Assessing and Reducing Risks at the Montague and Goldenville Gold Districts in Nova Scotia

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Workshop on the Role of Geochemical Data in Ecological and Human Health Risk Assessment
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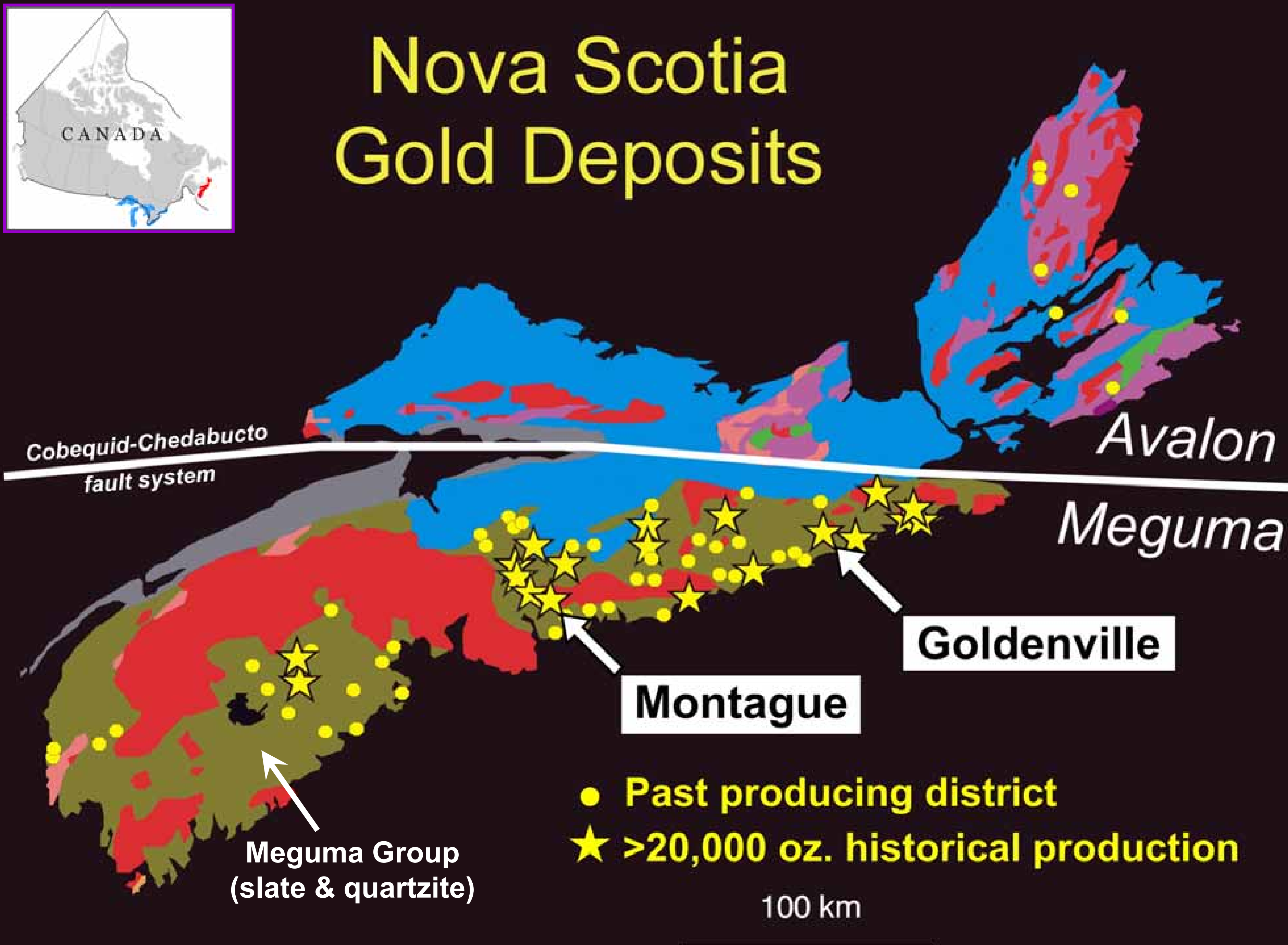
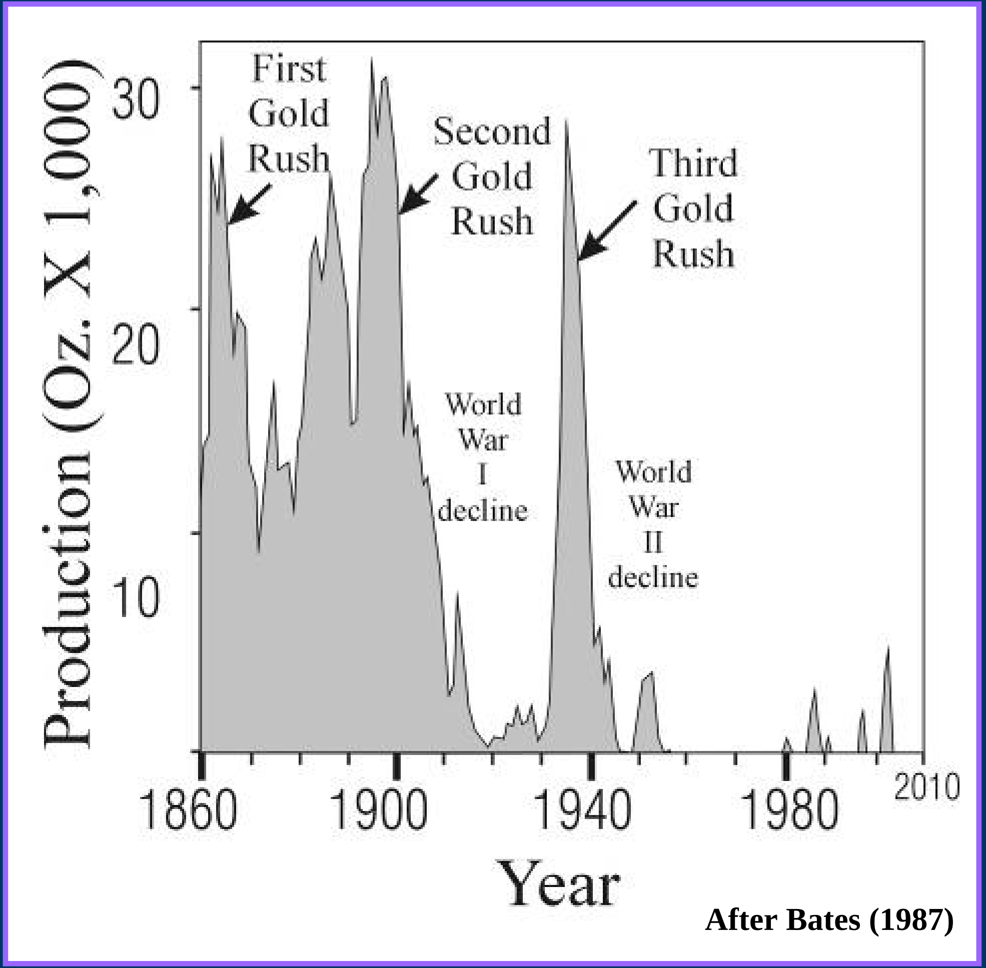
Nova Scotia Gold Deposits



History of Nova Scotia Gold Mining

- From 1861 to the mid-1940s, gold was produced from 64 mining districts, yielding ~1.2 million oz. from 3 million tonnes of crushed rock
- Both mercury amalgamation and cyanidation (post-1898) were used to extract gold
- Arsenic occurs naturally in the ore and surrounding wallrocks as arsenopyrite (FeAsS)



Nova Scotia gold production, 1861-2010

Tailings disposal at the Micmac Mill & Cyanide Plant, Leipsigate Gold District, 1904

Human Exposure to Gold Mine Tailings @ Montague

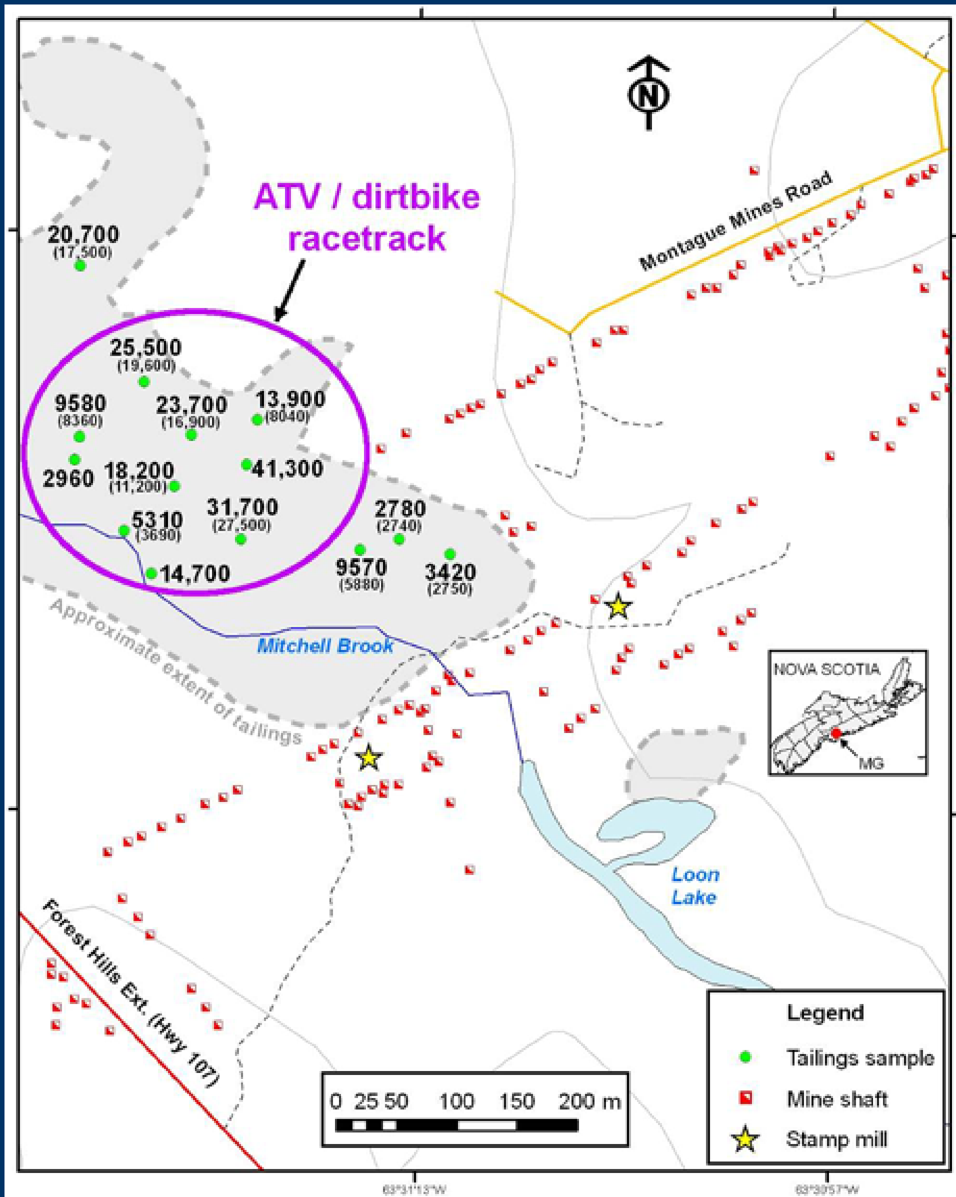


Fig. XX: As concentrations (ppm) in Montague tailings (maximum and (mean) concentrations; <2 mm size fraction).

Human Exposure to Gold Mine Tailings @ Goldenville

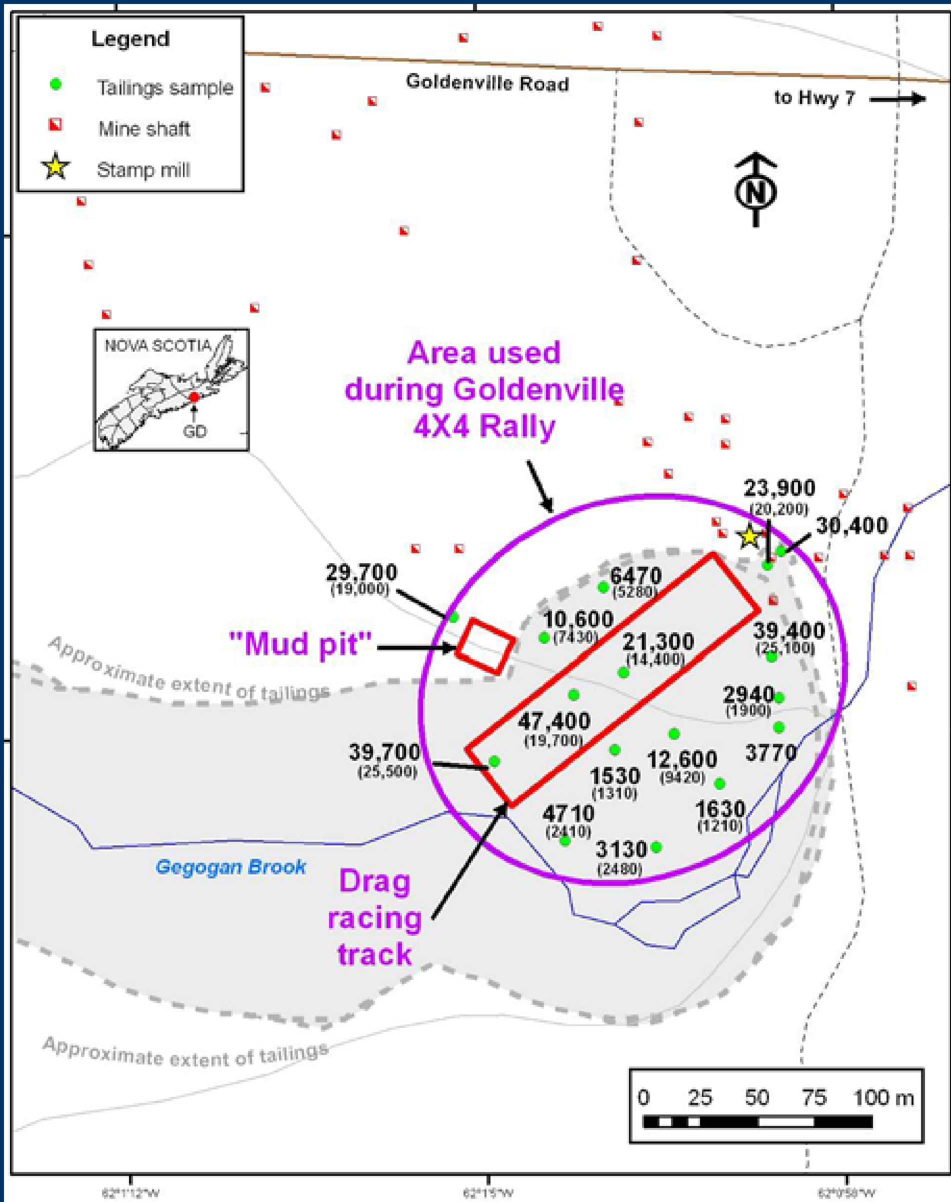


Fig. XX: As concentrations (ppm) in Goldenville tailings (maximum and mean) concentrations; <2 mm size fraction).

Research Objectives

Assess Risk

- Determine the role of mineralogy in controlling the bioaccessibility of As in weathered gold mine tailings (in collaboration with Royal Military College and others).
  - Focus on publicly accessible tailings sites used for recreation
- Determine the district-scale background concentrations of As and Hg in soils at Montague and Goldenville.

Reduce Risk

- Develop science-based guidelines to help optimize remediation strategies for high-As mine wastes.
- Communicate key project results to the Historic Gold Mines Advisory Committee in Nova Scotia to help inform risk assessment and management decisions.

Bioaccessibility Sampling (2005 & 2006) & Analysis

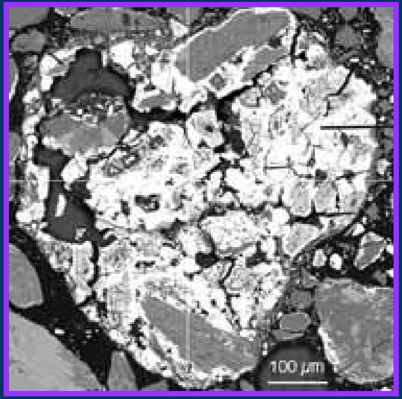
- Collected tailings and forest soils from five mine sites
- Sampling depth:
  - 0-5 cm (soils)
  - 0-10 cm (tailings)
- Air dried and dry-sieved to <150 μm
- Chemical and mineralogical analyses
- Bioaccessibility extractions (PBET)

Characterization of Mineral Hosts for As

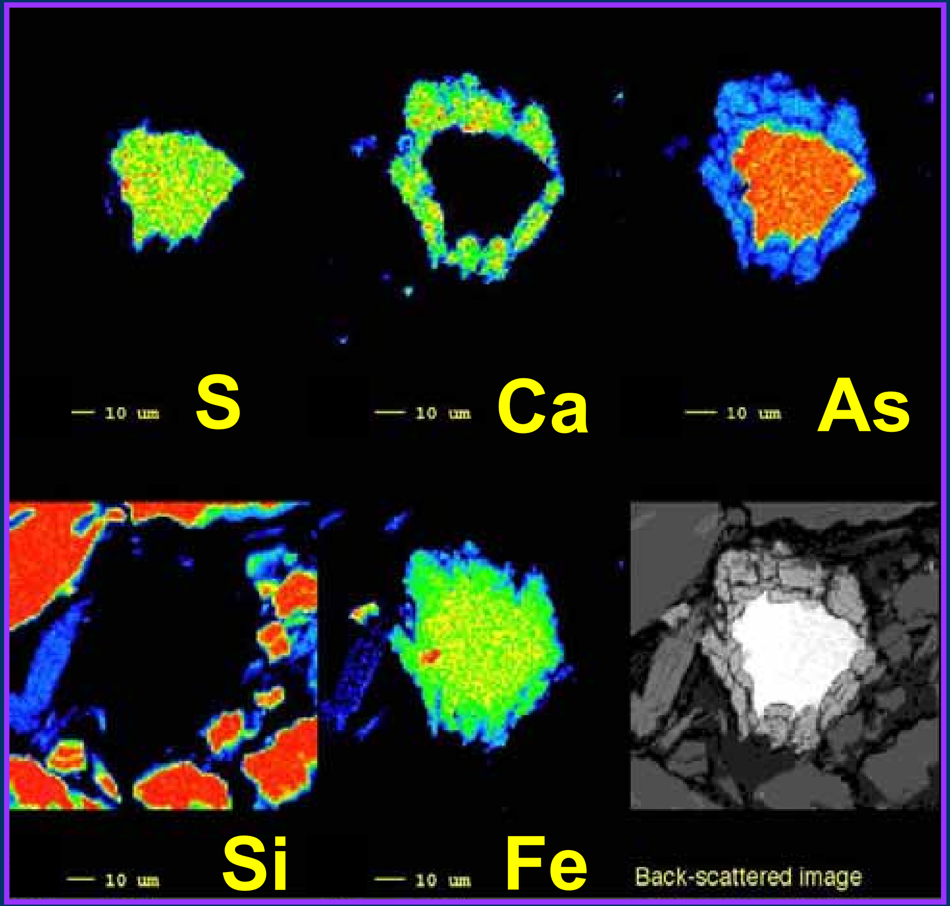
Arsenopyrite
(FeAsS)

Crystalline
scorodite
($FeAsO_4 \cdot 2H_2O$)

Amorphous
Fe arsenate
cement

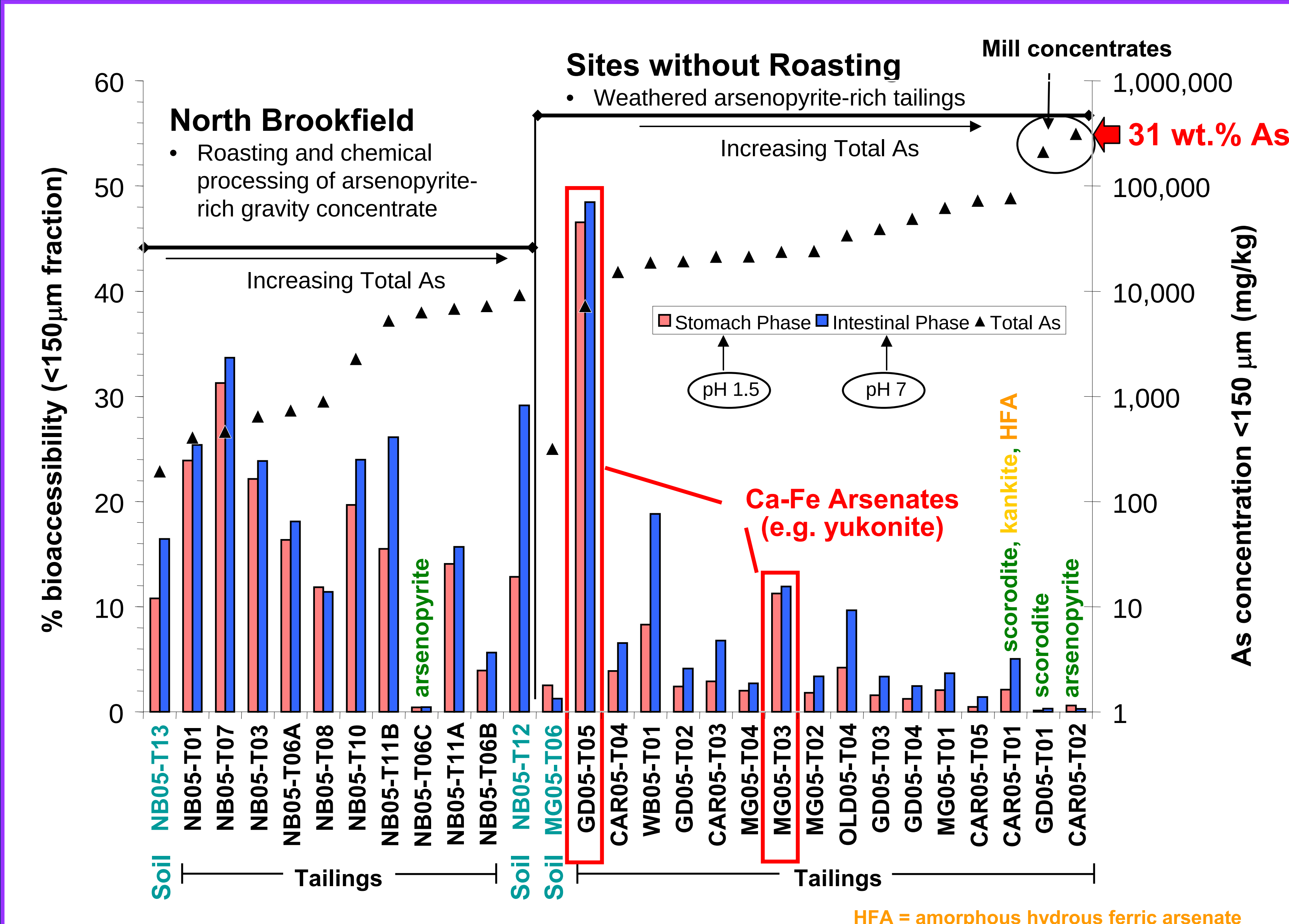


Compositional maps from electron microprobe



As-Ca bearing Fe oxyhydroxide
reaction rim on arsenopyrite

%Arsenic Bioaccessibility (from Meunier et al. 2010)



Key References

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ARSENIC MINERALOGY OF NEAR-SURFACE TAILINGS AND SOILS: INFLUENCES ON ARSENIC MOBILITY AND BIOACCESSIBILITY IN THE NOVA SCOTIA GOLD MINING DISTRICTS

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ABSTRACT

The mineral form, grain size and texture of As-bearing particles are important factors influencing the risk to human health associated with exposure to As-contaminated soils, sediments and mine wastes. Mining of arsenopyrite-bearing gold ores in Nova Scotia in the late 1800s and early 1900s has left a legacy of weathered, As-rich tailings deposits in more than 60 gold districts across the province. Fourteen samples of near-surface tailings and one of soil from several former gold mines frequented by the public were sieved to <150 μm and characterized using conventional mineralogical techniques (XRD, microscopy and EPMA) and synchrotron micro-analysis (μ-X-ray diffraction, μ-X-ray fluorescence and μ-X-ray absorption spectroscopy). Two high-As (>20% As) mill concentrates exposed at the surface within the tailings deposits are dominated by a single As mineral, fine-grained scorodite ($FeAsO_4 \cdot 2H_2O$) in one case, and massive unweathered arsenopyrite in the other. In the tailings (0.7 to 7% As), scorodite and amorphous hydrous ferric arsenate (HFA) are the most common As-bearing major components, occurring as discrete grains or grain coatings on gangue minerals. Other major As phases identified in the tailings include As-bearing amorphous hydrous ferric oxyhydroxides (HFO), kaňkite ($FeAsO_4 \cdot 3.5H_2O$), pharmacosiderite [$KFe_4(AsO_4)_3(OH)_4 \cdot 6–7H_2O$], yukonite [$Ca_7Fe_{12}(AsO_4)_{10}(OH)_{20} \cdot 15H_2O$], amorphous Ca–Fe arsenates, and arsenopyrite. Minor or trace constituents include: As-bearing ferric oxyhydroxides with up to 10% As (HFO, goethite, lepidocrocite and akaganeite), As-bearing sulfates (jarosite [$(K,Na,H_3O)Fe_3(SO_4)_2(OH)_6$], tooeleite [$Fe_6(AsO_3)_4(SO_4)(OH)_4 \cdot 4H_2O$]) and realgar ($As_4S_4$). Arsenic-bearing HFO (2.5% As) and goethite (0.08% As) were identified in the single B-horizon soil sample. This study is part of a broader coordinated effort by a multi-department federal and provincial advisory committee formed to coordinate the study of ecosystem and human health risks associated with historical gold mine sites in Nova Scotia. Our study shows that (i) the mineralogy of As in weathered tailings is highly variable, with aggregates of more than one As-bearing phase common in a given sample, and (ii) major differences in As mineralogy in the tailings are mainly controlled by factors that influence the weathering history (*e.g.*, presence or absence of mill concentrates, degree of water saturation, and abundance of relict carbonate minerals). The variable solubility of these primary and secondary As-bearing minerals influences both the environmental mobility and the bioaccessibility of As in near-surface tailings and soil samples.

Keywords: arsenic-rich tailings, gold mining, bioaccessibility, arsenopyrite, secondary minerals, scorodite, amorphous iron arsenate, yukonite, pharmacosiderite, iron oxyhydroxides, Nova Scotia.

Environ. Sci. Technol. **XXXX**, *xxx*, 000–000

Effects of Soil Composition and Mineralogy on the Bioaccessibility of Arsenic from Tailings and Soil in Gold Mine Districts of Nova Scotia

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Bioaccessibility tests and mineralogical analyses were performed on arsenic-contaminated tailings and soils from gold mine districts of Nova Scotia, Canada, to examine the links between soil composition, mineralogy, and arsenic bioaccessibility. Arsenic bioaccessibility ranges from 0.1% to 49%. A weak correlation was observed between total and bioaccessible arsenic concentrations, and the arsenic bioaccessibility was not correlated with other elements. Bulk X-ray absorption near-edge structure analysis shows arsenic in these near-surface samples is mainly in the pentavalent form, indicating that most of the arsenopyrite (As^{1-}) originally present in the tailings and soils has been oxidized during weathering reactions. Detailed mineralogical analyses of individual samples have identified up to seven arsenic species, the relative proportions of which appear to affect arsenic bioaccessibility. The highest arsenic bioaccessibility (up to 49%) is associated with the presence of calcium–iron arsenate. Samples containing arsenic predominantly as arsenopyrite or scorodite have the lowest bioaccessibility (<1%). Other arsenic species identified (predominantly amorphous iron arsenates and arsenic-bearing iron(oxy)hydroxides) are associated with intermediate bioaccessibility (1 to 10%). The presence of a more soluble arsenic phase, even at low concentrations, results in increased arsenic bioaccessibility from the mixed arsenic phases associated with tailings and mine-impacted soils.

Introduction

Gold mines were in operation in the province of Nova Scotia, on the eastern coast of Canada, from the 1860s to the mid-1940s (*1*). During this time, naturally occurring arsenopyrite was processed and deposited with some three million tonnes of mine tailings within 64 gold-mining districts in Nova Scotia (*2*). Postdepositional erosion and weathering processes have redistributed and oxidized most of the near-surface (0–10 cm) arsenic-rich tailings. Samples of tailings collected in Nova Scotia have arsenic concentrations ranging from 9.0 $mg \cdot kg^{-1}$ to 310,000 $mg \cdot kg^{-1}$ (31 wt %), (n = 433; mean = 10,000 $mg \cdot kg^{-1}$) (*3*), 99% of which exceed the local regulatory level of 12 $mg \cdot kg^{-1}$ (*4*). The presence of a contaminant in excess of these guidelines may prompt a risk assessment (*5*), especially when the sampled locations are adjacent to residential properties and used for recreational activities, such as in Nova Scotia. A major pathway contributing to human health risk, especially in children, is incidental soil ingestion (*6*). Once ingested, a portion of the arsenic may solubilize (i.e., become bioaccessible) in the gastrointestinal tract, and some of this may be absorbed (i.e., become bioavailable) into systemic circulation (*7*). The solubilized arsenic forms (predominantly trivalent and pentavalent arsenic compounds) are known to be toxic and carcinogenic (*8*). Estimating the bioaccessibility of arsenic from site-specific soil samples provides a more accurate approximation of the relevant dose and as such is an important component of risk assessment (*9*).

In this study, the bioaccessibility of arsenic was determined using an *in vitro* physiologically based extraction test (PBET). This method is based on Ruby et al. (*10*) and Rodriguez et al. (*6*) and is similar to previously published tests (*11, 12*). For arsenic-contaminated mine waste samples, results obtained using a similar PBET were well correlated to *in vivo* (rats and cattle) bioavailability (*13*). Wide variations in arsenic bioaccessibility from previous PBET studies (from 0.50 to 66 wt %) may be attributed to soil elemental composition and arsenic speciation (*7, 14*). This variability can also result from a number of parameters, including the pH of the simulated solution (*10*), the chosen liquid-to-solid ratio (*15*), and sample particle size (*16*). Such variability introduces uncertainty concerning the relevance of bioaccessibility measurements (*9*) and limits the acceptance of bioaccessibility measurements by end users and regulators (*17*).

Furthermore, the effect of mineralogical composition on arsenic bioaccessibility has not been thoroughly determined, and previous studies have focused on pure mineral forms and model soils. Arsenic sulfides (e.g., arsenopyrite FeAsS) are among the least bioaccessible forms of arsenic from soil (<1%) (*7*). Iron–arsenic oxides (especially amorphous iron oxides and hydroxides) tend to have intermediate bioaccessibility (<5%) (*18*), and arsenic trioxide is considered comparatively more bioaccessible (*7*). The solubility of arsenic-bearing minerals may be influenced by encapsulation or coating of grains, affecting their bioaccessibility (*7, 17*), and the presence of dissolved organic carbon may promote the solubility of arsenic in soils (*19*).

The present study focused on the multiple arsenic mineral forms present in the arsenic-enriched tailings and soils of abandoned gold mine sites. The first objective was to assess the influence of various PBET method parameters (e.g., liquid-to-solid ratio, particle size) in evaluating the bioaccessibility of arsenic in mine tailings and soils. The second objective was to determine the extent to which soil composition (organic carbon, elemental composition) and arsenic mineralogy (oxidation state(s), bulk, and detailed speciation) affect the bioaccessibility of arsenic. X-ray Absorption Near-Edge Structure (XANES) analysis was used to determine the

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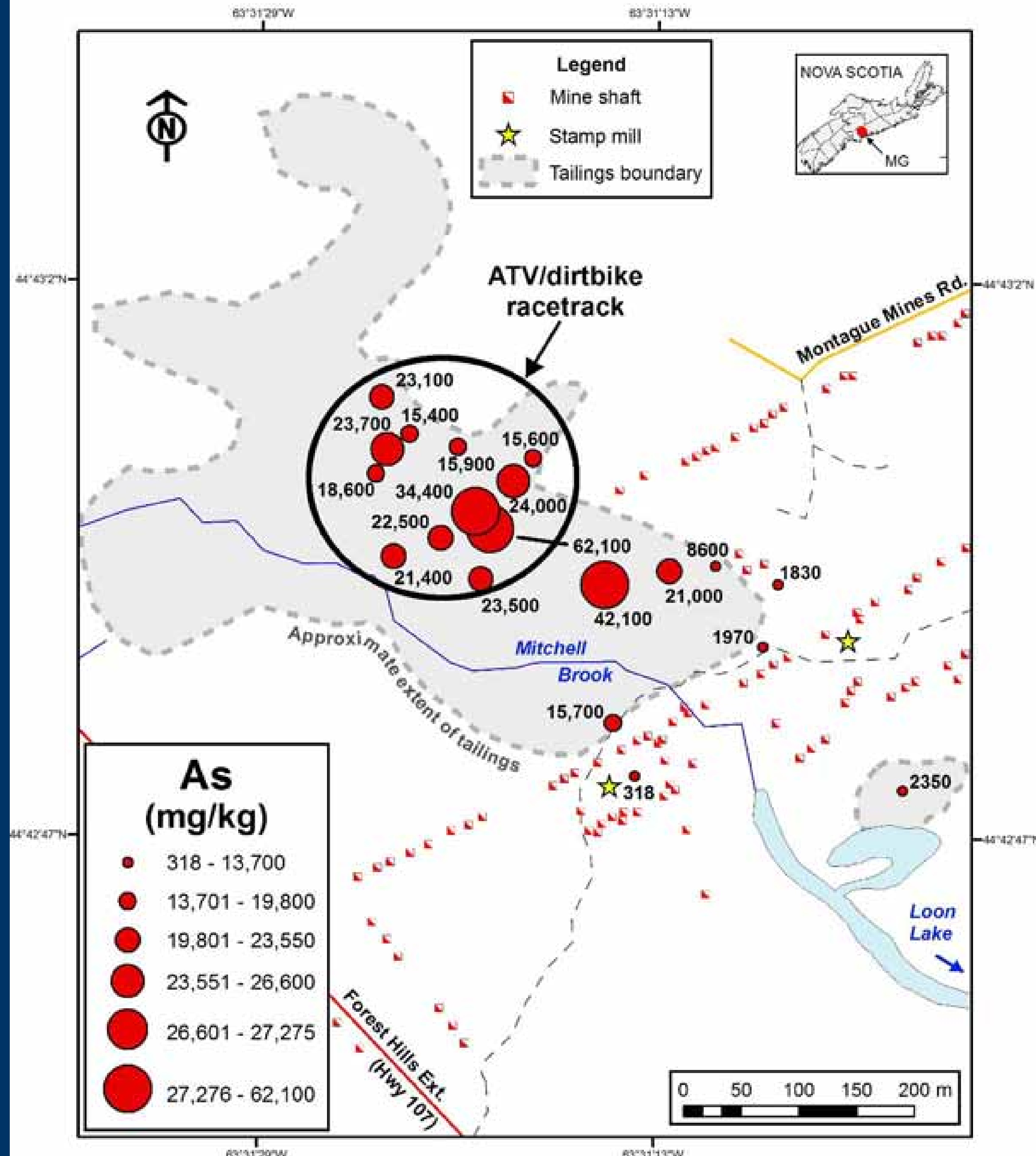
|| Natural Resources Canada, Geological Survey of Canada (Atlantic).

Montague

Total As (mg/kg) in near-surface tailings & soils

(<150 µm size fraction)

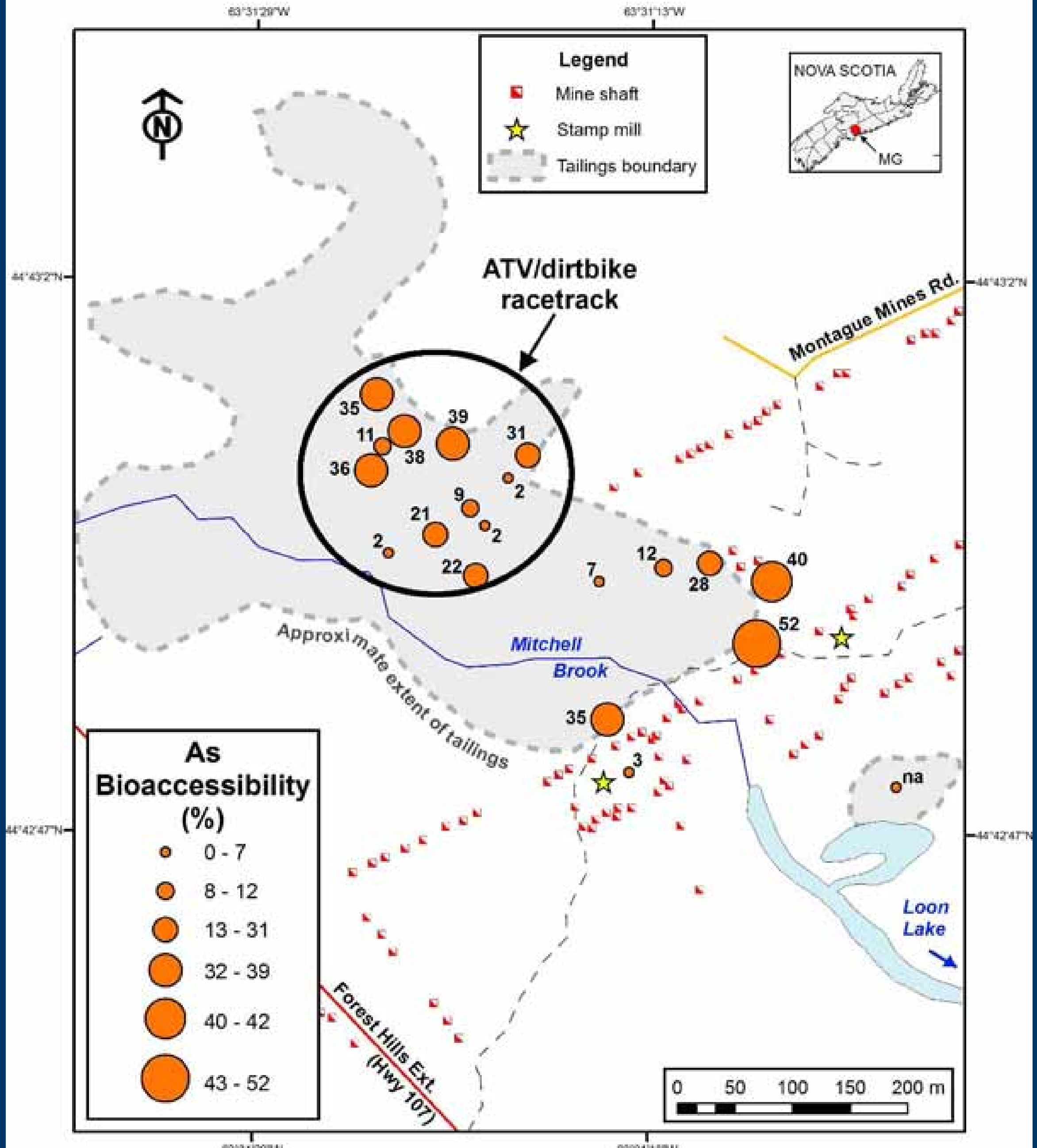


Arsenic (As) concentrations (mg/kg, <150 µm size fraction) in tailings from Montague Gold District, 2005-2006.

Montague

Bioaccessible As (%) in near-surface tailings & soils

(<150 µm size fraction; data from Matt Dodd, Royal Roads University)

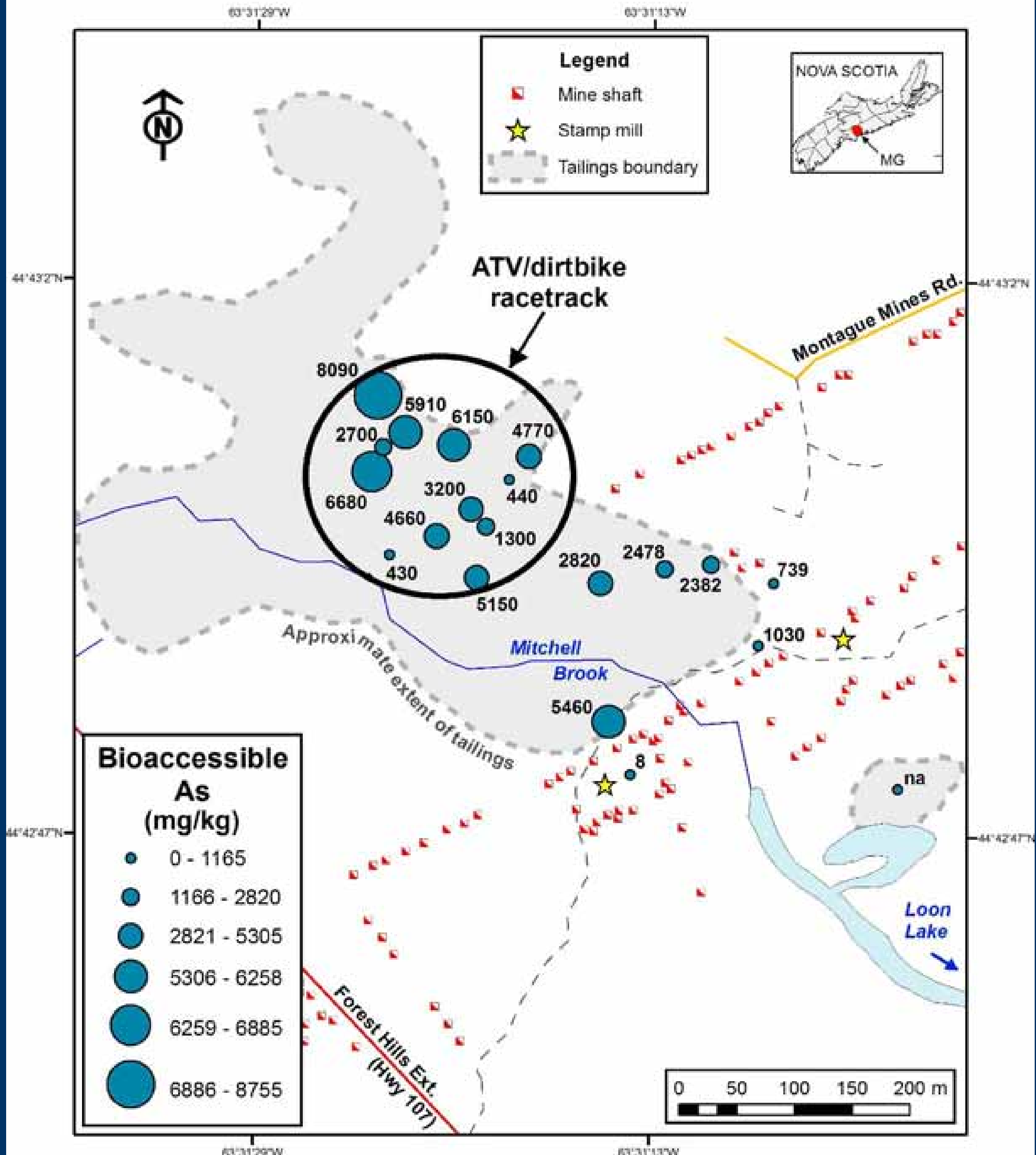


Percent arsenic (As) bioaccessibility in tailings (<150 µm size fraction) from Montague Gold District, 2005-2006.

Montague

Bioaccessible As (mg/kg) in near-surface tailings & soils

(<150 µm size fraction; data from Matt Dodd, Royal Roads University)

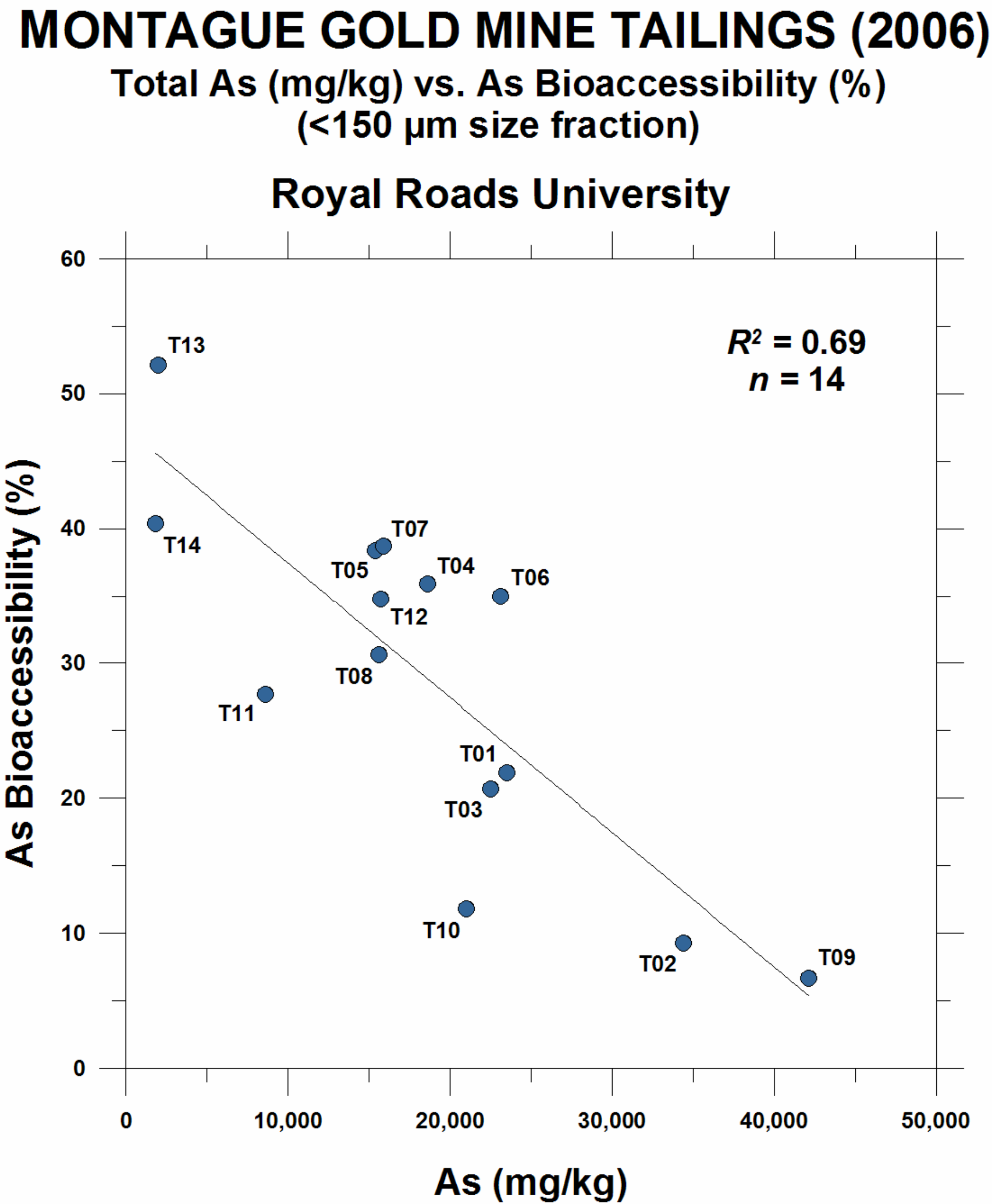


Bioaccessible arsenic (mg/kg dry wt., <150 µm size fraction) in tailings from Montague Gold District, 2005-2006.

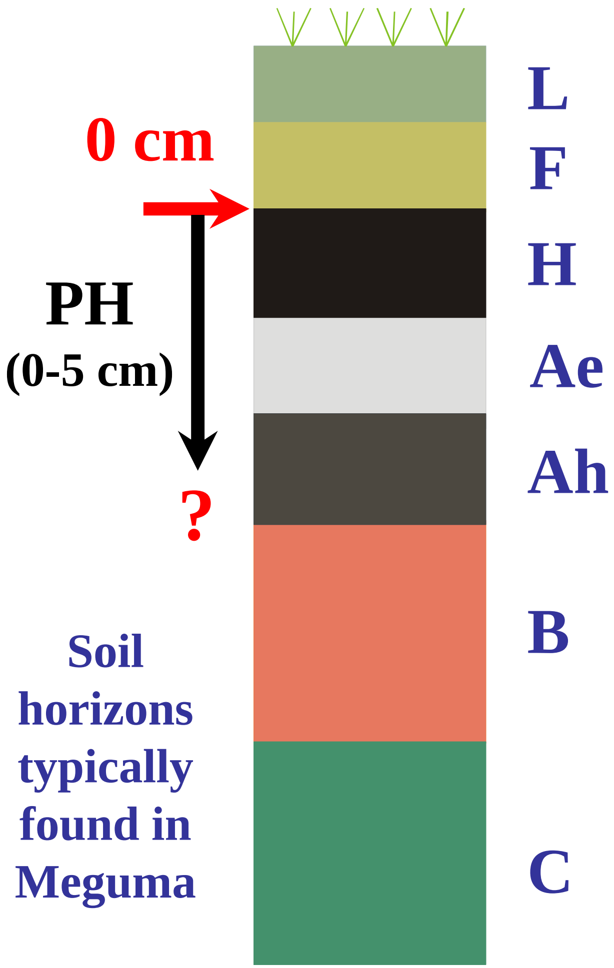
Montague

Total As (mg/kg) vs Bioaccessible As in near-surface tailings & soils

(<150 µm size fraction; data from Matt Dodd, Royal Roads University))



Background soil sampling



- In 2007, NRCan collected samples of the top 0-5 cm of soil (the Public Health (PH) layer) from 46 sites near Montague, and 39 sites near Goldenville
- Samples of individual soil horizons (H, Ae, B, and C) were also collected from 10 sites in Montague, and 6 sites in Goldenville
- Samples were air dried, sieved to various grain size fractions (<2 mm, <150 µm, <63 µm), and digested and analyzed for As and Hg using USEPA Method 3050B (HNO_3-H_2O_2) and a modified *aqua regia* digestion (HNO_3-HCl, 1:1)
- Organic and inorganic carbon were measured using a LECO combustion analyzer

Typical soil horizons at Montague

Public Health Layer

(0-5 cm)

L

F

H

Ae

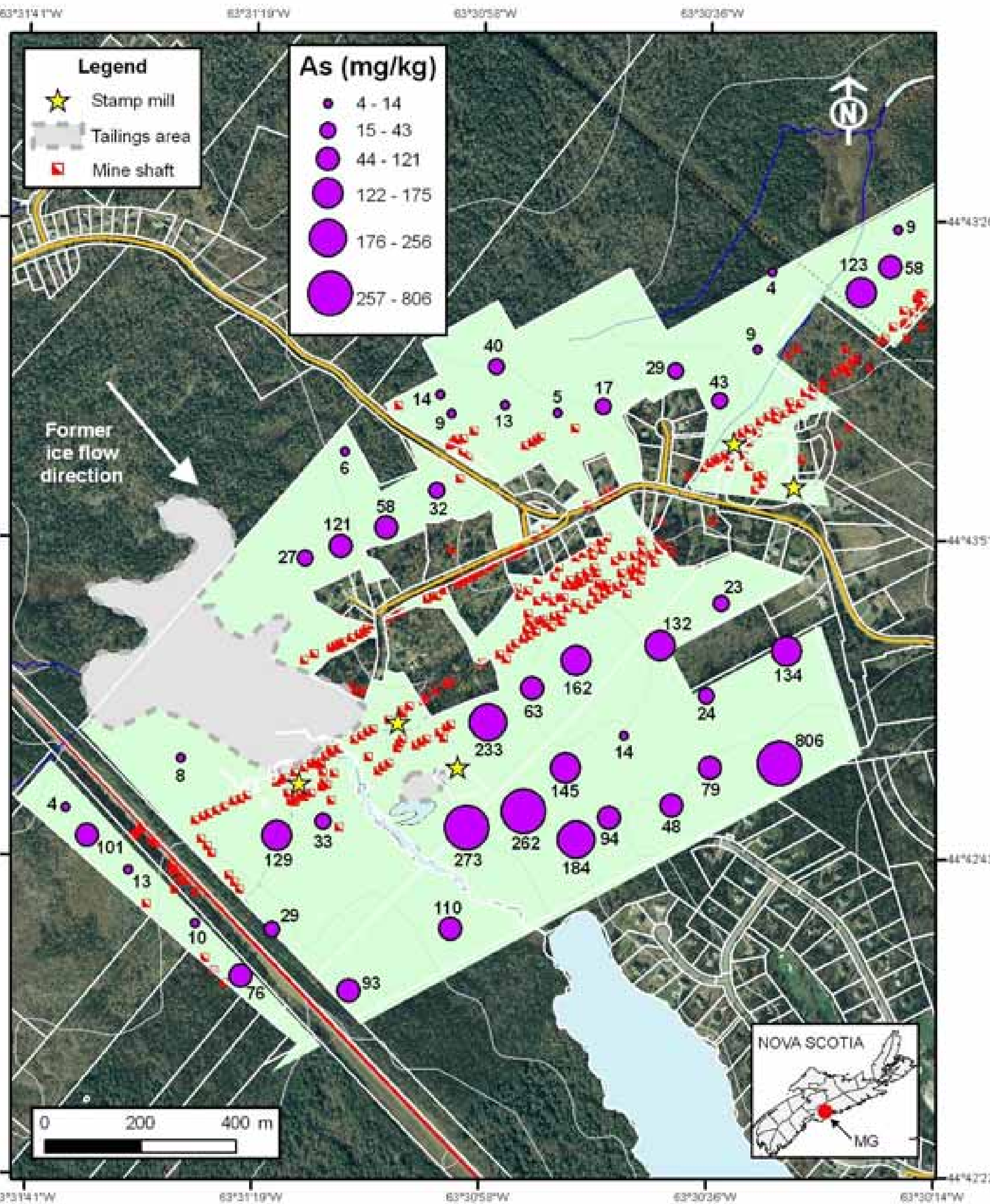
B

C

Montague

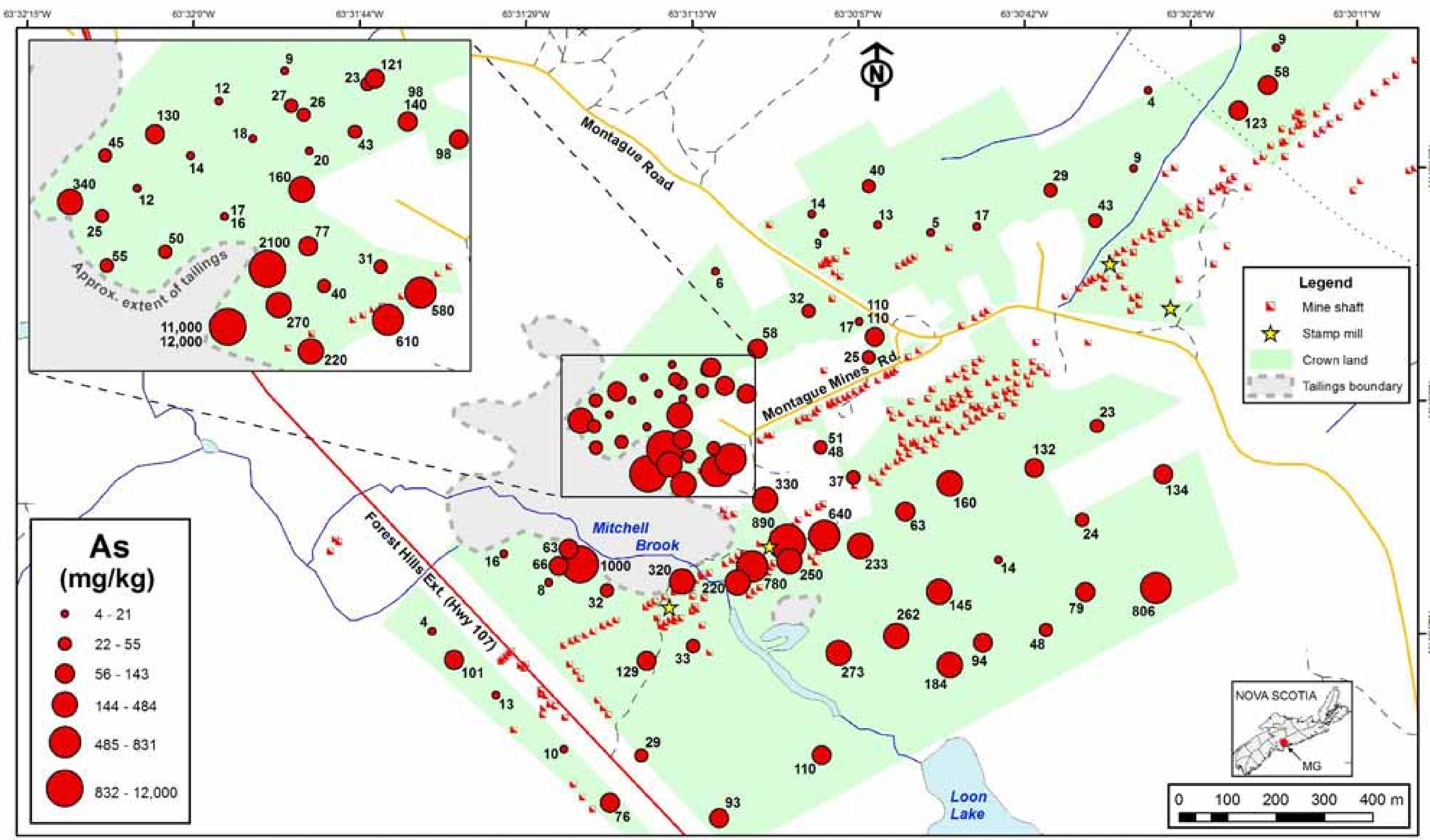
As (mg/kg) in the PH layer (0-5 cm)

(<2 mm size fraction, 3050B digestion)



As concentrations (mg/kg) in the top 0-5 cm of soils (<2 mm size fraction) near Montague Gold Mines. The extent of Crown Lands is indicated by light green shading.

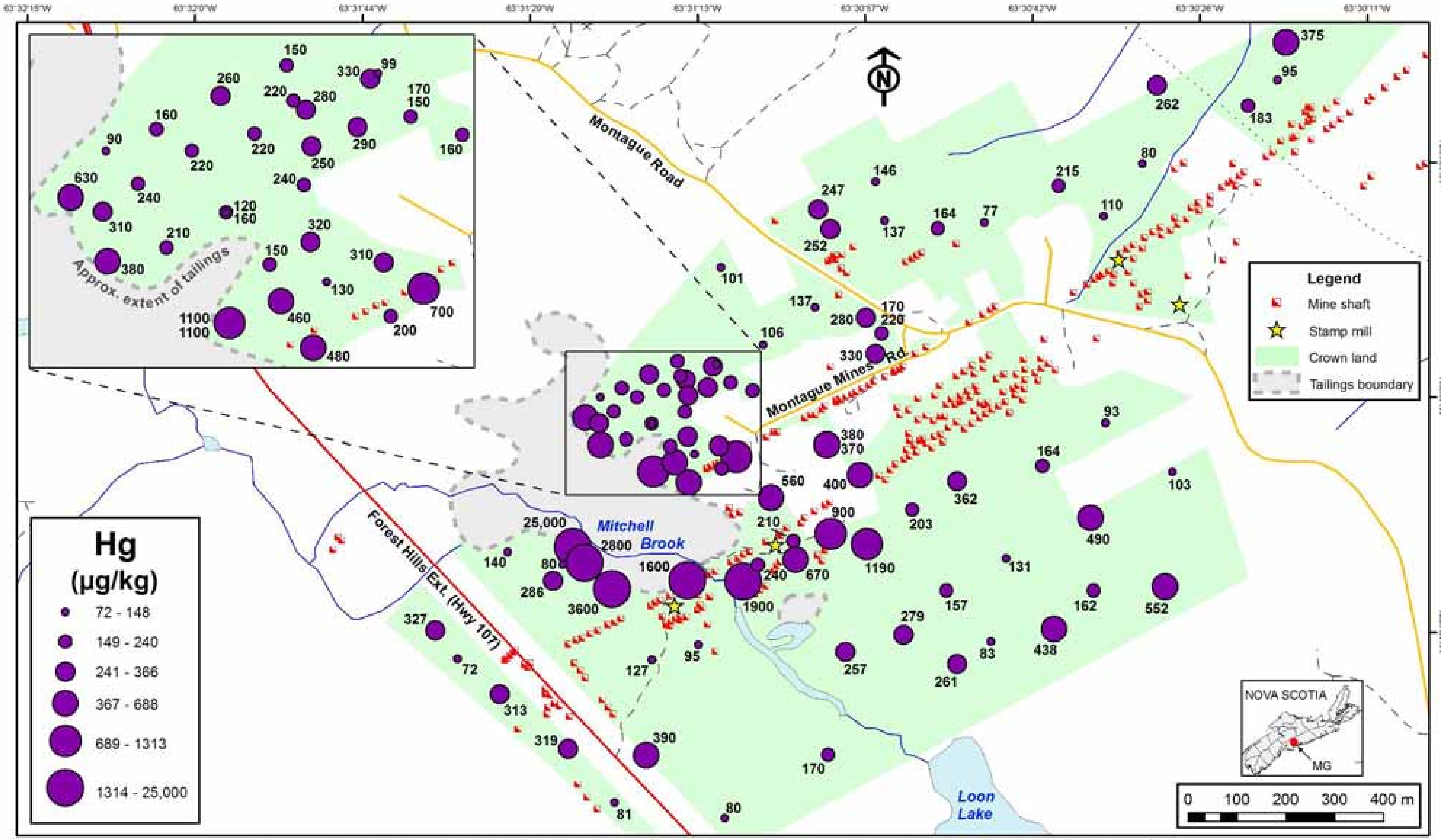
Montague: As (mg/kg) in the PH layer (0-5 cm, < 2 mm)



Arsenic concentrations (mg/kg) in the top 0-5 cm of soils (<2 mm size fraction) from Montague Gold District, 2007-2008.

Near-field data from Environmental Site Assessment Report (Maritime Testing, 2009)

Montague: Hg (µg/kg) in the PH layer (0-5 cm, < 2 mm)



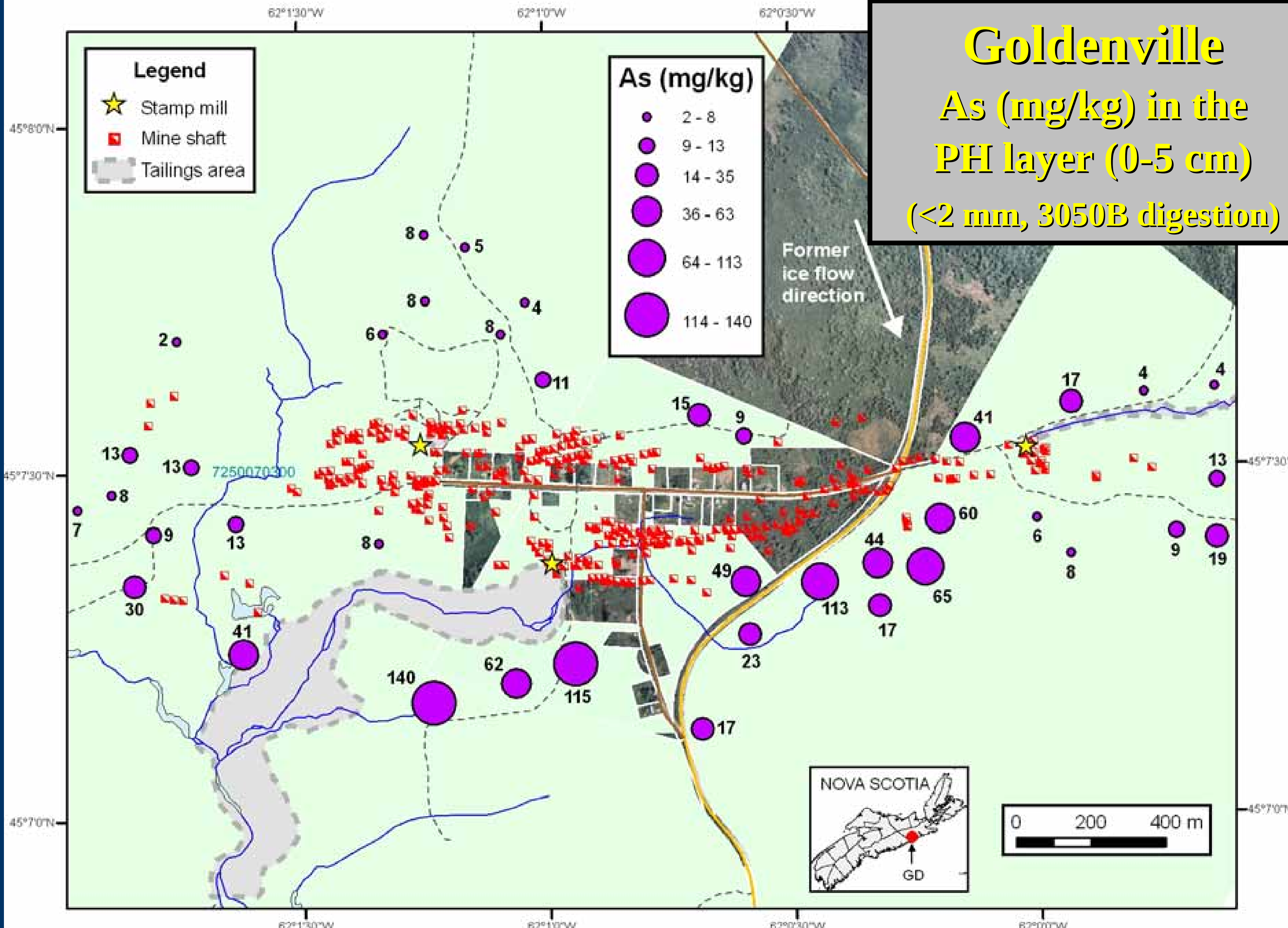
Mercury concentrations (µg/kg) in the top 0-5 cm of soils (<2 mm size fraction) from Montague Gold District, 2007-2008.

Near-field data from Environmental Site Assessment Report (Maritime Testing, 2009)

Goldenville

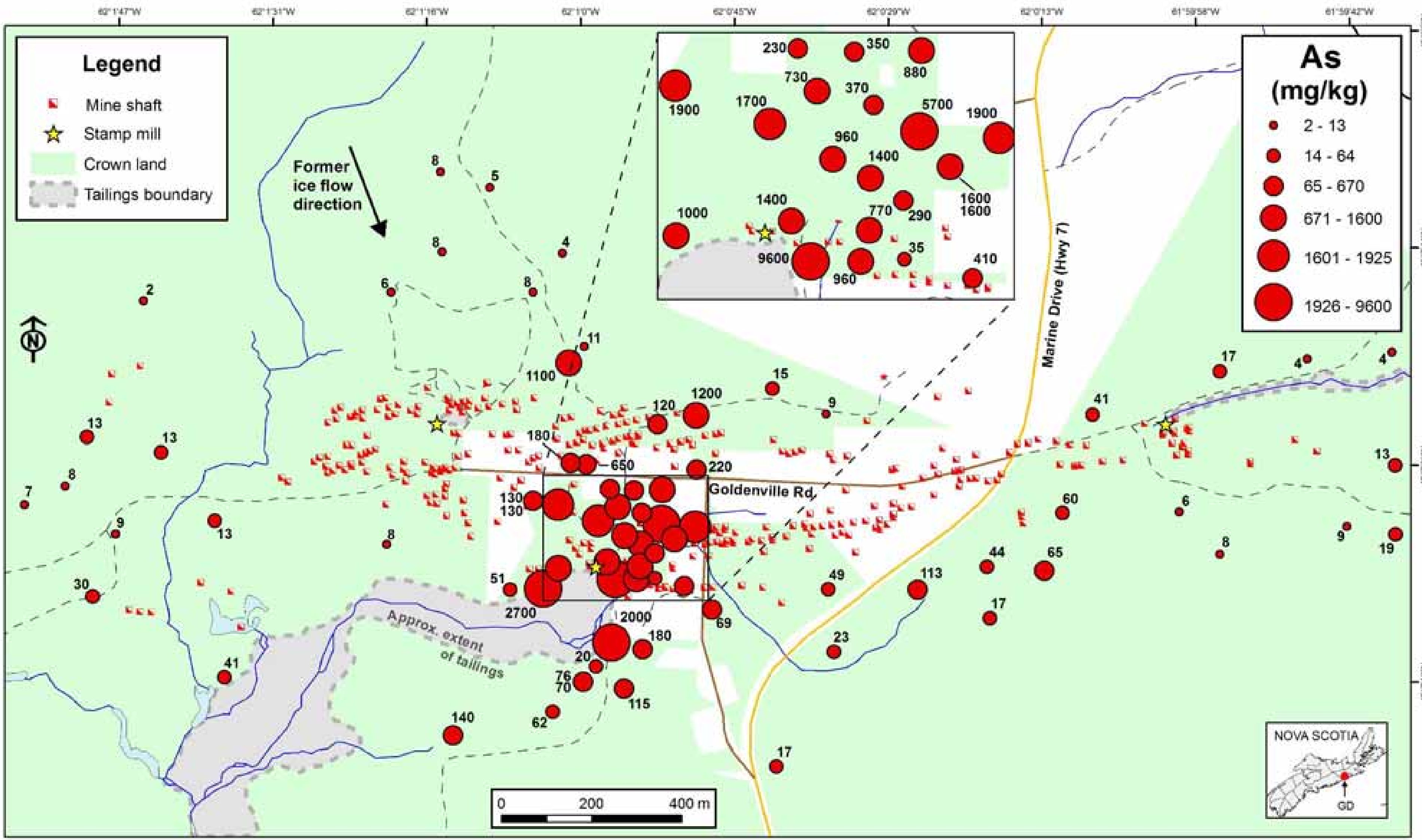
As (mg/kg) in the PH layer (0-5 cm)

(<2 mm, 3050B digestion)



As concentrations (mg/kg) in the top 0-5 cm of soils (<2 mm size fraction) near Goldenville Gold Mines. The extent of Crown Lands is indicated by light green shading.

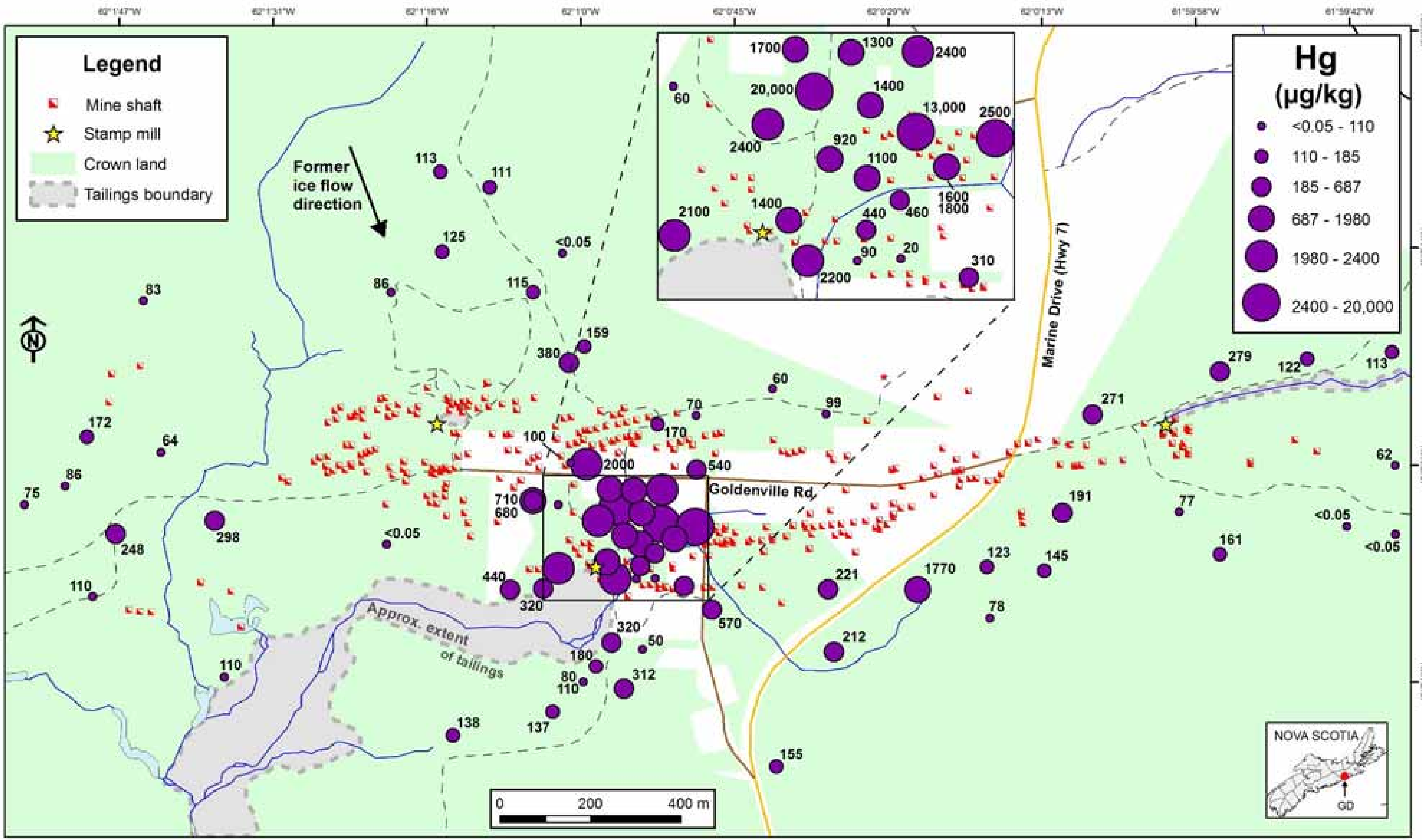
Goldenville: As (mg/kg) in the PH layer (0-5 cm, < 2 mm)



Arsenic concentrations (mg/kg) in the top 0-5 cm of soils (<2 mm size fraction) from Goldenville Gold District, 2007-2008.

Near-field data from Environmental Site Assessment Report (C.J. MacLellan & Associates, 2009)

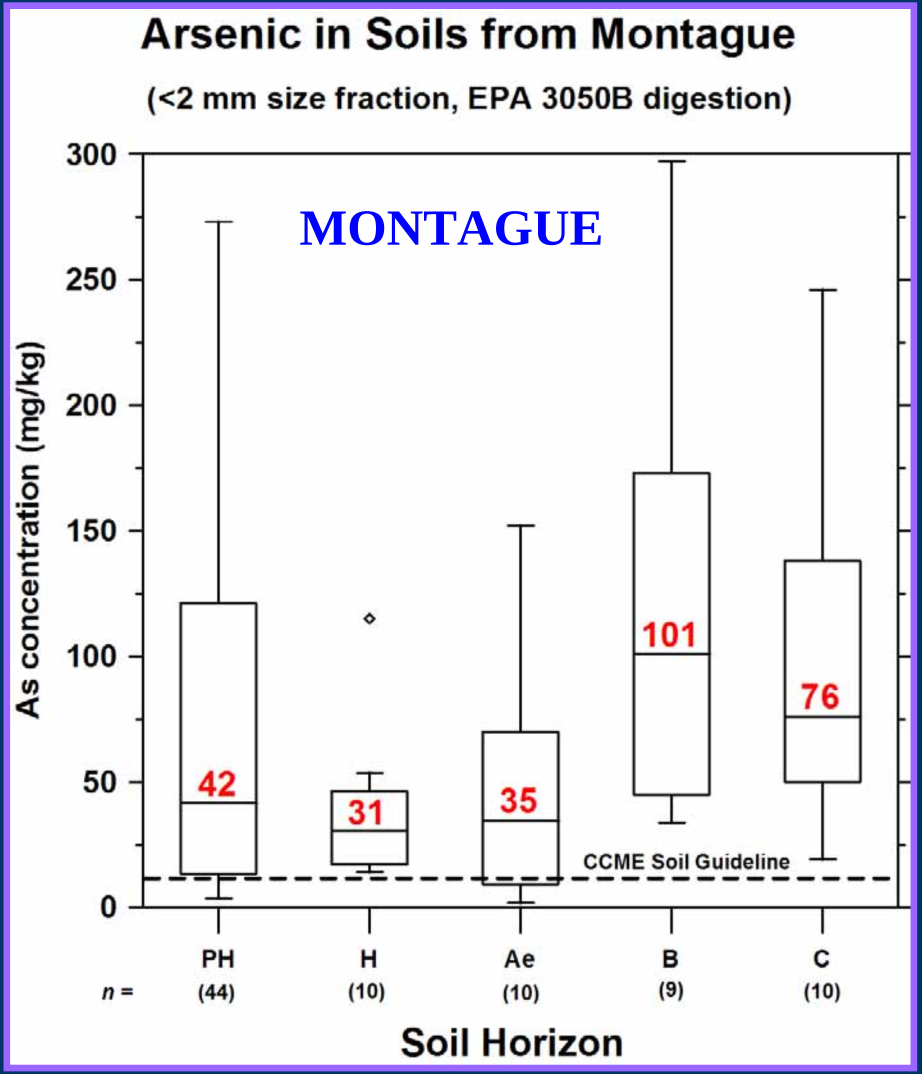
Goldenville: Hg (µg/kg) in the PH layer (0-5 cm, < 2 mm)

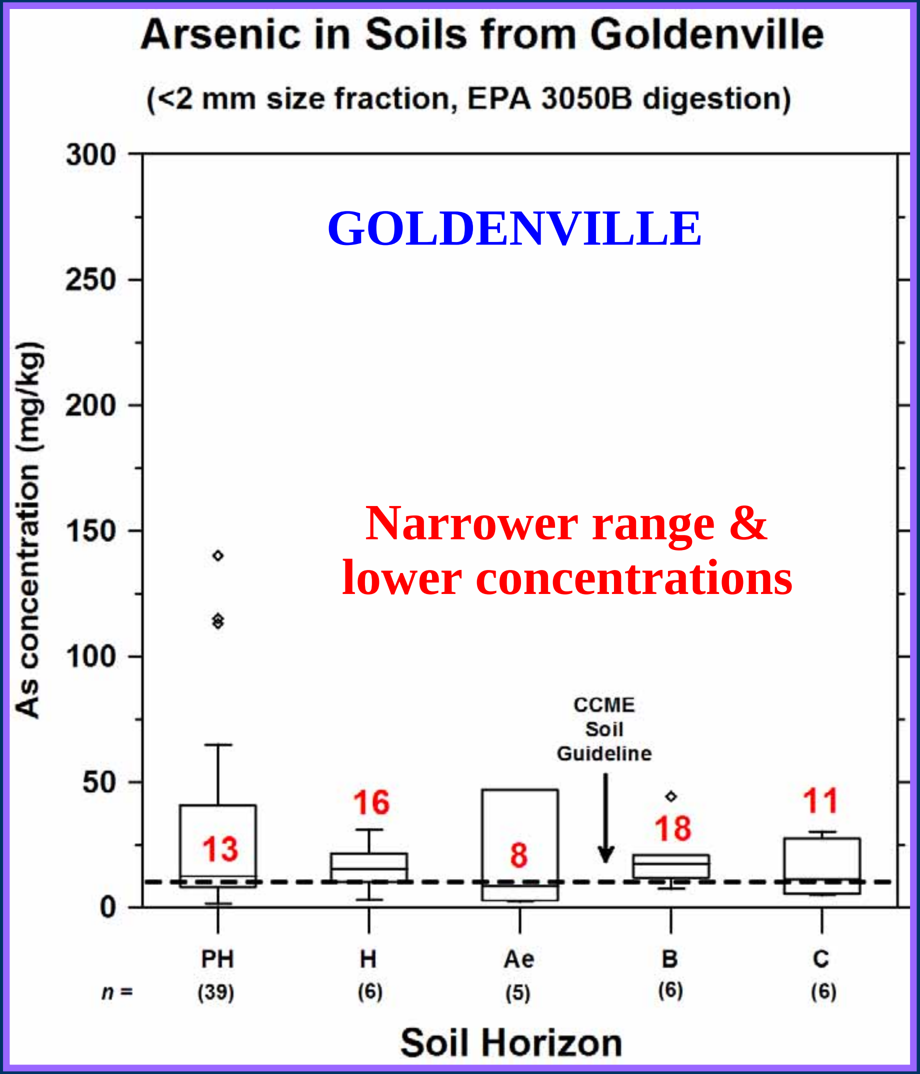


Mercury concentrations (µg/kg) in the top 0-5 cm of soils (<2 mm size fraction) from Goldenville Gold District, 2007-2008.

Near-field data from Environmental Site Assessment Report (C.J. MacLellan & Associates, 2009)

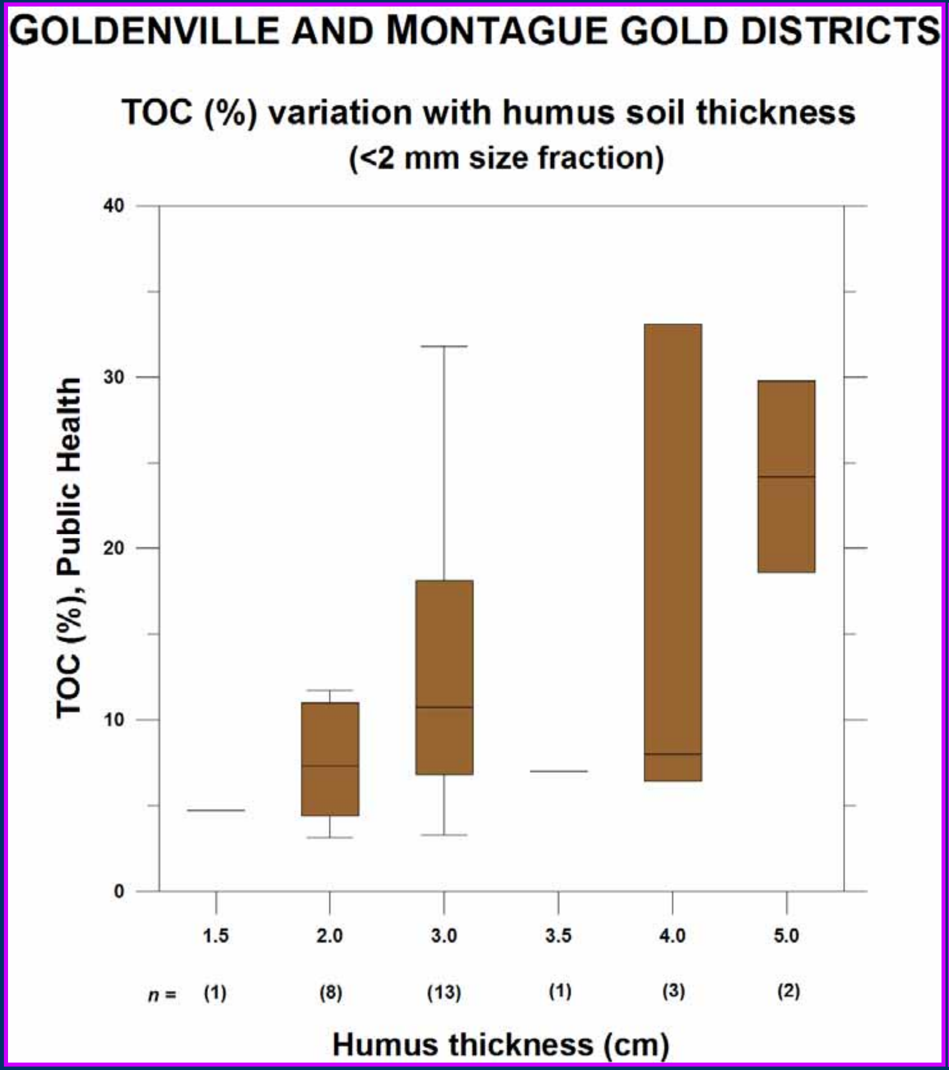
As in Soil Horizons at Montague and Goldenville

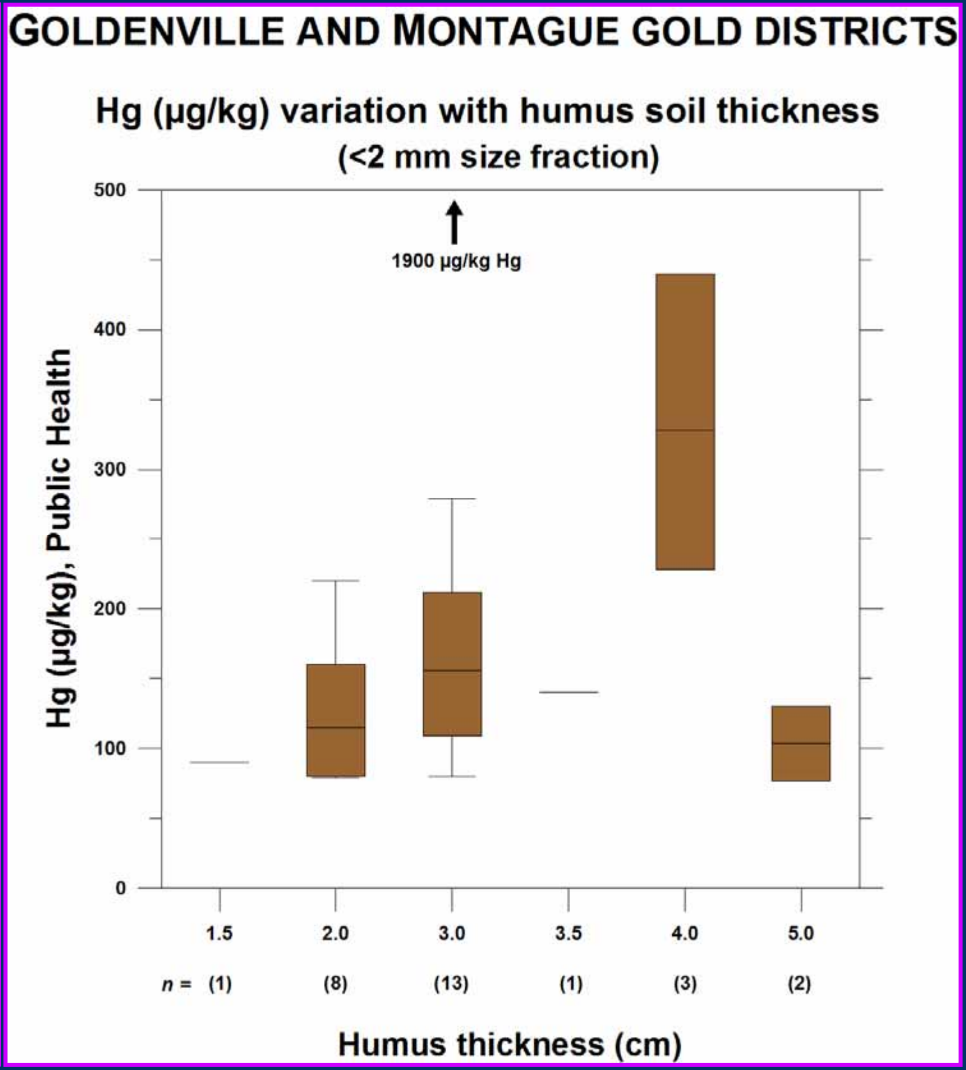




CCME Soil Quality Guideline for As: 12 mg/kg

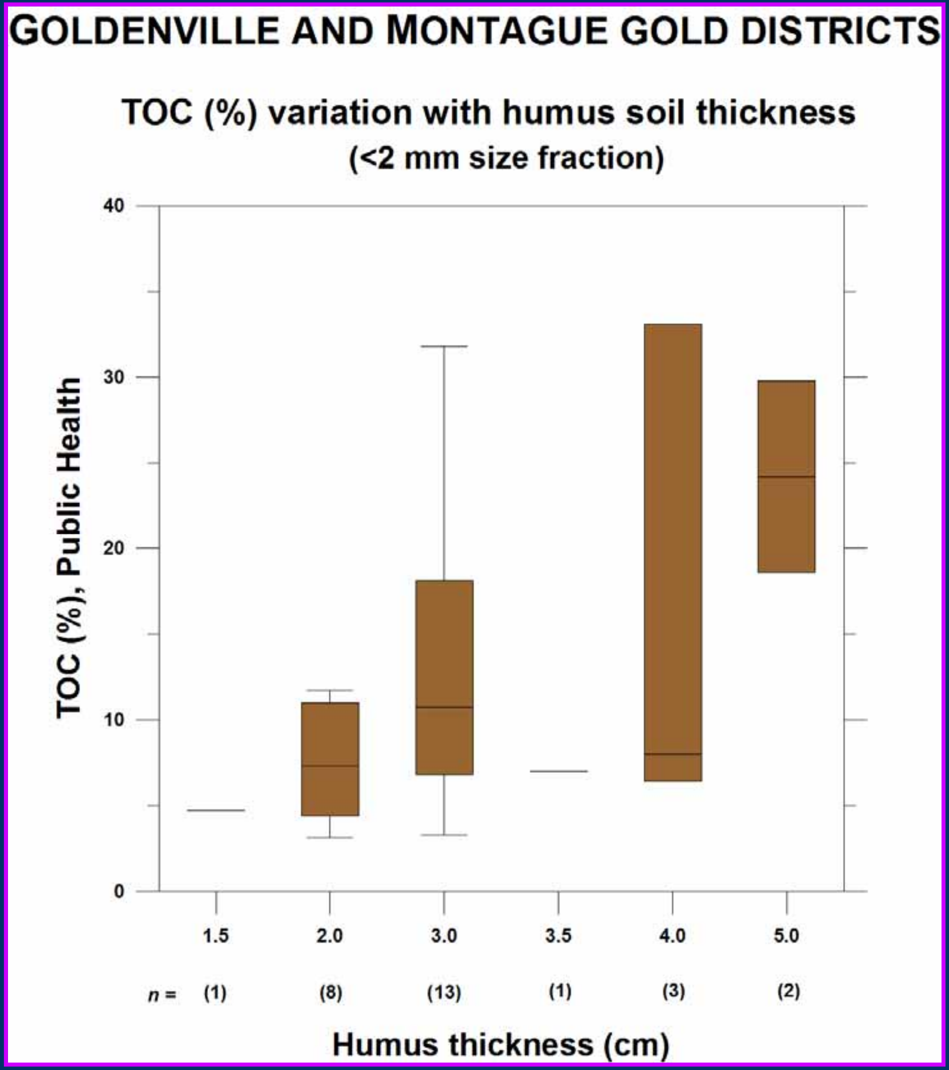
TOC and Hg Variation with Humus Layer Thickness

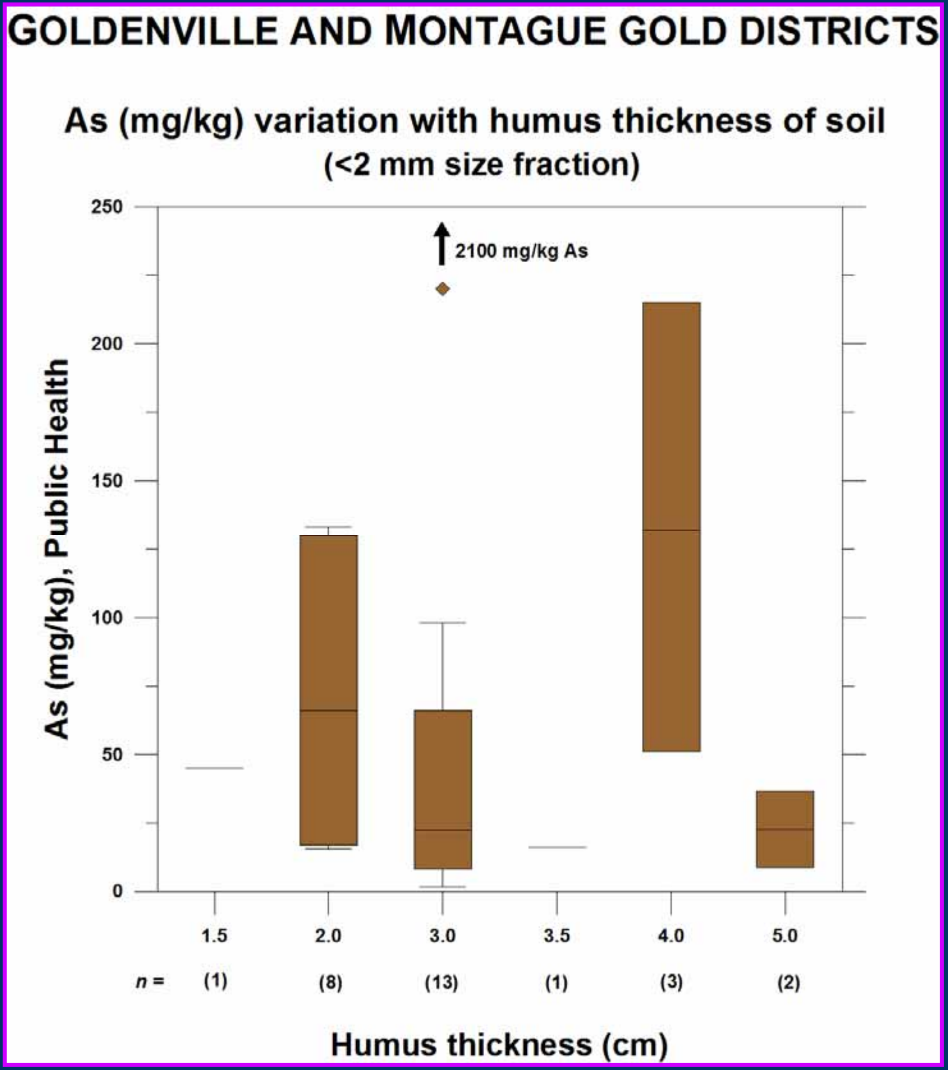




In general, thicker H-horizon = higher Hg content

TOC and As Variation with Humus Layer Thickness

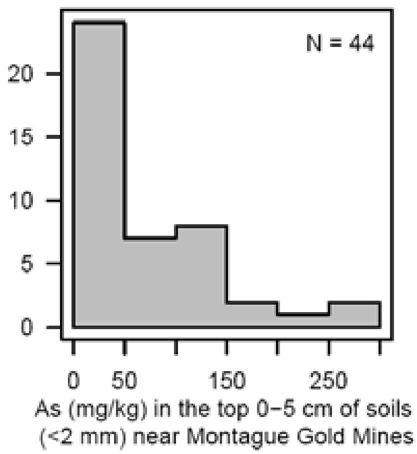




Higher As content with thicker H thickness may reflect inclusion of some mineral soil in samples

Estimation of As threshold in PH Layer
(outer limit of background variation)

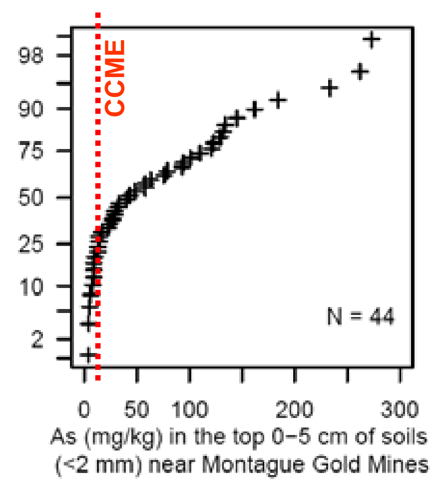
MONTAGUE



Summary Statistics

Maximum	273
98th Percentile	263.5
95th Percentile	225.7
90th Percentile	156.9
3rd Quartile	112.8
Median	41.5
1st Quartile	13.75
10th Percentile	8.3
5th Percentile	5.15
2nd Percentile	4
Minimum	4
Median Abs. Deviation	48.9
IQR Est. of Std. Dev.	72.9
Mean	70.3
Standard Deviation	71.3

% Probability Plot

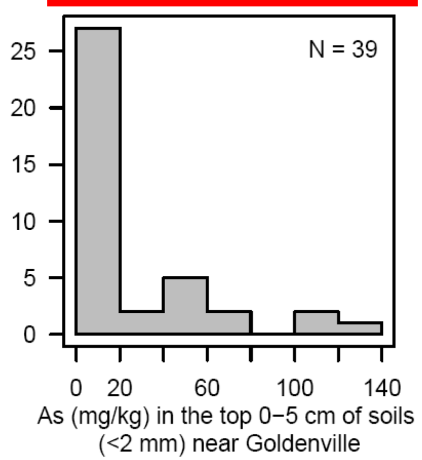


Range
4-273 mg/kg

98th %tile
264 mg/kg

95% UPL
255 mg/kg

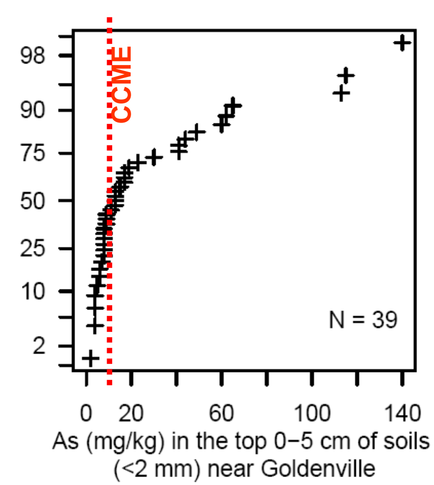
GOLDENVILLE



Summary Statistics

Maximum	140
98th Percentile	121
95th Percentile	113.2
90th Percentile	62.6
3rd Quartile	35.5
Median	13
1st Quartile	8
10th Percentile	4.8
5th Percentile	4
2nd Percentile	2.76
Minimum	2
Median Abs. Deviation	8.9
IQR Est. of Std. Dev.	20.2
Mean	26.8
Standard Deviation	33.1

% Probability Plot



Range
2-140 mg/kg

98th %tile
121 mg/kg

95% UPL
115 mg/kg

Objectives of Current Study

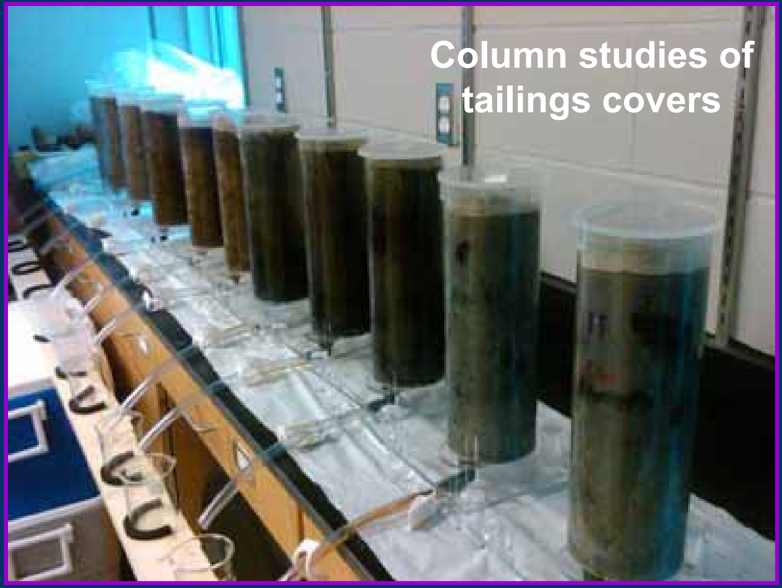
(A partnership between NRCan, Queen's, UOttawa, Trent Univ., AMEC, SRK Consulting, and the Province of Nova Scotia)

- Design appropriate remediation strategies for As-rich historical gold mine tailings in Nova Scotia that (i) prevent As concentrations increasing in downstream surface and groundwater, and (ii) reduce health risks to local residents and recreational users of these sites.

- Define the geochemical and microbial controls on the stability of different As-hosting minerals in weathered gold mine tailings, and develop remediation options that can minimize the release of As from both oxidized and unoxidized tailings deposits.

- Develop general guidelines that can be used to optimize the management and remediation of high-As mine wastes at active and abandoned gold mines across Canada, and at other sites worldwide.

NSERC Strategic Grant Project (2009-2012)



Tailings Leaching Experiments at GSC-Atlantic


Collection of four end-member tailings


Filling lysimeters in field


"Garbage-can" lysimeters


Leachate collection system

Acknowledgements

- NRCan Environmental Geoscience Program
- Health Canada Safe Environments Programme
- Nova Scotia Historic Gold Mines Advisory Committee

  (http://www.gov.ns.ca/nse/contaminatedsites/goldmines.asp)

- MITHE-SN (Metals in the Human Environment Strategic Network, http://www.mithe-sn.org) and the NSERC Strategic Grants Program

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Questions?
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