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*R.A. Klassen, S.L. Douma, A. Ford, A. Rencz, and E. Grunsky*

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# Geoscience modelling of relative variation in natural arsenic hazard potential in New Brunswick

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**Abstract:** In eastern Canada, natural arsenic concentrations in bedrock, soil, and water exceed levels associated with acceptable human health risk, and they are linked with enhanced risk for disease. Despite complex and varied exposure pathways, geoscience supports health risk assessment by informing on regional-scale variation in relative geochemical hazard potential, and by providing a stable environmental reference framework that guides decision making. For New Brunswick, a preliminary arsenic hazard model based on bedrock type, mineral composition, geological history, and regional geochemical data supports a two-level hazard code classification, but may be improved to four-level by incorporating information compiled in higher resolution geological maps. In an exploratory, collaborative project with the New Brunswick Department of Health, a revised model will be tested as a predictor for arsenic in well water, an environmental media more closely associated with exposure pathways, and for spatial variation in occurrences of human cancers known to be arsenic related.

**Résumé :** Dans l'Est du Canada, les concentrations naturelles d'arsenic dans la roche, les sols et l'eau dépassent les niveaux considérés acceptables pour la santé humaine et sont donc associées à des risques accrus de maladie. Malgré la complexité et la diversité des voies d'exposition à l'arsenic, les géosciences appuient l'évaluation des risques pour la santé en renseignant sur les variations relatives de l'aléa géochimique potentiel à l'échelle régionale et en fournissant un cadre environnemental stable pour guider la prise de décisions. Au Nouveau-Brunswick, un modèle préliminaire de l'aléa arsenic en fonction du type de roche, de la composition minérale, de l'histoire géologique et des données géochimiques régionales vient appuyer un système de classification des codes d'aléa à deux niveaux, auquel on pourrait toutefois ajouter deux autres niveaux si on y incorpore l'information des cartes géologiques à plus haute résolution. Dans le cadre d'un projet conjoint réalisé avec le ministère de la Santé du Nouveau-Brunswick, un modèle révisé sera mis à l'essai en qualité d'indicateur des concentrations d'arsenic dans l'eau des puits, milieu plus étroitement associé aux voies d'exposition, et de la variation spatiale dans les incidences de cancers liés à l'arsenic chez l'être humain.

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## INTRODUCTION: GEOSCIENCE AND PUBLIC HEALTH

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Arsenic is a naturally occurring, nonessential trace element known as a causative agent for a wide range of diseases (Smith et al., 2002), and it is identified as a toxic substance in the Canadian Environmental Protection Agency's *Priority 1 Substances List* (Canadian Environmental Protection Act, 1993). Originating in minerals of the Earth's crust, its potential for harm is further increased through natural weathering and soil-formation processes that promote its wider dispersal in the biosphere.

It has long been known that large areas (thousands to ten thousands of square kilometres) of the Appalachian Geological Province of northeastern North America are characterized by natural arsenic concentrations exceeding levels associated with acceptable risk. In addition to bedrock (Petruk, 1964; Roscoe, 1971; New Brunswick Department of Natural Resources and Energy, 2002), arsenic is also naturally enriched in soil media (Presant and Tupper, 1966; Presant, 1971; Kettles et al., 2008; Adcock et al., 2009) and water (Bottomley, 1984; Puppe and Grove, 1989; Pronk, 1992; Pilgrim and Schroeder, 1997; R.A. Brinsmead, New Brunswick Department of Environment and Local Government, unpub. internal report, 2000; Peters, 2008). Most importantly, the arsenic enrichments in geological media have been linked to increased risk for arsenic-related diseases. In soil, acceptable risk levels for arsenic are 12–15 ppm (mg/kg) and in drinking water 10 ppb ( $\mu\text{g}/\text{kg}$ ) (Canadian Council for Ministers of the Environment, 1999).

Although exposure pathways for arsenic may include air, water, soil, and plant media; for human health, drinking water may be the most important pathway (Smedley and Kinniburgh, 2005). In water solution, arsenic has a toxicity potential at any exposure level (Andrew et al., 2006), with the risk of death for some cancer types (e.g. bladder) increasing by almost 12-fold at more than 170 ppb arsenic (Chen et al., 1985, 1992). In New Hampshire, U.S.A., increased risk for nonmelanoma skin cancer occurs even where arsenic concentrations in well water are less than the current primary drinking water standard of 50 ppb (Brown et al., 1989; Karagas et al., 2002). For other cancer types, increased health risk has been shown even where arsenic is less than 10 ppb (Smith et al., 1992).

In New Brunswick, where 64% of the population depend on groundwater, approximately 6% of wells may be arsenic contaminated, with more than 30 300 people potentially exposed to concentrations greater than the Canadian and United States EPA (Environmental Protection Agency) guidelines (Puppe and Grove, 1989). In New Brunswick well waters, arsenic values range up to 850 ppb (New Brunswick Department of Environment, 2008).

To assess arsenic health risk, there is a need to establish the natural origins of arsenic as well as to estimate the magnitude and extent of arsenic contamination in exposure pathways. Although environmental media, such as water and food, may be tested directly for arsenic, such testing is expensive to conduct, relies on the co-operation of property owners, and must be periodically repeated because chemical properties of water and food change over time, reflecting seasonal variation in biosphere processes.

In New England, knowledge of basic geochemical-mineral associations in bedrock guides health protection by linking spatial variation in relative arsenic hazard potential to specific types of geological terranes (Ryker, 2002; Ayotte et al., 2003, 2006a, b; Frost et al., 2003; Lipfert et al., 2006; Robinson and Ayotte, 2006; Peters, 2008). Likewise in Nova Scotia, geological factors have also been used to construct a two-level arsenic hazard potential map (e.g. high, low; Nova Scotia Department of the Environment (2005)). In defining a stable environmental reference framework, geoscience-based hazard potential models indicate geographic areas that may require testing of exposure pathways most likely subject to natural arsenic contamination.

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## ARSENIC HAZARD POTENTIAL MODELLING

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As part of the Environmental and Human Health Program of Natural Resources Canada, the value of geoscience-based hazard potential models in support of health risk assessment and decision making is being investigated. This preliminary report of progress considers the design, construction, and testing of an arsenic hazard potential model (HPM) for New Brunswick.

### Model design and construction

A map for relative arsenic hazard potential expressed in a four-level code (e.g. low (1) to high (4)) is based on geological factors known to affect the natural occurrence and distribution of arsenic, including bedrock lithotype, geochemical-mineral associations, and crustal processes (Fig. 1; Table 1). Greatest arsenic hazard potential may be attributed to black shale and iron-rich metasedimentary bedrock, and to bedrock characterized by sulphide mineralization, manganese oxides, uranium, phosphorite, and coal. Least hazard potential is attributed to inorganic, clastic sedimentary bedrock.

The scale of geological map compilation affects the extent to which natural bedrock variation may be reflected in hazard coding. The preliminary arsenic hazard potential model, for example, is based on geological information compiled at 1:500 000 (Fyffe and McCutcheon, 2000), but may be further improved by incorporating information from 1:250 000 and finer scale maps that better distinguish the

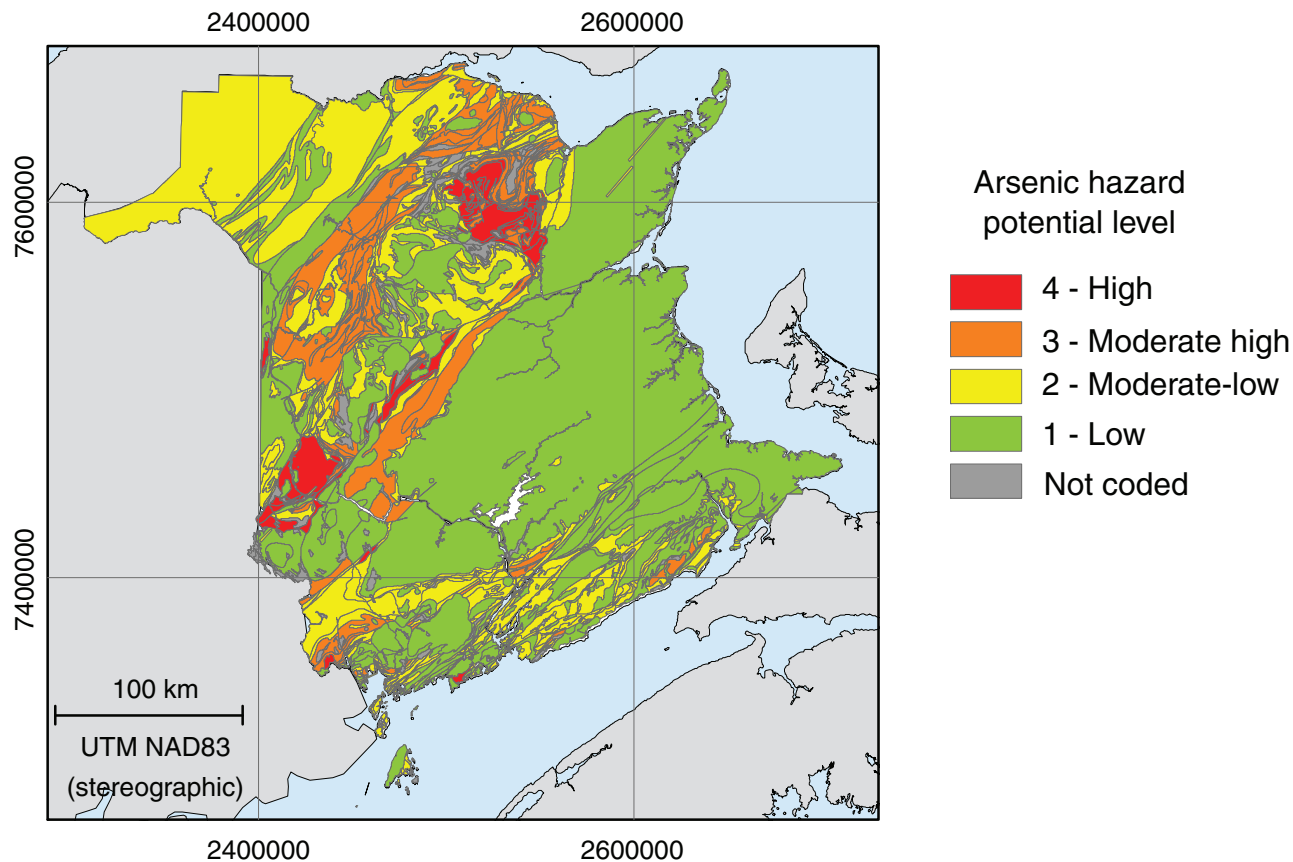


Figure 1. Arsenic hazard potential map for New Brunswick.

Table 1. Geological interpretation of relative arsenic hazard potential based on geochemical-mineral associations reported for bedrock of New Brunswick and elsewhere.

Hazard code	Bedrock associations
High - 4	Black shale, coal, and high-Fe sedimentary rock, including ironstone, and bedrock in which >50% of the units are characterized by enrichments in manganese, coal, uranium, phosphorite, and sulphide minerals.
Moderate - 3	Extrusive igneous rock (including rhyolite) and marine-derived sedimentary rock in which <50% of the units are characterized by coal and/or enrichments in manganese, uranium, phosphorite, and sulphide minerals.
Moderate-low - 2	Extrusive igneous rock (excluding rhyolite), and marine sedimentary rock in which <10% of the units are characterized by enrichments in manganese, coal, uranium, and sulphide minerals.
Low - 1	Intrusive igneous rock, including high and low Ca-granite (undifferentiated), and non-marine sedimentary rock, including sandstone, argillaceous rock, shale, limestone (carbonate), and in which <10% of the units are characterized by enrichments in manganese, coal, phosphorite, iron, uranium, and sulphide minerals.

References Turekian and Wedepohl, 1961; Rose et al., 1979; Ure and Berrow, 1982; Nicolli et al., 1989; Korte and Fernando, 1991; Brownlow, 1996; Fyffe and McCutcheon, 2000; Frankenberg, 2002; Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006; Peters, 2008.

distributions of arsenic-bearing coal formations, mine sites that may indicate a potential for arsenic mineralization, contact aureoles for igneous bodies associated with secondary deposition of arsenic-rich minerals, and geochemical differentiation that may accompany cooling of intrusive rock, among other geological factors.

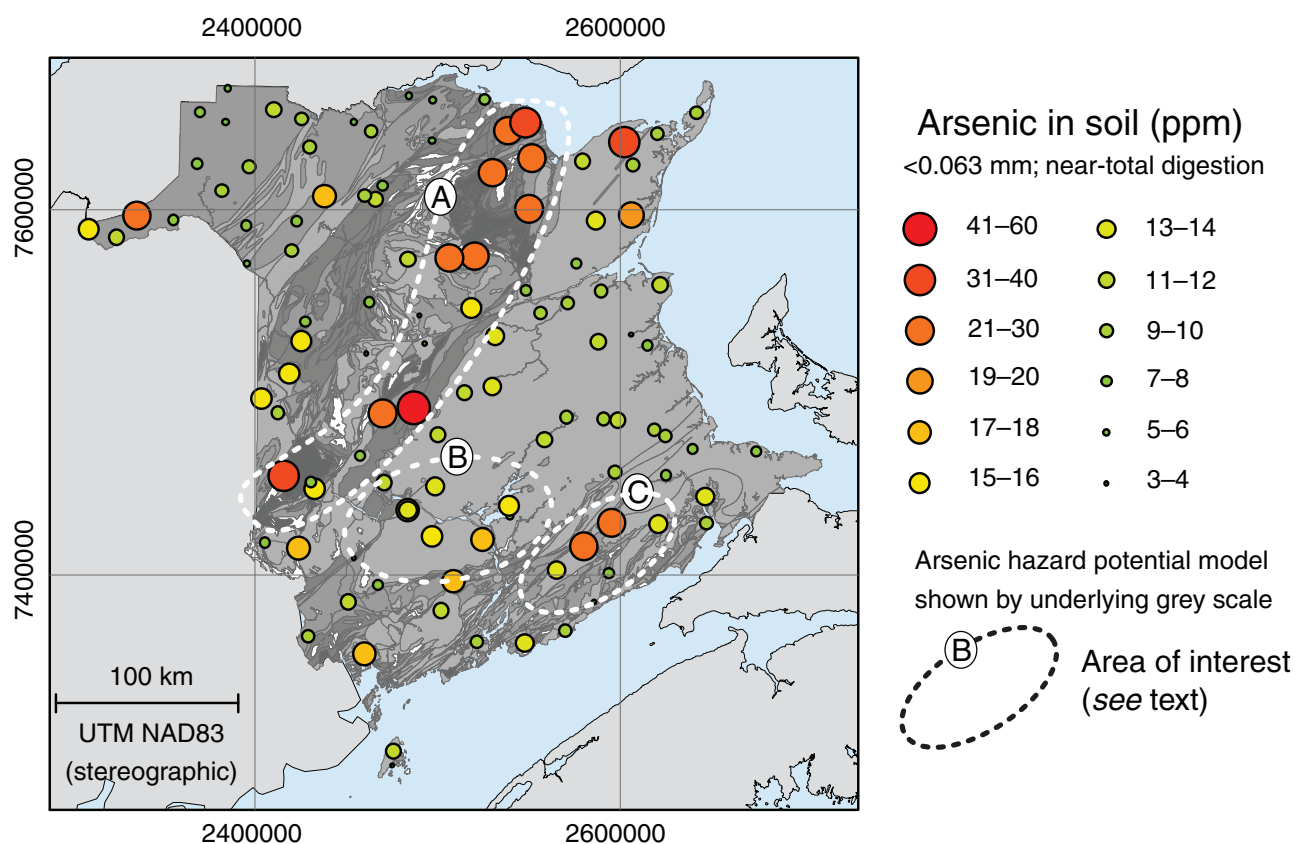
Indirect evidence for geochemical variation in New Brunswick bedrock provided by regional geochemical surveys establishes a secondary basis for refining the arsenic hazard potential model. Data sources include surveys of till in areas of economic mineral potential (sampling density 1/4 km<sup>2</sup>) (Adcock et al., 2009), and of soil parent materials throughout the province carried out for the North American Soil Geochemical Landscape Project (sampling density 1/1600 km<sup>2</sup>) (Kettles et al., 2008) (Fig. 2). The latter soil samples represent most geological terranes of New Brunswick, whereas the till samples are derived principally from terranes having an enhanced potential for economic mineralization. Both data sets are based on analyses of the more than 0.063 mm grain size fractions after a near-total, four acid digestion.

Till geochemical data represent about 8400 samples of the least-weathered material exposed at the base of hand-dug sampling pits, equivalent to the C-soil horizon. Due to the depth of sample collection, geochemical

variability originating in soil formation is minimized. In till, arsenic values range from less than detection limit (1 ppm) to 1240 ppm, with a mean of 19.4 ppm and standard deviation (SD) of 33.6 (Fig. 3a). More than 50% of the samples contain arsenic at concentrations greater than the recommended guideline of 12–15 ppm for residential soils in Canada (Soil Quality Guidelines; Canadian Council for Ministers of the Environment (1999)).

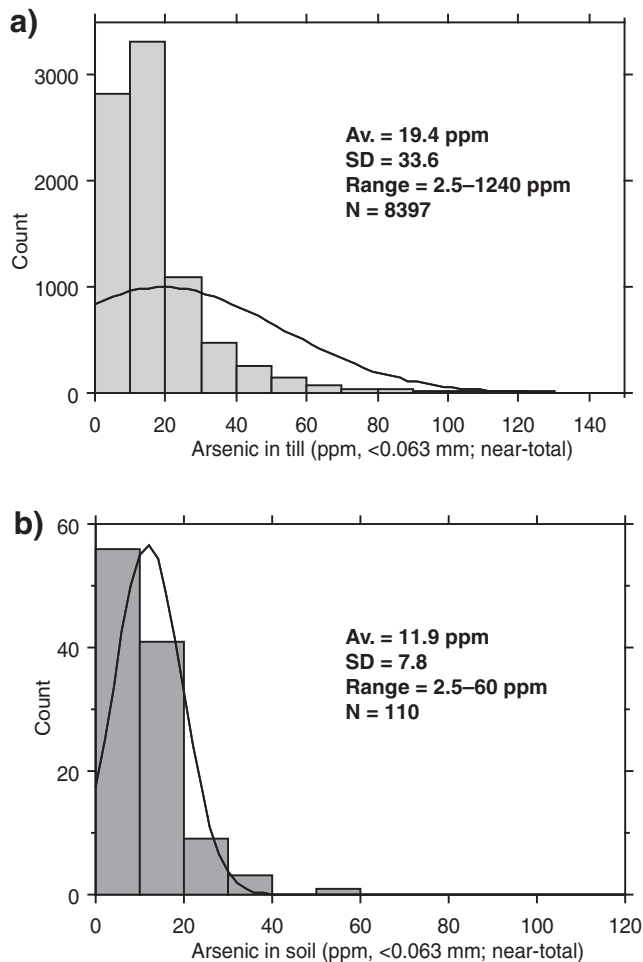
In contrast to the till surveys, North American Soil Geochemical Landscape Project data represent 110 samples of C-soil horizon for a wide range of glacial deposit types, including till. In the North American Soil Geochemical Landscape Project samples, arsenic concentrations range from less than detection limit (1 ppm) to 60 ppm, with a mean of 12 ppm and standard deviation of 7.8 (Fig. 2, 3b). Although having more limited range in arsenic, like the till survey more than 50% of the samples contain arsenic at concentrations greater than recommended Soil Quality Guidelines. Despite low sampling density, the Tri-National geochemical map distinguishes arsenic-rich and arsenic-poor areas.

In preliminary examination, unpaired statistical comparisons of North American Soil Geochemical Landscape Project geochemical data indicates minimal to no differences among igneous (N = 15), metamorphic (N = 4), metasedimentary



**Figure 2.** Regional geochemical survey for arsenic in C-soil horizon of glacial deposits in New Brunswick. Sampling was carried out as part of the Tri-National Soil Geochemical Landscapes Project of the Geological Survey of Canada.

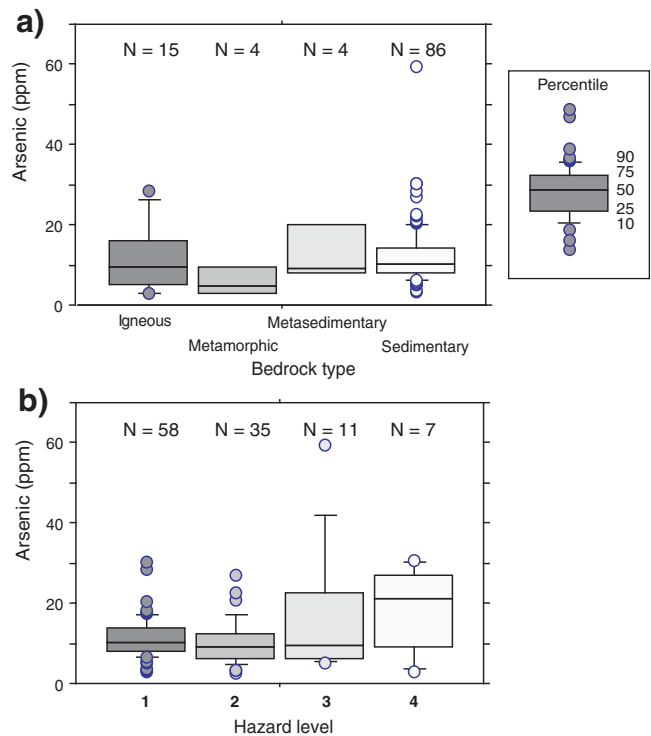




**Figure 3.** Histograms for arsenic in **a)** till and in **b)** C-soil horizon parent materials for New Brunswick.

(N = 4), and sedimentary bedrock terranes (N = 86), with minimal likelihood (75–80% probability) for metamorphic bedrock to be relatively depleted in arsenic (p-values <0.25) (Fig. 4a). Sedimentary bedrock terrane has a wide range in arsenic concentration that may correspond to wide variation in coal distribution. A lack of clear geochemical differences among such grossly defined bedrock terranes indicates that a simplistic geological subdivision of geochemical data cannot reliably support hazard modelling.

Subdivision of North American Soil Geochemical Landscape Project geochemical data by association between sampling site and hazard code (Fig. 1) indicates mean arsenic concentrations are 11.3 ppm (SD 5.1; N = 58) for zone 1; 10.1 ppm (SD 5.6; N = 35) for zone 2; 16.3 ppm (SD 16.6; N = 11) for zone 3; and 18.1 (SD 9.6; N = 7) for zone 4 (Fig. 4b). Unpaired statistical comparisons indicate no significant geochemical differences either between zones 1 and 2, or between zones 3 and 4, but a 94% probability that zones 1 and 2, and zones 3 and 4 represent different geochemical populations (p-value <0.0621). The analyses indicate that geological hazard coding based on 1:500 000 scale bedrock maps can support at least two-level modelling of relative arsenic hazard potential, similar to Nova Scotia.



**Figure 4.** Box-and-whisker plots for arsenic in C-soil horizon media distinguished by **a)** underlying bedrock type and **b)** arsenic hazard code. Unpaired statistical comparisons indicate no significant differences between data sorted by bedrock type, but distinguish hazard code levels 1 and 2 from 3 and 4.

In addition to low sample numbers, weak relations between arsenic in soil parent material and hazard coding level may reflect gross simplifications inherent in 1:500 000 scale geological maps. Qualitative comparison of the arsenic hazard potential model and Tri-National Soil Geochemical Landscape project geochemical map indicates the greatest arsenic concentrations (>19 ppm) preferentially occur along the southeastern limb of a belt of metamorphic shale and metavolcanic bedrock associated with hazard zones 3 and 4 (Fig. 2; area A). Comparison of the more detailed till geochemical and 1:250 000 scale bedrock maps indicates the greatest arsenic values are preferentially associated with Ordovician rhyolite and early Devonian and Silurian marine metasedimentary rock.

In southeast New Brunswick, slight arsenic enrichment in soil parent material (Fig. 2; area B) is preferentially associated with coal in Pennsylvanian to late Carboniferous nonmarine sedimentary rock, sandstone, potash-bearing sedimentary bedrock, and Mississippian siliceous sedimentary bedrock (Fig. 2; area B). Although coal is commonly enriched in arsenic, its preferential occurrence in southeast New Brunswick is not reflected in 1:500 000 scale geological maps, further indicating how the arsenic hazard potential model may be improved through reference to the combination of finer scale geological maps and regional geochemical survey data.



## Model testing: environmental media

For risk assessment, the value of the arsenic hazard potential model may be tested by how well it serves to predict spatial variation for arsenic in environmental media more closely associated with exposure pathways.

During flow and storage, groundwater is modified through contact with its bedrock host through subsurface chemical weathering. Despite complexities in subsurface flow regimes, weathering environments, and bedrock composition, broad correspondence between groundwater chemistry and bedrock composition has long supported success in mineral exploration based on hydrogeochemical prospecting (Taufen, 1997). Although difficult to model, regional scale (tens to hundreds of kilometres) variation in groundwater chemistry — hence, groundwater hazard potential — reflects geological context.

In New Brunswick, two data sets report arsenic concentrations for groundwater. In both, the samples were collected and analyzed between 1994 and 2007 (New Brunswick Department of Environment, 2008). The smaller data set represents arsenic levels in well water of 172 provincial institutions, including schools and government buildings, with 23 characterized by concentrations greater than 10 ppb, and one having arsenic levels of 780 ppb (Fig. 5a). The larger set represents 10 555 private wells, approximately 10% of the total such wells in the province, and it shows arsenic concentrations range from less than detection limit to a high of 850 ppb (Fig. 5b).

Direct comparison of water well and soil parent material geochemistry is made difficult because water wells are not uniformly distributed and their locations are distinct from those of the North American Soil Geochemical Landscape Project soil sample sites. Furthermore, soil parent material reflects the composition of bedrock surfaces, whereas groundwater reflects that of the subsurface. Comparison of the arsenic hazard potential model (Fig. 1), arsenic in soil (Fig. 2), and arsenic in groundwater (Fig. 5a, b) indicates that areas coded for high arsenic hazard potential in bedrock may not directly correspond with arsenic enrichments in either glacial deposits or groundwater. In southern New Brunswick, where arsenic-bearing coal formations may be extensive in the subsurface, sedimentary bedrock terranes coded low to moderate-low hazard are associated with arsenic-contaminated groundwater (Fig. 1; Fig. 2, areas B, C).

Although hazard potential models may be refined by incorporating more detailed-scale geological and geochemical knowledge, certainty in risk assessment and in the prediction of individual exposure and bio-uptake potential cannot be increased without a corresponding increase in knowledge of environmental pathways and processes. Soil hazard potential models, for example, are refined through knowledge of sample depth, soil-horizon association, soil

type, and soil-forming processes. Groundwater hazard potential models are refined through geoscience knowledge of both surface and subsurface bedrock composition.

## Model testing: human health data

Given the complexity of exposure pathways and processes, and the wide variations in cultural, political, economic, and geographic factors affecting exposure and human health, relations between geoscience-based hazard potential models and health are inherently stochastic. For decision making, their value is ultimately established by how well they simplify the interpretation of spatial variation in disease; hence, health risk. In linking geological factors with disease through reference to a single element, however, the importance of other causative environmental agents for disease that confound apportionment of disease burden maybe overlooked.

To test the value of a revised arsenic hazard potential model in collaboration with the New Brunswick Cancer Registry, a retrospective cohort epidemiological study using human health data for prostate, lung, liver, melanoma, bladder, and kidney cancers symptomatic for arsenic exposure will be undertaken. The health data distinguish age and sex, are stratified for the years 2002, 2003, 2004, 2005, and 2006, and are geographically grouped by 6-digit postal code.

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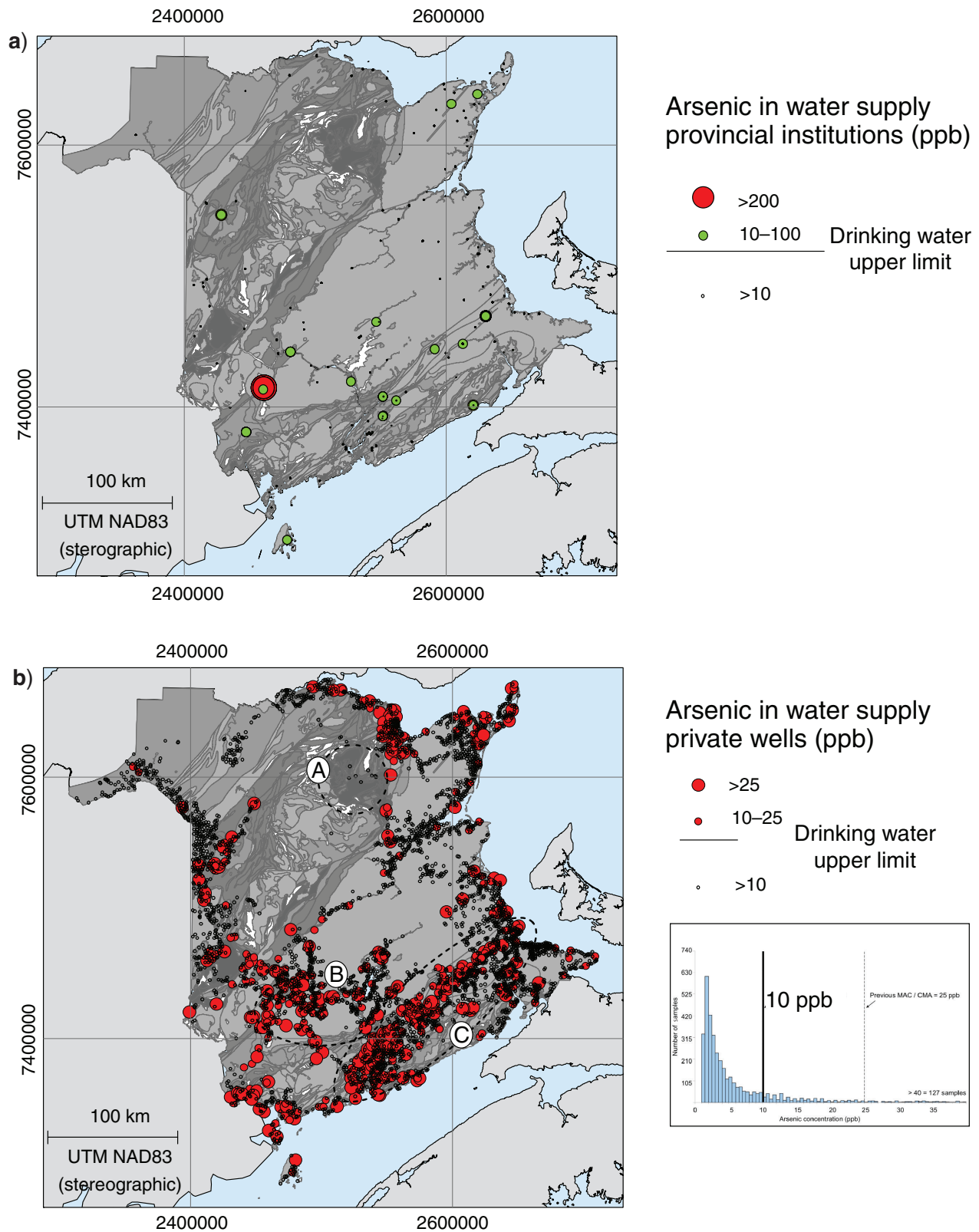
## SUMMARY AND CONCLUSIONS

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This study is based on the premise that geoscience can provide a stable environmental reference framework that supports regional-scale (tens to hundreds of kilometres) modelling of relative arsenic hazard potential, and, through that, can support population health risk assessment.

Although geoscience-based hazard potential models cannot be used to assess individual exposure, they guide risk assessment by establishing relative variation in hazard potential. In doing so, they establish the origins of hazard and permit the testing of environmental media targeted in geographic areas where exposure pathways have the greatest potential for contamination. Through that, they support proactive decision making designed to mitigate risk. Such models may also have a potential, currently unexplored, to provide unexpected insight on spatial variation in environmental burdens of disease in terms of low-level geochemical background variation and combinations of geochemical factors may otherwise influence health outcomes through biological and environmental synergies.

In such an exploratory collaboration between geoscience and health science, the core challenges are twofold. Foremost, there is a need to communicate. Despite the continuum of processes linking geology with health, in a world where “...few researchers span the interdisciplinary divide between the earth sciences and public health sciences...”



**Figure 5.** Arsenic in New Brunswick groundwater supply of **a)** provincial institutions and **b)** private wells. In approximately 6% of the private wells tested, arsenic concentrations exceeded 10 ppb (New Brunswick Department of Environment, 2008).

(Committee on Research Priorities for Earth Sciences and Public Health, 2007, p. 7), there is a need to establish common understanding of how the natural sciences can support health risk assessment. Secondly, where the value of geoscience-based hazard models can be demonstrated for risk assessment, there remains a need to establish how to incorporate such models as a basis for proactive decision making designed to mitigate future risk.

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