively unaffected (Hall et al. 1996; Henderson et al. 1998). Organic substances have a high scavenging capacity because of the presence of carboxylic acid functional groups as well as amine and thiol groups (Papp et al. 1991; Hall et al. 1996; Hall and Pelchat 1997). Sodium pyrophosphate can effectively remove easily extractable organic matter due to its ability to chelate with Ca and trivalent cations. The removal of cations bound to humates results in the conversion of polyanions into soluble Na salts which may then be leached out (Papp et al. 1991). Conversely, aqua regia is a much stronger leach that can dissolve sulfide and oxide minerals, organic matter and airborne fallout dust and therefore is better at providing an estimate of the spatial extent of anthropogenic contamination in humus.

The strong negative correlation between LOI and V, Cr, Th, U and REEs by both aqua regia and Na pyrophosphate suggests that these elements in humus may be derived from the underlying soil and/or mineral matter. Furthermore, there is a strong positive correlation between LOI and Bi, Cd, Hg, Ni and Se (analysed by Na pyrophosphate ICP-MS) in humus samples and some samples with the highest ‘smelter metal’ content also contain high amounts of organic matter. This suggests that metals such as As, Bi, Cd, Hg, Ni and Pb are present in the organic matter in humus and may be the result of breakdown of smelting-derived sulfide mineral particulates that are subsequently adsorbed by humic and fulvic acid complexes in the humus. This finding is supported by the observations of Hutchinson and Whitby (1977) who reported >3000 ppm Ni and >2000 ppm Cu in soil in the Sudbury region, causing a drop in pH and an increase in the acidity of humus and upper soils over time. The increased acidity consequently led to an increase in the mobility of metals and an increased metal-binding capacity of soils and the fulvic component of humus (Hutchinson and Whitby 1977). The implication is that ‘smelter metal’ accumulation in the organic matter in humus will remain high relative to background and may overprint the naturally high metal contents due to the presence of proximal Ni–Cu–PGE mineralization, even with the use of Na pyrophosphate.

At Rouyn-Noranda, Knight and Henderson (2006) used electron microbeam analysis to identify the presence of historic and recent smelter dust trapped in humus; elements detected in the smelter-derived dust include Si, Al, Fe, Mg, Na, K, Ca, Cu, Zn, Pb and Ti. The authors also observed that the spatial distribution of smelter dust coincided with elevated concentrations of As, Cd, Cu, Pb and

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**Fig. 6** (a) Graduated colour and proportional dot map of Ni (ppm) content in B- and C-horizon till samples determined by aqua regia ICP-MS, respectively; (b) graduated colour and proportional dot map of Cu (ppm) content in B- and C-horizon till samples determined by aqua regia ICP-MS, respectively. Sample sites mentioned in text are labelled. Bedrock geology legend same as in **Figure 2**.
Zn in humus (Henderson et al. 2002) and inferred that, soon after deposition, weathering processes had released metals and other elements from the dust to the humus (Knight and Henderson 2005, 2006). Similarly, Bajc and Hall (2000a) also noted elevated Ag, As, Au, Bi, Co, Cr, Pd, Pt, Se and Te content in humus samples collected near smelters, which the authors attributed to be a direct result of anthropogenic atmospheric fallout of colloid sulfide particles from local smelters. Oxidation of these sulfide mineral colloids results in the bioavailability of the associated metals, which are rapidly scavenged by humic and fulvic acids in organic matter (i.e. decaying forest litter and humus), resulting in elevated metal content in humus samples (Bajc and Hall 2000a). Therefore, it is likely that the high concentrations of elements such as As, Cd, Cu and Pb in humus, as determined using the Na pyrophosphate leach, may in part be derived from the breakdown of smelter-derived sulfide minerals. Overall, Na pyrophosphate was not successful in diminishing the anthropogenic masking of the geogenic signal.

Fig. 7. Profile sampling of humus, B- and C-horizon completed at select sites and their respective geochemistry. The blue, yellow and green columns indicate the depth of the humus, B-horizon and C-horizon, respectively. (a) Samples at site 2015-HS-002 were collected over metasedimentary rocks of the Elliot Lake Group; (b) samples at site 2019-HS-124 were collected over the Worthington Offset; (c) samples at site 2015-HS-007 were collected over metasedimentary rocks of the Hough Lake Group; (d) samples at site 2015-HS-034 were collected over mafic intrusive rocks of the Nipissing mafic intrusive suite; (e) samples at site 2019-HS-042 were collected over the metavolcanic rocks of the Elliot Lake Group; (f) samples at site 2015-HS-125 were collected over mafic intrusive rocks of the Nipissing intrusive suite.
Lastly, the geochemistry of humus may reflect long-term accumulation; even processes such as yearly evaporation and leaching (by rainwater) can enrich the humus horizon with Ag, Au, Be, Zn, Cd, Sc, Tl, Ge, Sn, Pb, As, Mn, Co and Ni (i.e. Goldschmidt enrichment principle; Goldschmidt 1937; Sucharová and Suchara 2004; Minolfi et al. 2017).

Comparison between the B- and C-horizon soil geochemistry

The mobility of Au, Cu, Ni and PGEs and associated chalcophile elements is variable in the surficial environment; factors such as pH (and redox conditions) (Stoffregen 1986; Hattori and Cameron 2004; Borch et al. 2010; Leybourne and Cameron 2010; Violante et al. 2010; Rivera et al. 2018), presence of S (Hawkes 1957; Rose et al. 1979; Violante et al. 2010; Kotze et al. 2019), ligands available for complexation (Fuchs and Rose 1974; Plyusnin et al. 1980; Bowell et al. 1993; Boyle 1995; Leybourne and Cameron 2010; Violante et al. 2010) and organic matter (Wood 1996; Kotze et al. 2019) play a vital role in metal mobility and enrichment in the B-horizon till. Overall, the highest ore element (Ni, Cu, Pt and Au) and associated element (including As, Cd, Co, Sb, Se, Hg and Pb; Naldrett 2004; Dare et al. 2010) content associated with Ni–Cu–PGE mineralization in the study area is recovered from C-horizon samples (Hashmi 2018b). Furthermore, downhole profile plots show that Au, PGEs, Ni and Cu, and associated elements As, Cd, Co, Sb, Se, Hg and Pb, are depleted in the B-horizon compared to the C-horizon (Fig. 8a). This depletion in ore and associated elements is due to weathering and subsequent hydromorphic dispersion (Hawkes 1957), suggesting that these elements are mobile in the surficial environment to variable extents. However, concentrations of ore and associated elements are higher in the B-horizon than in the C-horizon at some sites in the study area. These samples were collected at depths of >20 cm and therefore reprecipitation of metals from the Ae horizon or anthropogenic contamination by airborne particulates are not factors responsible for the enrichment in the B-horizon. Only Pd is consistently depleted in the B-horizon, because it is mobile over a wide range of Eh and pH conditions in the surficial environment (Fuchs and Rose 1974; Cabral et al. 2007; Rivera et al. 2018) and readily forms neutral and/or anionic (hydroxide) complexes with water (i.e. rainwater and/or soil moisture) (Hattori and Cameron 2004; Cameron and Hattori 2005; Rivera et al. 2018). Both Pt and Pd can be transported in solution via groundwater (Bowles et al. 2017) but Pd is more mobile in the surficial environment than Pt (Hattori and Cameron 2004; Cameron and Hattori 2005). At one site, Pt is enriched in the B-horizon relative to the C-horizon (sample 2015-HS-090; Fig. 8b). McCallum et al. (1976) also documented this phenomenon at the New Rambler Mine, Wyoming, where Pt was enriched in the oxidized zone relative to the fresh ore, which they suggested may be due to secondary enrichment by supergene processes in the oxidized horizon. Similarly in our study, Pt may have been liberated from platinum group minerals (PGMs) during weathering of the C-horizon till, forming secondary PGE-oxides or hydroxides (McCallum et al. 1976; Suárez et al. 2008, 2010), and resulting in higher Pt content in the oxidized B-horizon till. Gold
contents are both relatively depleted (2015-HS-158; Fig. 8c) and enriched (2015-HS-090; Fig. 8b) in the B-horizon with respect to the C-horizon. Breakdown of sulfide minerals associated with Ni-Cu-PGE mineralization would result in the formation of metastable thiosulfate complexes, encouraging Au mobility in soil–water solution (Goldhaber 1983). Subsequently, the instability of thiosulfate would result in Au reprecipitation, resulting in elevated Au content in the B-horizon. Oxidation of sulfide minerals (which bind the ore and associated chalcophile elements) in the surficial environment releases H+ ions, causing a drop in pH and consequently encouraging the mobility of metals such as As, Cu, Ni, Cd, Co and Pb. Reduction of cations (Cu2+ to Cu+, Pb3+ to Pb2+ etc.) by Fe2+ or H2S may also mobilize them by forming sulfide colloids. Antimony is enriched in the B-horizon relative to C-horizon at one site (2016-HS-003; Fig. 8a). In the case of Sb, desorption increases with increasing pH as it is mobile under alkaline conditions (Violante et al. 2010). An increase in pH would result in Sb getting adsorbed onto clay and Fe- and Mn- oxyhydroxides, removing it from the soil–water solution and reprecipitating in the B-horizon. Mercury is predominantly elevated in the B-horizon (2016-HS-003, 2015-HS-090; Fig. 8a and c). This may be because it can occur in various forms in the soil, including: (1) dissolved as soluble complexes, (2) non-specifically adsorbed (electrostatic forces), (3) specifically adsorbed (adsorption increasing with reducing pH), and (4) precipitated as a sulfide complex (Schuster 1991). Mercury has a strong affinity for building Cl−-, OH- and S2− complexes (Schuster 1991). Lastly, organic matter also has a high affinity for Hg (e.g. Zhu and Zhong 2015). LOI results suggest that there is more organic matter present in the B-horizon (compared to the C-horizon) which means that Hg can also form strong bonds with both organic and mineral matter present within the B-horizon, also resulting in higher Hg present in the B-horizon with respect to the C-horizon.

**Anthropogenic v. geogenic sources of metals in the surficial media**

Humus can be an effective surficial medium for geochemical sampling for both contamination and mineral exploration because of its capacity to accumulate trace metals, thereby providing a strong contrast in the composition of background v. anomalous samples (Fortescue 1985). However, its application to mineral exploration surveys can be limited if the source of its geochemical signature is challenging to determine due to the complexity of the interactions between geogenic and anthropogenic factors in established mining camps (McMartin et al. 1999; Minolfi et al. 2017). Factors that are responsible for elevated metal content in humus in the study area include: (1) the natural geochemical signature of the surrounding bedrock and till; (2) soil-forming processes such as biogeochemical enrichment in the O-horizon (McMartin et al. 1999); (3) accumulation of metals in decaying plant litter (Goldschmidt 1937); (4) atmospheric, smelter-derived fallout and post-depositional oxidation of smelter particles and mobilization of metals (Fig. 9) (Lanteigne et al. 2014).
Although there is a strong anthropogenic overprint, humus samples collected over Ni–Cu–PGE mineralization and/or over till samples down-ice from known Ni–Cu–PGE mineralization contain elevated to anomalous ore metal content that is highly likely to have been derived from mineralization. For example, humus samples collected over the Worthington Offset (sample 2015-HS-124; Fig. 7b) and Nipissing Intrusive Suite (2015-HS-034 and 2015-HS-125; Fig. 7d and f) have elevated Au, Pt, Ni and Cu content, which is highly likely to have been derived from the underlying Ni–Cu–PGE mineralization. Similarly, elevated Ni, Cu, Pt and Au content is also noted in a humus sample (2015-HS-002; Fig. 7a), where the C-horizon till sample collected for indicator mineral separation recovered a high number of gold (26) and sperrylite (55) grains (Hashmi et al. 2021).

Future work
A humus sampling survey completed by Theyer (2006) Ni–Cu–PGE mineralization in the Mayville Igneous Complex in southeastern Manitoba demonstrated that the mobility of Pd and its adsorption to organic matter makes it an excellent pathfinder element to detect local PGE prospects (Theyer 2006). Similarly, Cameron and Hattori (2005) also concluded that Pd is an excellent indicator of PGE mineralization at Lac des Iles PGE deposit. Although the suite of elements analysed for in humus in this study did not include Pd, future humus sampling surveys exploring for PGE mineralization would benefit from including PGEs (such as Pd) in the analytical work.

In parts of the SIC where the humus is dominated by anthropogenic metal accumulations from atmospheric fallout out of smelter particles, sampling of tree cores may work in determining the natural geochemical background (van Geffen et al. 2012; Schmidt et al. 2017). Tree roots can tap into deeper soils, groundwater and bedrock for nutrients and subsequently uptake and redistribute elements (Rogers and Dunn 1993; Dunn 2007; van Geffen et al. 2012). Deeper and older ‘heartwood’ within the inner tree cores can provide a natural regional geochemical condition of the time in which the heart rings grew, provided that the trees chosen for sampling predate smelting operations (Dunn 2007; van Geffen et al. 2012). Furthermore, Pb isotope ratios also have the potential to document provenance (Ayuso et al. 2013). Lead is a pathfinder element to Ni–Cu–PGE mineralization in the study area (Hashmi et al. 2021); therefore, Pb isotopes can potentially be used to discriminate Pb associated with geogenic Ni–Cu–PGE occurrences v. anthropogenic Pb derived from smelter emissions. Lead isotope ratios have been used successfully to discriminate between anthropogenic (smelter-derived) and geogenic (Pb–Zn mineralization) sources in surficial media near the Talbot prospect (van Geffen et al. 2013). Incorporating Pb isotope ratios with dendrochronology is a powerful tool that has the potential to characterize multiple sources of anthropogenic contamination as demonstrated by Savard et al. (2006). The authors used 208Pb/206Pb and 206Pb/204Pb in tree rings to identify Pb from geogenic (mineral soil) and two different anthropogenic (Horne smelter and coal-burning power plant) sources (Savard et al. 2006). Future surficial exploration in the Sudbury Mining Camp may benefit from incorporating Pb isotope ratios in determining the geochemical provenance of surficial media (especially humus) for targeting Ni–Cu–PGE mineralization.

Conclusions
A surficial media sampling study was completed in the Denison and Drury townships in the southwestern corner of the SIC. The objectives of the study were to determine: (1) whether the use of partial extractions can minimize or eliminate the anthropogenic signal in humus, and (2) compare the geochemical signature of humus and B- and C-horizon soils to determine whether they can delineate geochemical anomalies associated with mineralization.

Results of this study suggest that the natural geochemical signature from Ni–Cu–PGE deposits in humus is strongly overprinted by the anthropogenic signal; despite anthropogenic contamination, the geogenic Ni–Cu signature in humus is apparent in samples collected in the vicinity of Ni–Cu–PGE mineralization. Overall, humus sampling geared towards mineral exploration is not recommended in the SIC and other established mining regions where the surficial soils are heavily contaminated by smelter emissions. The use of Na pyrophosphate leach does not minimize the anthropogenic metal contribution in humus, and the use of aqua regia ICP-MS highlights its extent.

Apart from humus, anthropogenically-derived atmospheric fallout also seems to affect the upper B-horizon but not the lower B-horizon till (at >20 cm depth) nor the C-horizon till. Generally, metal concentrations are depleted in the B-horizon compared to the C-horizon; however, at some sites, ore and associated elements Au, As, Ni, Cu, Co, Cd, Pt, Pd, Se, Sb, Hg and Pb are enriched in the B-horizon with respect to the C-horizon. The enrichment of these elements is due to normal redox and pH-related soil forming processes, that result in the liberation of these elements and their subsequent reprecipitation.

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Data availability
The datasets generated during and/or analysed during the current study are available in the Ontario Geological Survey repository: http://www.geologyontario.mndm.gov.on.ca/mndmaccess/mndm_dir.asp?type=pub&
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