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THE INFLUENCE OF BEDROCK AND MINERAL OCCURRENCES ON ARSENIC CONCENTRATIONS IN GROUNDWATER WELLS IN THE GANDER BAY AREA, NEWFOUNDLAND

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ABSTRACT

Results from chemical water analyses, collected from private drinking wells in the Gander Bay area, have revealed arsenic concentrations above the maximum acceptable concentration (MAC), as established by Health Canada Guidelines for Drinking Water Quality. The purpose of this study is to offer an explanation for the source of the elevated arsenic concentrations in the groundwater.

One hundred and sixteen (116) water samples were collected from existing water wells, drilled into bedrock of the Dunnage and Gander zones, to determine if the bedrock was a source of the arsenic. More than 50 percent of the water samples analyzed were found to have arsenic concentration above the MAC of 0.010 mg/L. Additionally, these samples also showed concentrations of lead, iron and zinc above the MAC of 0.01, 0.3 and 5 mg/L, respectively. The concentrations of arsenic varied between 0 and 0.790 mg/L.

Geostatistics were applied to study the public health hazard posed by arsenic in the well water. The ordinary kriging estimates of arsenic were plotted on arsenic distribution maps using lake-sediment, till- and bedrock-geochemistry data. Indicator kriging for groundwater-well samples was applied to characterize the health hazard caused by arsenic concentration at a threshold value of 0.01 mg/L through a threshold map. These arsenic distribution and threshold maps will provide a decision-support tool to define the areas where it will be safe to drill new groundwater wells.

The elevated concentrations of arsenic within the bedrock in the Gander Bay area suggest that there are other sources, other than rock type, for the elevated arsenic levels found in the well water. Adjacency to mineralization and arsenic chemistry both play important roles in this process. The analytical results show a strong correlation between the occurrence of arsenic contamination in groundwater samples and the occurrence of copper and gold in the area. However, more samples need to be analyzed (till, bedrock, soil and vegetation) to evaluate the impact of arsenic contamination on the drinking water, as well as related issues of agricultural sustainability and food quality.

INTRODUCTION

The Gander Bay area was identified as having the potential for moderate to high concentrations of arsenic in the groundwater resources of the area (Newfoundland and Labrador Department of Environmental and Conservation website: *www.wrmd.env.gov.nl.ca*; viewed 2008). Figure 1 shows that this area has high concentrations of arsenic in groundwater and consequently in private wells in the area. Although this data was collected initially for the purposes of mineral exploration, it provided a useful means of mapping natural chemical variation over the province. Data coverage was extensive; 6569 lakes were sampled in insular Newfoundland and analyzed for a variety of elements (Davenport *et al.*, 1994).

Arsenic concentrations in public drinking-water supplies are regulated by Health Canada (1996). In 2003, the Federal-Provincial-Territorial Committee on Drinking Water, revised the maximum allowable concentration (MAC) from 0.025 mg/L to 0.010 mg/L for arsenic in drinking water because it was determined that the existing standard did not satisfactorily protect the public from the adverse health effects of long-term exposure (Safiudin and

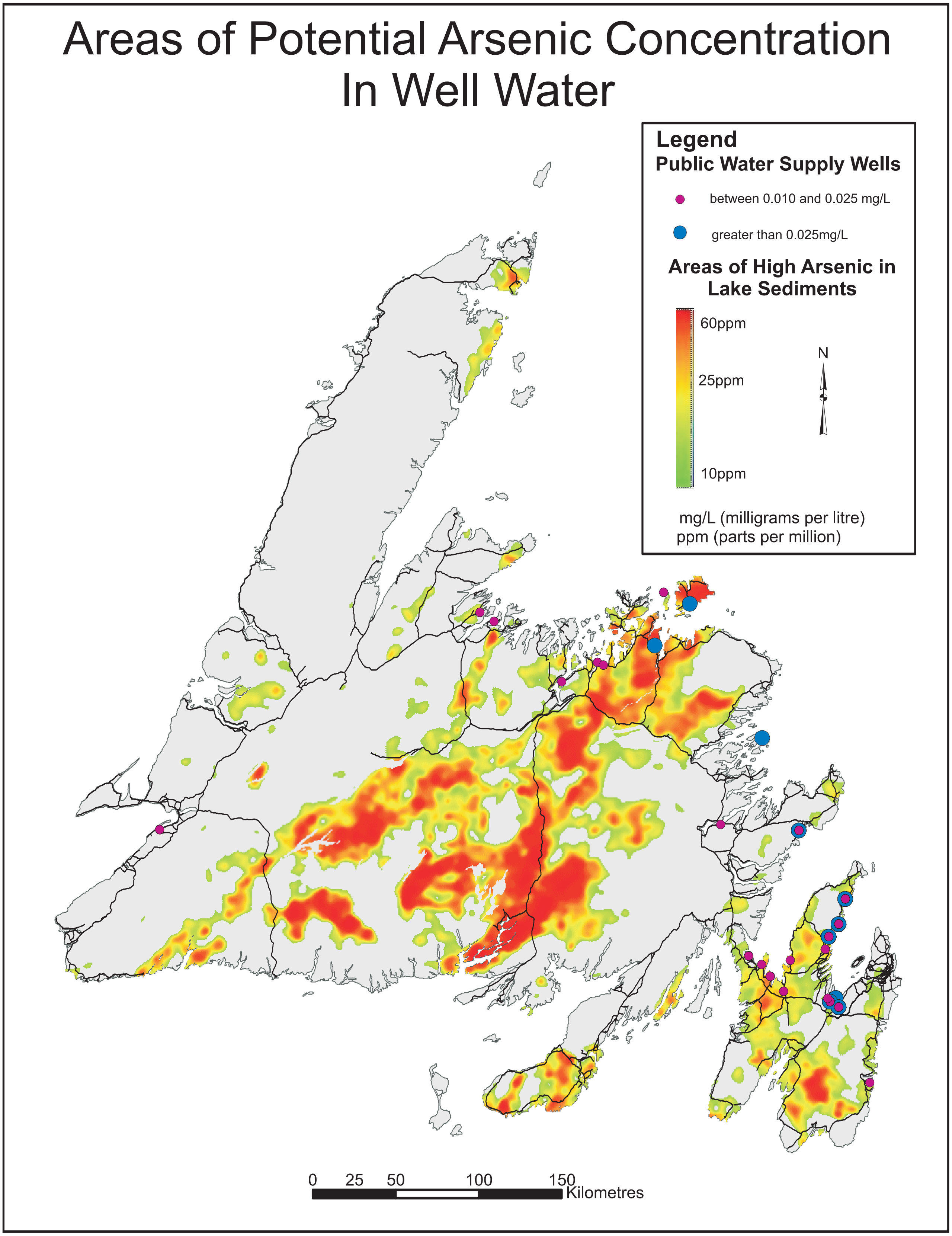


Figure 1. *Areas of potential arsenic concentration in well water (Department of Environment–Department of Natural Resources).*

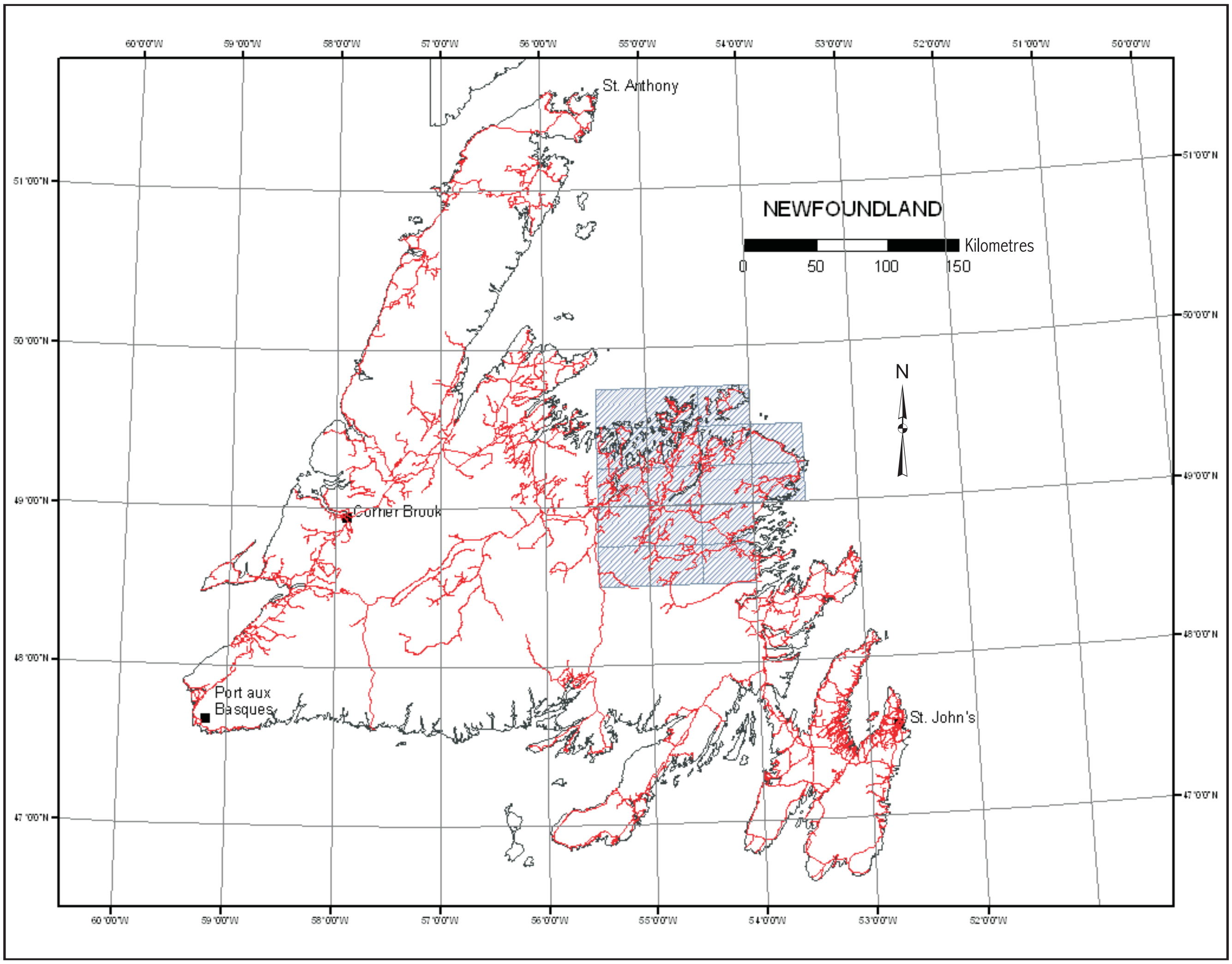


Figure 2. *Index map showing sampling area.*

Karim, 2001). Private water-supply wells are rarely sampled for arsenic or other chemical constituents unless individual well owners choose to do so.

To provide private well owners and provincial environmental and health officials with accurate information on arsenic concentrations from private wells in the Gander Bay region, the departments of Environment and Conservation, (Water Resources Management Division) and of Natural Resources (Geological Survey) conducted an arsenic occurrence and distribution study.

This report describes the investigation regarding the sources of arsenic contamination in the Gander Bay area, which includes discussion of analyses of water samples collected from private wells chosen at random, and analyses of samples of lake sediment, till and bedrock.

LOCATION

The study area comprises the Gander Bay and Bonavista Bay north areas, which are located in central Newfoundland (Figure 2), and covers fifteen 1:50 000-NTS map sheet areas: these are Glovertown (NTS 2D/9), Dead Wolf Pond (NTS 2D/10), Eastern Pond (NTS 2D/11), Mount Peyton (NTS 2D/14), Gander (NTS 2D/15), Gambo (NTS 2D/16), Weir's Pond (NTS 2E/1), Gander River (NTS 2E/2), Botwood (NTS 2E/3), Port Leamington (NTS 2E/6), Comfort Cove (NTS 2E/7), Carmanville (NTS 2E/8), Fogo (NTS 2E/9), Twillingate (NTS 2E/10), Exploits (NTS 2E/11), Wesleyville (NTS 2F/4) and Musgrave Harbour (NTS 2F/5).

PREVIOUS INVESTIGATIONS

Arsenic is widely distributed throughout the Earth's crust. The presence of elevated concentrations of arsenic in Newfoundland has been known since 1990 when 16 569 lake-sediment samples were collected as part of Canada's National Geochemical Reconnaissance Program. Results of this project included a map of arsenic distribution in lake sediment for the Island of Newfoundland (Davenport *et al.*, 1994) that showed considerable variation from region to region, and its clear relation with bedrock geology. Elevated arsenic concentrations are shown in central Newfoundland and on the Avalon Peninsula. Papezik (1967) described the origin of native arsenic in two copper mines in the Springdale area.

In 2002, the first reported concentration of arsenic above the federal drinking-water guidelines was reported from the Harbour Main–Chapel's Cove–Lakeview area of the Avalon Peninsula, just after public wells first started to be tested. Arsenic concentrations were found to be up to 12 times greater than the MAC.

Rageh *et al.* (2007) studied arsenic concentrations exceeding the MAC level in many wells and some from surface water bodies in eastern, central and western Newfoundland. Their study showed that the analyses revealed differences among water sources in the eastern, central and western regions of Newfoundland, mainly due to the different type of bedrock geology of the areas.

HEALTH EFFECTS OF ARSENIC

Long-term ingestion of arsenic has been linked to certain types of cancer, particularly skin, lung and bladder cancer. The symptoms and signs that arsenic causes appear to differ between individuals, population groups and geographic areas. Thus, there is no universal definition of the disease(s) caused by arsenic. Similarly, there is no method to identify those cases of internal cancer that were caused by arsenic from cancers induced by other factors (World Health Organization, *http://www.who.int/mediacentre/factsheets/fs210/en/*; viewed 2008). The risks of developing health problems are the same for everyone, including children and pregnant women. There is minimal absorption of arsenic through the skin, and thus washing with water high in arsenic does not present a health risk (World Health Organization, *op. cit.*)

Arsenic is a naturally occurring groundwater contaminant in Canada, especially in Prince Edward Island, Québec, Ontario, British Columbia, Saskatchewan and Nova Scotia (Health Canada, 2006). Internationally, high concentrations have been reported in the western United States, especially around Los Angeles, the Sierra Nevada Mountains, the Salt River Basin, and areas of Michigan and Wisconsin (Peters and Blum, 2003). There is widespread contamination in southeast India, and the worst occurrence of the health effects of groundwater arsenic contamination is in Bangladesh.

GEOCHEMISTRY AND SOURCES OF ARSENIC

Arsenic occurs naturally in several oxidation states (-3, 0, +3 and +5), but in natural waters is mostly found in inorganic forms, such as Arsenite As (III) and Arsenate As (V) (Holm *et al.*, 2004). Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Inorganic arsenic species are more mobile and toxic than organic forms of arsenic to living organisms, including animal, plants and humans (Bell *et al.*, 2000).

The occurrence and variability of arsenic in groundwater from wells drilled into bedrock in the study area are related to a number of factors, including: a) underlying bedrock composition and mineralization, b) soils and sediments derived from weathering of bedrock, c) anthropogenic sources related to past pesticide use and/or mining processes, d) leaching of tailings, and e) resident time of groundwater in contact with the bedrock.

In the Gander Bay area, arsenic occurs in bedrock, as well as in the shallow glacial sediment that covers the area. Arsenic is dissolved naturally from these materials and enters the groundwater through natural recharge. Naturally occurring arsenic concentrations in igneous, metamorphic and sedimentary rocks vary considerably; sedimentary rocks generally contain more arsenic than igneous and metamorphic rocks (Banglapedia, 2006). Also, arsenic can be found in association with several ore minerals, *e.g.*, arsenopyrite (FeAsS), or associated with gold, antimony or iron. Finally, arsenic is also associated with geothermal areas and high evaporation rates, most likely because trace elements such as arsenic are more readily mobilized and transported by warm or hot water (Welch *et al.*, 2000).

The Gander Bay area is characterized by massive sulphide zinc–copper–lead–gold–silver; epithermal zones of gold and silver; porphyry copper–molybdenum; low-sulphidation antimony; porphyry copper–gold; zinc and copper deposits (Figure 3).

BEDROCK GEOLOGY

Newfoundland and Labrador is subdivided into four tectonic zones, namely the Humber, Dunnage, Gander and Avalon zones. The Humber Zone could include components of the North American continental margin or the western margin of Iapetus. More easterly zones are geologic entities, added to the North American margin during the closing of

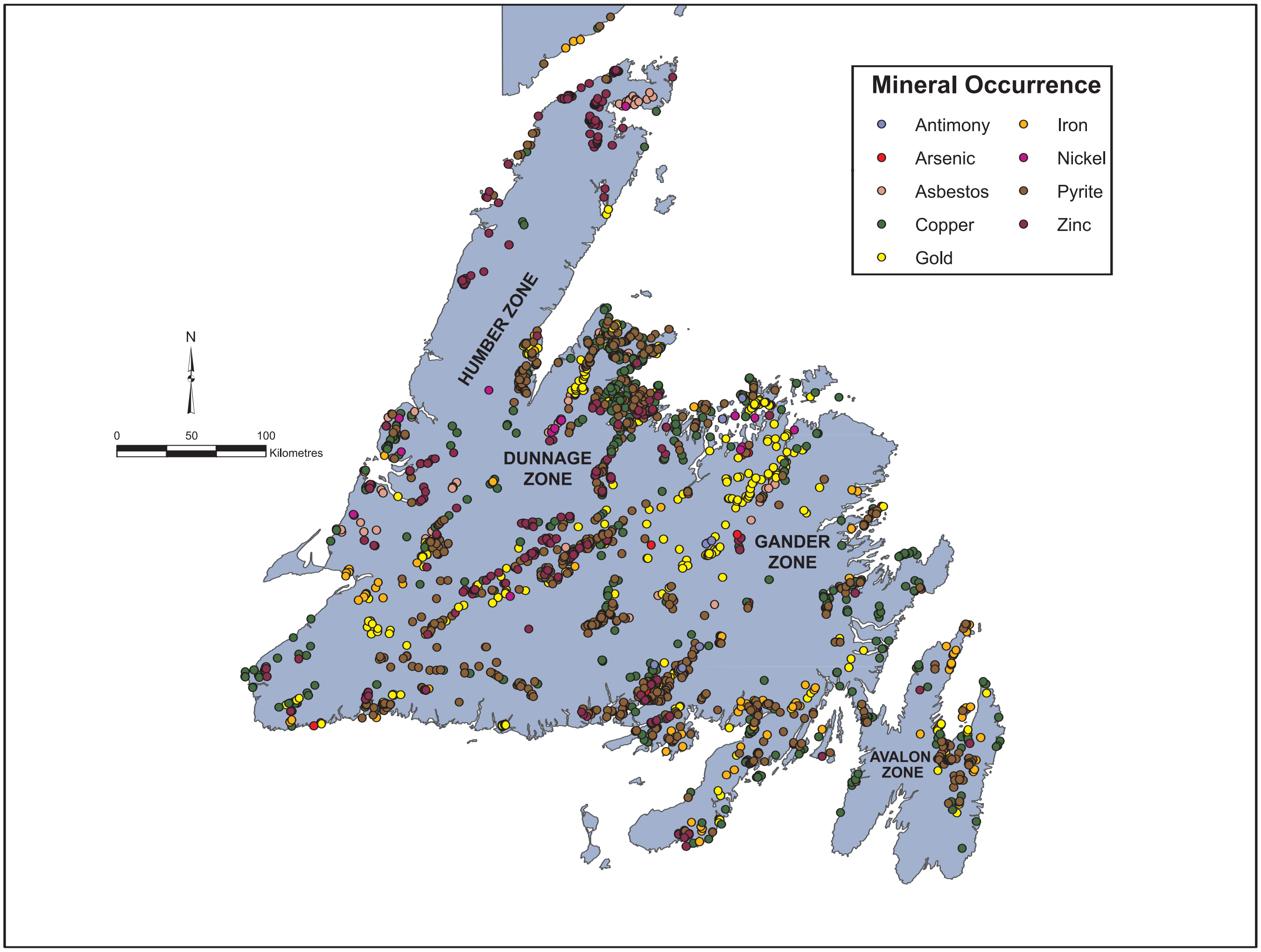


Figure 3. *Mineral occurrences in Newfoundland. Mineral Occurrence Data System (MODS).*

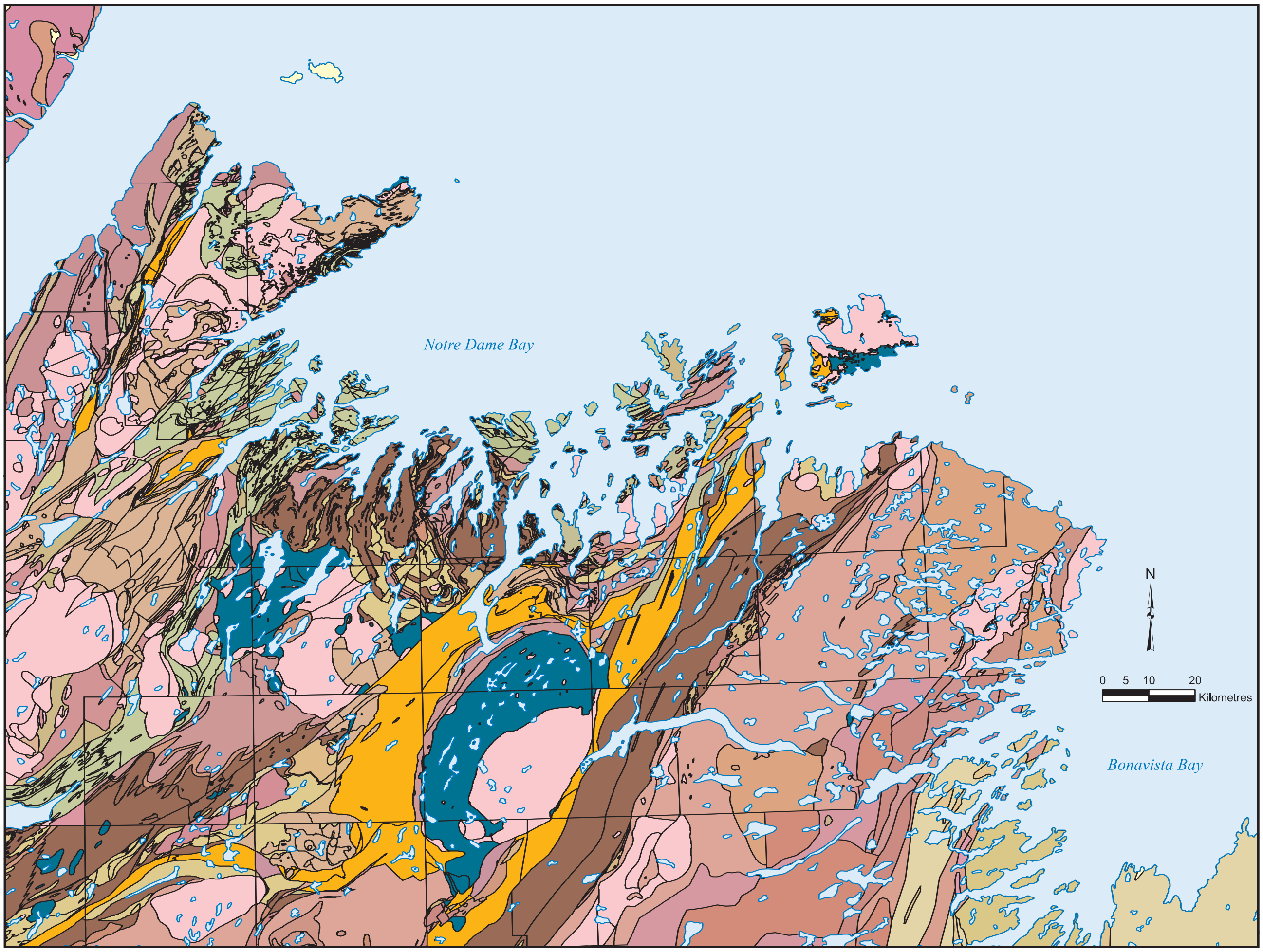
the Iapetus Ocean. Thus, the Dunnage Zone represents vestiges of Iapetus; the Gander Zone represents the eastern margin of Iapetus, while the Avalon Zone was originally part of the North African Plate. Between these two are components of the ancient Iapetus Ocean that once separated these continents. The Gander Bay area straddles the Gander and Dunnage (tectonic) zones. The Gander Zone in the east includes mainly Cambro-Ordovician metasedimentary rocks that were formed in proximity of the Gondwanan continental margin (Colman-Sadd, 1980). In the west, the Gander Group is interpreted to be overlain by the Gander River Complex and Davidsville Group. Between the two continental margin terranes, the Dunnage Zone includes plutonic and volcanic rocks and volcaniclastic to epiclastic sedimentary rocks that together represent remnants of early to middle Paleozoic oceanic terranes (Figure 4).

The Dunnage Zone is divided by a series of faults called the Red Indian Line. These faults make a natural two-fold subdivision of the Dunnage Zone, assigning rocks in the northwestern part of the Red Indian Line to the Notre Dame Subzone, and rocks in the southeastern part to the Exploits Subzone (Williams *et al.*, 1988).

The Exploits Subzone consists mainly of the Davidsville Group, a sequence of Cambro-Ordovician siliciclastic rocks that contain a large proportion of mafic clasts (Blackwood, 1982). In the east, the Davidsville Group lies upon the Gander River Complex, which is composed of plutonic and ophiolitic rocks (O'Neill and Blackwood, 1989). The upper part of the Davidsville Group is overlain by the Indian Islands Group mainly composed of Silurian shallow-marine sedimentary rocks (Williams *et al.*, 1993; Dickson, 2006).

GEOLOGICAL DATASETS

This study synthesizes the existing groundwater-quality data from the Department of Environment and Conservation database, collects and analyzes additional water samples



DUNNAGE ZONE

Devonian

■ Loon Bay Batholith: Plutonic felsic rocks

Silurian

■ Mount Peyton Granite
■ Mount Peyton Gabbro
■ Wild Bight Group: Mafic volcanic marine rocks
■ Botwood Group: Red, grey and green micaceous sandstone

Ordovician – Silurian

■ Badger Group: Grey, well-bedded greywacke, conglomerate layers
■ Badger Group: Felsic volcanic with sedimentary rocks

Silurian – Early Devonian

■ Indian Islands Group: Siliclastic sedimentary, with sandstone, shale and conglomerate
■ Ten Mile Lake Fm: Siliclastic non marine

Ordovician

■ Davidsville Group: Siliclastic sedimentary, slate, argillite, siltstone, sandstone, etc
■ Hamilton Group: Melange with sedimentary and volcanic blocks
■ Hamilton Group: Marine siliclastic sedimentary rocks
■ Hamilton Group: Main Point Fm: Siliclastic black shale

Cambro Ordovician

■ Gander River Complex: Plutonic ultramafic
■ Gander River Complex: Plutonic ultramafic
■ Gander River Complex: Plutonic ultramafic

GANDER ZONE

Devonian

■ Middle Ridge Granite

Cambro Ordovician

■ Gander Group: Metasedimentary quartzite, psammite and pelite

Figure 4. *Lithology of bedrock geological units north of Gander Lake, Newfoundland. Geology compiled by Colman-Sadd and Crisby-Whittle (2002).*

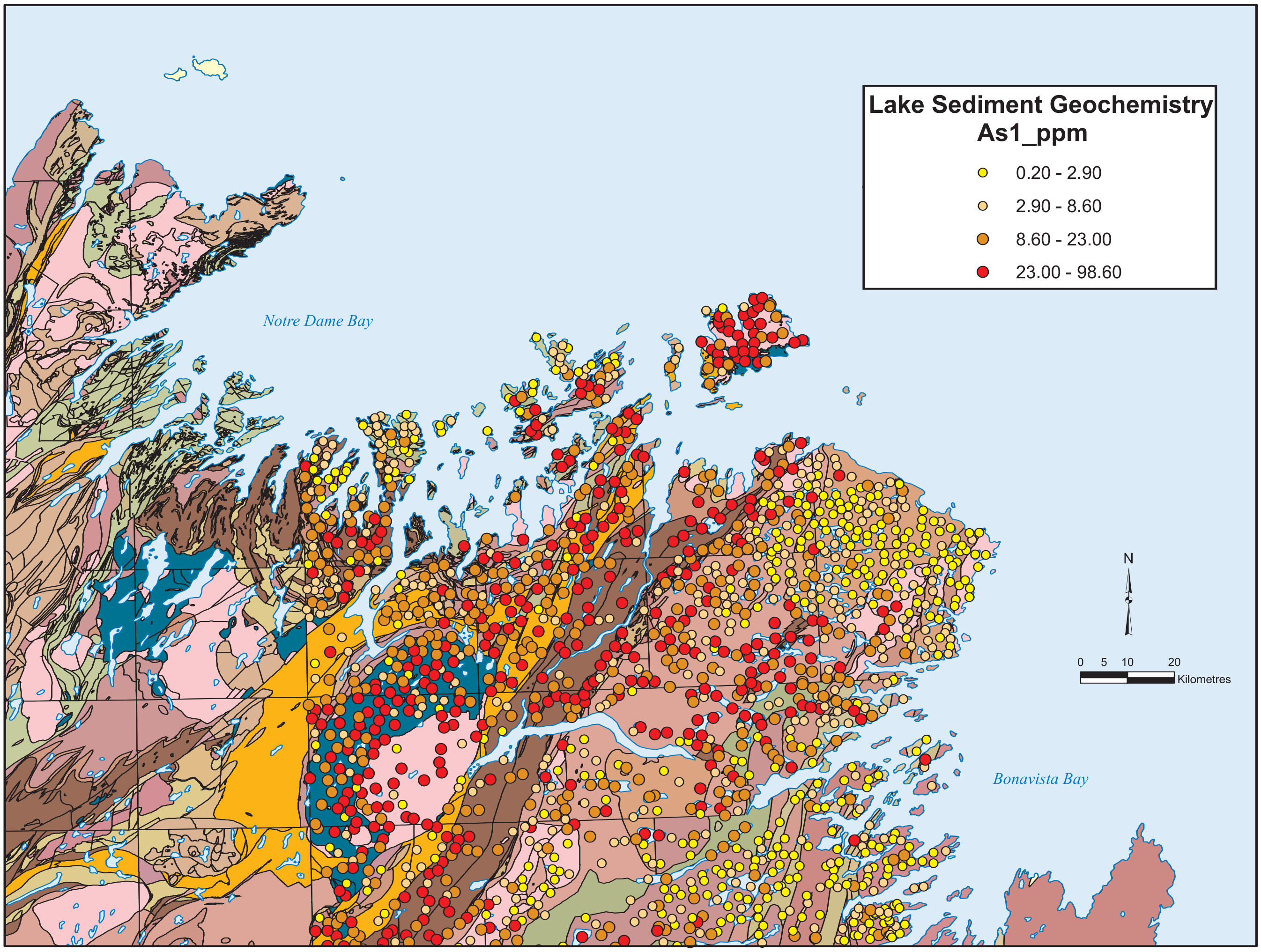


Figure 5. *Location of lake-sediment samples analyzed for arsenic. Legend as in Figure 4.*

from public and private drinking-water supplies within the Gander Bay area, and compiles and reclassifies the lake-sediment, till and bedrock data from the provincial Geological Survey databases to determine if there is any geostatistical correlation between the regional geology and the occurrence of arsenic in the groundwater. This correlation can then be extrapolated into areas where the geology is known, but where groundwater-quality data are scarce or do not exist, to guide future development.

GEOLOGICAL MAPS

Bedrock and surficial geological data were compiled from geological maps by Colman-Sadd *et al.* (1990), Currie *et al.* (1997) and Batterson *et al.* (1998). Digital versions of the provincial geological map were obtained though the Resources Atlas from the Newfoundland and Labrador Geological Survey (*http://gis.geosurv.gov.nl.ca/*, viewed 2008). Because the geological maps were produced at different scales, the level of detail is variable. However, group and formation designations were respected and the data were reclassified to follow the unit patterns.

SAMPLE DATASETS

Till-, lake-sediment and bedrock-geochemical data for the Gander Bay area were retrieved from the Resources Atlas database archive of the Newfoundland and Labrador Geological Survey.

1. Arsenic in Lake-Sediment Dataset

The lake-sediment geochemistry dataset produced 1555 As determinations from the Gander Bay area (Figure 5). These samples were collected at a sample spacing of 1 sample per 6 km^2 and analyzed by INAA.

2. Arsenic in Till Dataset

Between 1987 and 1999 till samples were collected from the Gander Bay area. Sample spacing was 1 sample per

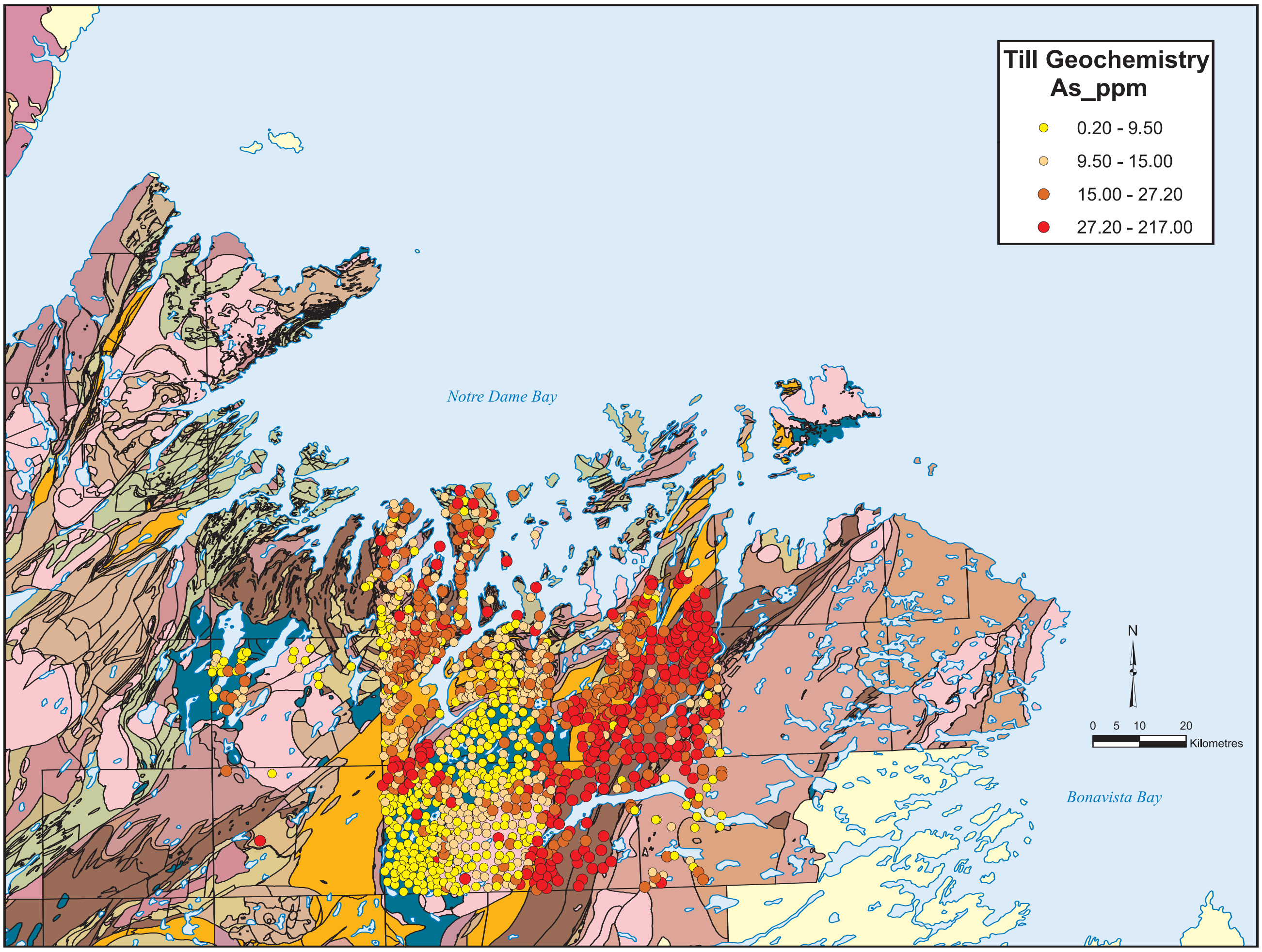


Figure 6. *Location of till samples analyzed for arsenic in the Gander Bay area. Legend as in Figure 4.*

1 to 4 km^2 depending on access, and samples were collected mostly from shallow hand-dug pits penetrating to the BC- or C-horizon (Batterson and Taylor, 2001; Liverman *et al.*, 2000). Till sampling across the area is not complete and samples were collected between the Gander River Ultrabasic Belt and Northern Arm Fault, in the Exploits Subzone (Figure 6).

3. Arsenic in Bedrock Dataset

Bedrock geochemical data for 350 bedrock samples were collected during 1993 for the Mount Peyton bedrock-mapping project (Dickson, 1993; Figure 7).

4. Arsenic in Groundwater Dataset

Arsenic data from public and private wells that are finished in bedrock, in the Gander Bay area, were obtained from the provincial records on public water-supply wells collected by the Department of Environment and Conservation for compliance with the Provincial Safe Drinking Water Act (2002) and earlier legislation to ensure the safe delivery of public drinking water. The samples were collected by department staff between 1995 and 2008.

A total of 86 previously collected groundwater samples from the Gander Bay area were obtained from the provincial records for water supplies of the Department of Environment and Conservation, and an additional 30 samples from private domestic wells. Most of the existing groundwater data were collected during well tests (also known as pumping tests, conducted to evaluate a well's potential yield by 'stimulating' the aquifer through constant pumping, and observing drawdown in the pumped well). Consequently, wells were pumped prior to sample collection; therefore, samples collected were likely from the aquifer, rather than from the well casing. Samples from private wells collected as part of this study were taken from the faucet of the kitchen sink after running the water for 3 minutes in order to ensure that the pipes and well stem were purged, and the water collected was representative of the aquifer. Well-depth information was generally available for all these samples (Figure 8).

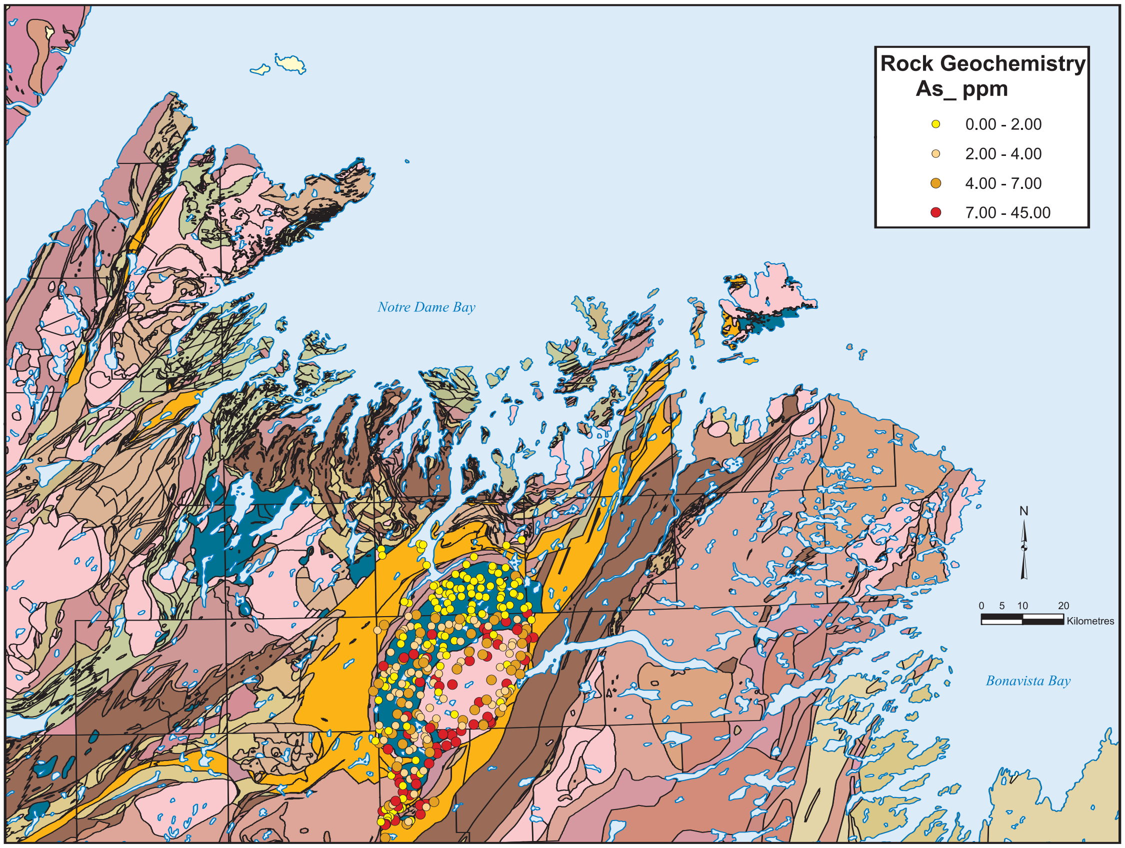


Figure 7. *Location of bedrock samples analyzed for arsenic in the Gander Bay area. Legend as in Figure 4.*

The water-quality samples collected were analyzed by Maxxam Analytical Inc. following the Guidelines for Canadian Drinking Water Quality, while existing water-quality samples were analyzed by the Department of Natural Resources Geochemical Laboratory.

All distribution maps (Figures 5 – 8) depict arsenic concentrations in quartiles. A quartile map is simply a colour-coded sampling map, where the symbols identify the sampling locations and their corresponding colours indicate the magnitude of the response variable. In this study, arsenic concentration measurements were classified into four distinct quartile ranges: Q1 (25%), Q2 (50%), Q3 (75%) and Q4 (100%). This method facilitates data interpretation, by comparing maps with arsenic concentrations displayed, using equal intervals.

ARSENIC STATISTICS

Concentrations of arsenic in lake sediment, till, bedrock and groundwater in bedrock that vary by more than four orders of magnitude are shown in Table 1 (*see* Robinson and Ayotte, 2007). The ranges of arsenic concentrations in all samples are from below the detection limit to 119 000 ppm. The highest concentration of arsenic was measured in bedrock samples from the Mount Peyton area in a sample of serpentine. The distribution of arsenic concentrations in groundwater range from below detection limit to a maximum arsenic concentration of 0.239 mg/L from samples collected from known locations and aquifer material. However, the maximum arsenic concentration (in the Department of Environment and Conservation's database) was from samples collected in the towns of Seldom and Little Seldom in September 2002. Analyses from these samples indicate arsenic concentrations of 0.790 mg/L (data taken from the records of the Department of Environment and Conservation). Unfortunately, neither the accurate location nor the depth of theses samples is known. While this value was used for modelling, its lack of coordinates made it impossible to be used as a single value. Instead, this concentration was averaged in with other arsenic results from the same area as a composite (0.01 mg/L for arsenic concentrations from samples from 37 wells).

SPATIAL ANALYSIS AND RESULTS

General statistical analyses of the geochemical arsenic data in drinking-water, lake-sediment, whole-rock, and till samples are described in this section. A spatial database was generated and is presented in an interpolated map form,

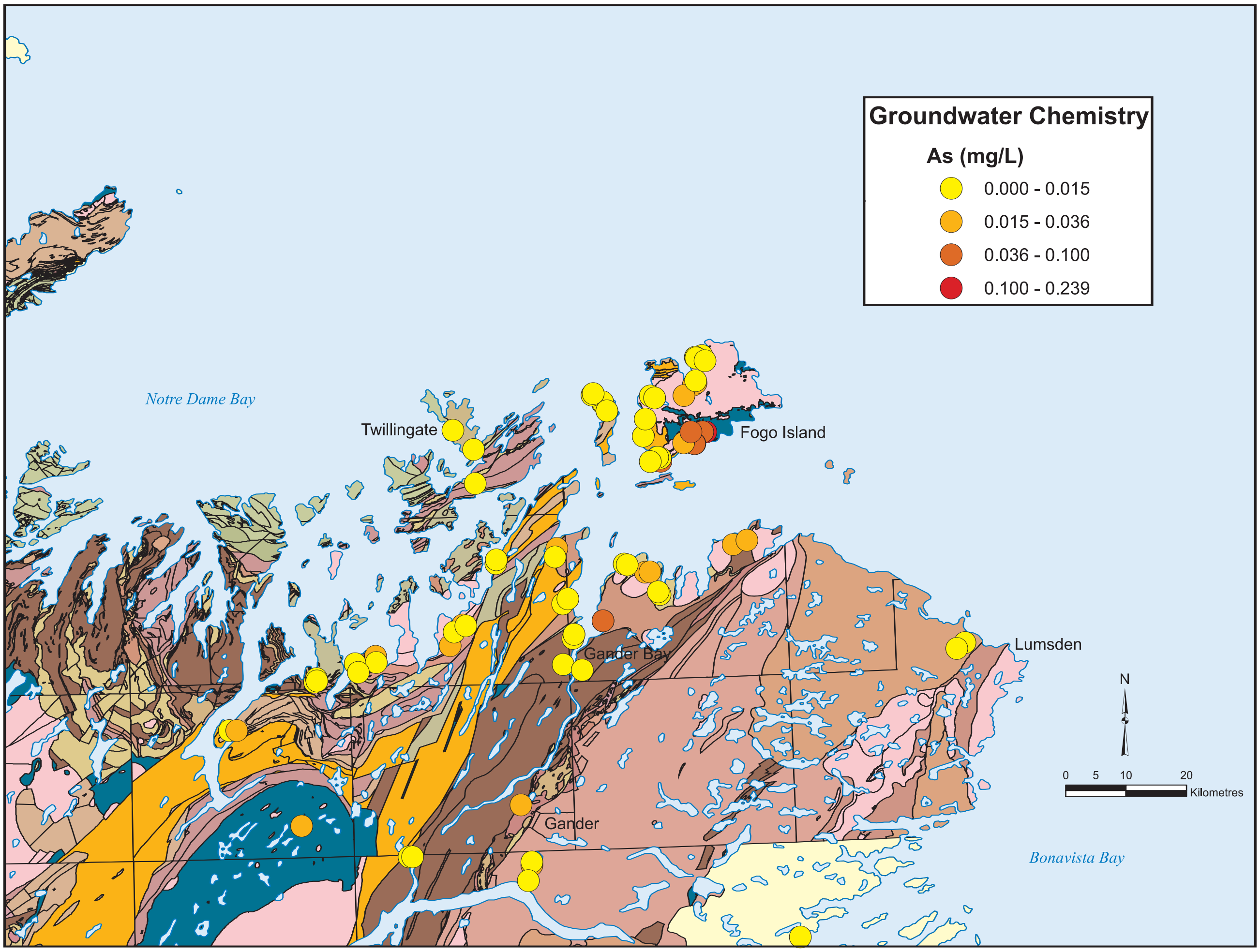


Figure 8. *Location of groundwater-quality samples in the Gander Bay area. Results of the analyses indicate that most of the groundwater samples exceed the Guidelines for Canadian Drinking Water Quality of 0.01 mg/L. Legend as in Figure 4.*

Table 1. Summary statistics of available arsenic concentration data (ppm = mg/L)

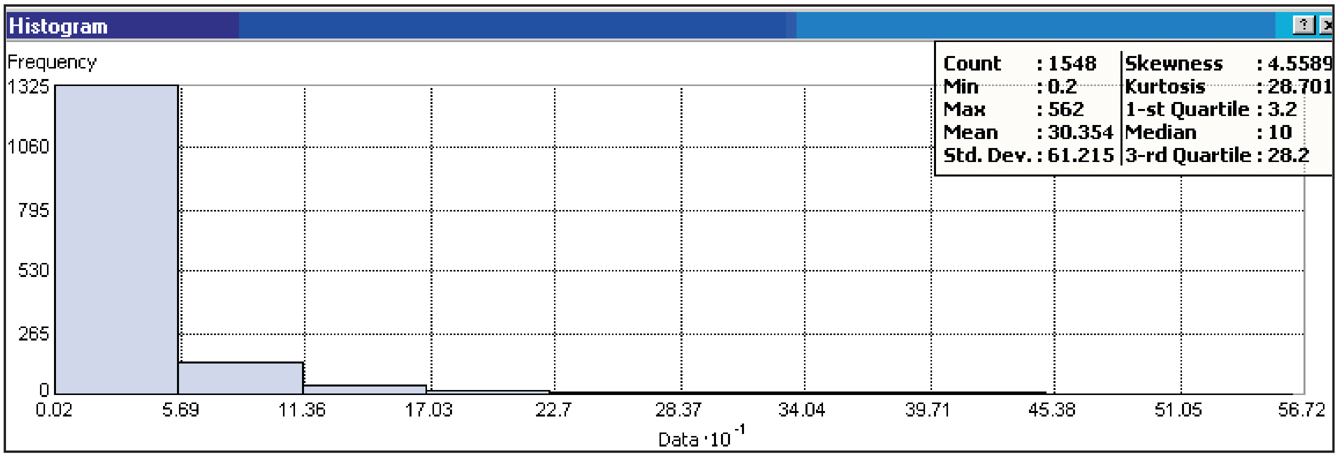
Type of Sample	#Samples	Min (ppm)	Max (ppm)	Median (ppm)
Groundwater	116	0.00	0.239	0.01
Lake sed.	1555	0.20	1550	10.00
Till	1357	0.20	480	15.00
Rock	350	0.00	119000	3.00

from which the relation (or lack of) between arsenic in drinking-water versus lake-sediment, bedrock and/or till samples is described. To examine the distribution of the arsenic data as a single element, histograms were created for each one of the different type of samples. A histogram is used to graphically summarize and display the distribution of a process dataset. For example, the histogram for lake-sediments dataset from the Gander Bay area is shown below (Figure 9).

Figure 9 shows the graphical summary of the shape of the lake-sediment data distribution. Generally, arsenic concentrations in lake-sediment, bedrock, till and groundwater well datasets were non-normally distributed and were positively skewed with extreme values.

The Q-Q plots were produced for all datasets to explore what parts of the data can be poorly estimated; these plots graphically compare the distribution of a given variable to the normal distribution (represented by the straight line). Figure 10 (left) shows that the highest arsenic values deviate from the normal model, tending to disappear; whereas Figure 10 (right) shows that transforming arsenic values logarithmically improves the fit at the high concentration levels, ensuring that the highest arsenic concentrations would be equally considered.

A multi-element correlation matrix was calculated for all data. Table 2 shows a summary of selected elements. This



Count : 1548
Min : 0.2
Max : 562
Mean : 30.354
Std. Dev. : 61.215
Skewness : 4.5589
Kurtosis : 28.701
1-st Quartile : 3.2
Median : 10
3-rd Quartile : 28.2

Figure 9. *Histogram showing unimodal arsenic concentration distribution in lake-sediment samples.*

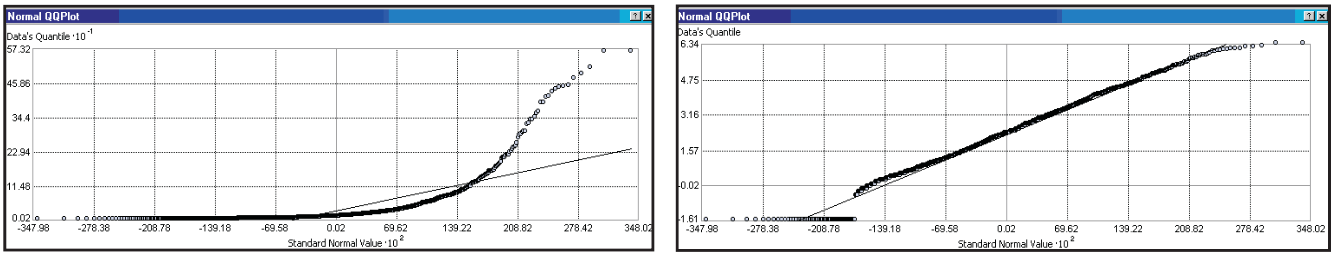


Figure 10. *Normal Q-Q plots for lake-sediment samples before (left) and after (right) logarithmic transformation.*

Table 2. Pathfinder minerals for As in lake sediment, till and bedrock from the Gander Bay area

	Lake Sediment	Till	Rock
Iron (Fe)	0.48		
Gold (Au)		0.43	0.85
Antimony (Sb)			0.92

correlation shows that As in the bedrock samples have a strong positive correlation with gold (0.85), as well as with antimony (0.92). These numbers suggests that gold and antimony might be used as pathfinder elements for arsenic in the Gander Bay area (Figure 11 and Table 2).

Additionally, important associations were found between the concentrations of sulphide minerals in nonfiltrated samples. Water samples showed associations between zinc, lead and iron concentrations, suggesting the possible presence of sulphide minerals at depth (Ishtiaque *et al.*, 2008).

Other elements also have strong correlation with arsenic. These elements, including Co, Cu, Fe and Sb, were compiled from the database for lake sediments, bedrock and till. The distribution and ranges of concentration of the multi-element geochemical dataset were examined and are presented in a multi-element boxplot to be visualized and compared among the different sample types.

Figure 12 and Table 3 shows that As, Co, Cu, Fe, Pb and Zn distributions in these samples are non-symmetric and have positive skewness. Outliers are observed for As, Cu, Co and Zn. The skewness indicates that there would be some problems in the interpolation of these data, especially for the highest concentrations.

Generally, the geochemical data are imprecise, multivariate, spatially auto-correlated and non-normally distributed, and pose specific problems to the choice of the data analyses methods. The choice of technique to use in this study is based on the characteristics of the data, as well on the purpose of the study. Ordinary kriging accommodates non-normal distributed data as long as spatial auto-correlation structure is not masked by extreme-valued outliers (Isaaks and Srivastava, 1989); as a result, these outliers can be removed without problem for temporal change analysis under most circumstances.

Exploratory data evaluation identified spatial outliers in all datasets. These outliers, if not handled appropriately, could severely mask underlying auto-correlation structure in the data and lead to poor or inaccurate kriging estimate. Thus, for lake-sediment samples for the Gander Bay area, eight outliers were eliminated. The remaining high values were taken into account and classified as 'extreme values' because, in contrast to statistical outliers, these high values do not violate the auto-correlation pattern of the dataset

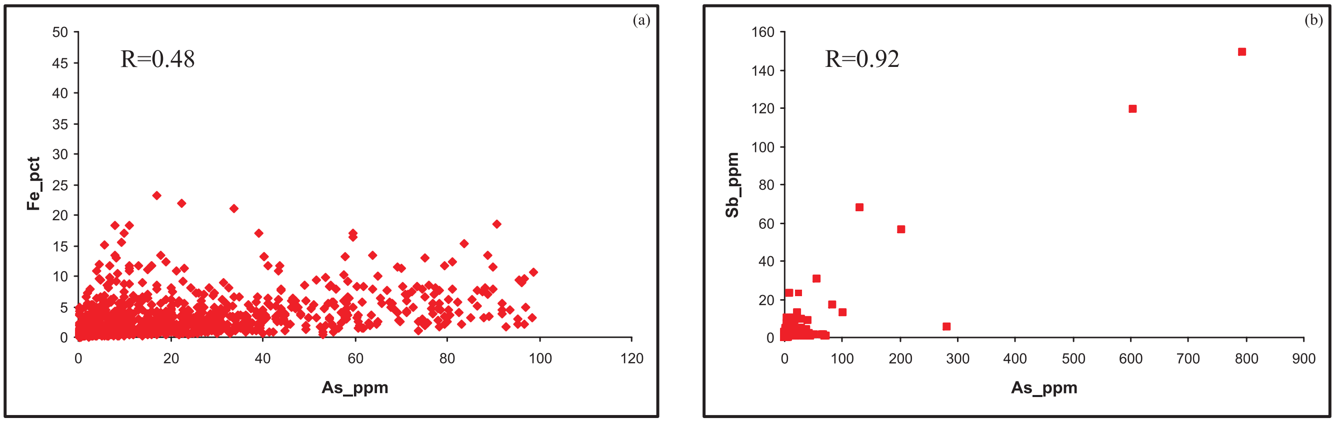


Figure 11. *Correlations between (a) Fe vs. Au (0.85) and (b) As vs. Sb (0.92) in bedrock samples from the Gander Bay area.*

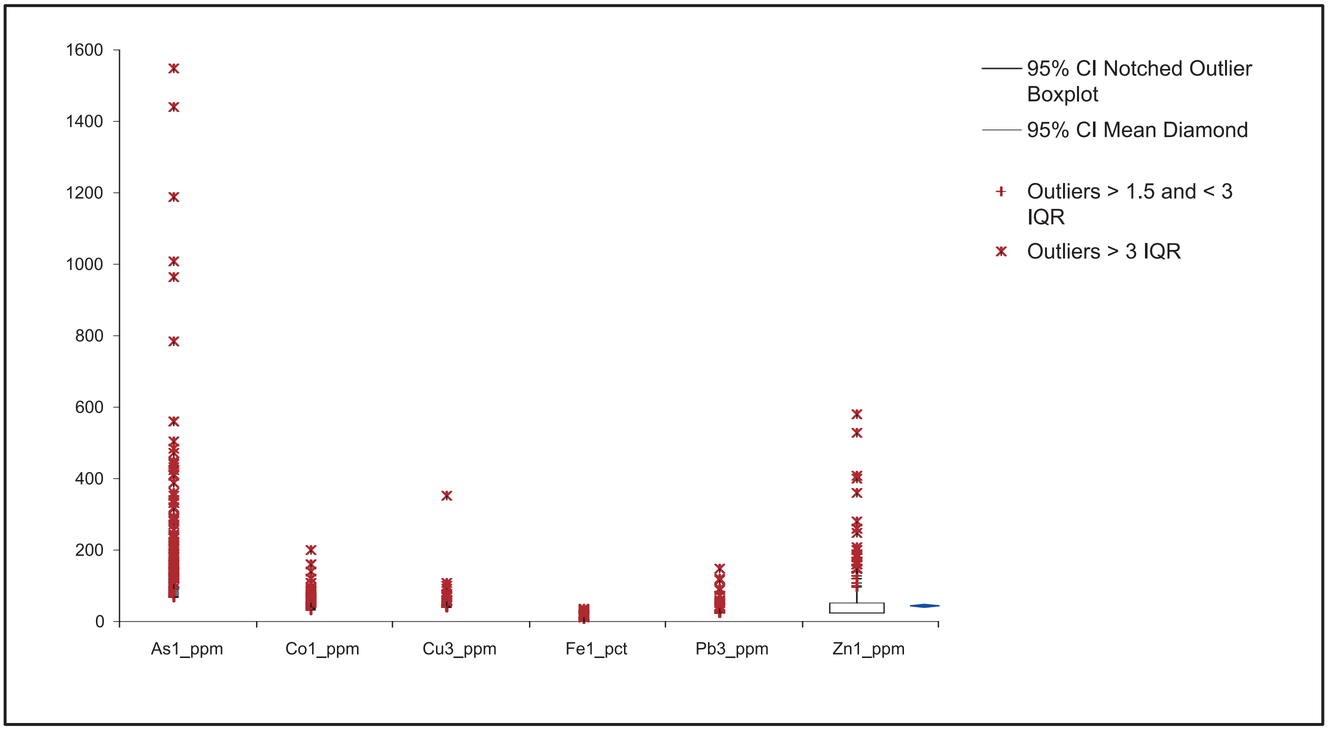


Figure 12. *Multielement boxplot (As, Co, Cu, Fe, Pb and Zn) from rock, till and lake-sediment samples from the Gander Bay area.*

Table 3. Statistics of As, Co, Cu, Fe, Pb and Sb for 9346 lake-sediment samples in the Gander Bay area

	n	Min	1st Quartile	Median	95% CI	3rd Quartile	Max	IQR
As1_ppm	1556	0.20	3.20	10.00	8.90 to 11.00	28.658	1550.00	25.46
Co1_ppm	1556	1.00	1.00	6.00	5.00 to 6.00	14.000	200.00	13.00
Cu3_ppm	1561	1.00	8.00	13.00	12.00 to 13.00	20.000	351.00	12.00
Fe3_pct	1556	0.05	0.75	1.60	1.50 to 1.70	3.600	36.00	2.85
Pb3_ppm	1561	1.00	3.00	7.00	6.00 to 7.00	11.000	150.00	8.00
Sb1_ppm	1556	25.00	25.00	25.00	25.00 to 25.00	54.000	580.00	29.00

Table 4. Statistics summary of arsenic concentrations in samples from the Gander Bay area after elimination of outliers

	Lake Sed (ppm)	Till (ppm)	Rock (ppm)	Gw (ppm)
# of Samples	1447	1351	335	53
Mean	17.32	24.70	6.67	0.022
Median	8.60	15.00	3.00	0.013
Min	0.20	0.20	0.00	0.0002
1st Q	2.90	9.50	2.00	0.003
2nd Q	8.60	15.00	3.00	0.013
3rd Q	22.80	27.80	6.00	0.030
Max	98.60	217.00	83.00	0.239

(Table 4). In fact, exploring the data using these extreme values provided many clues to the development of better models. For this case, a logarithmic transformation was completed to regulate these extreme values.

SPATIAL MAPPING

All mapping and geostatistical calculations were performed using ESRI Inc.'s ArcMap 9.2 GIS platform, ESRI Inc.'s Geostatistical Analyst and Spatial Analyst extensions, and Excel Data Analysis.

Geostatistics have been applied in investigating and mapping soil contamination by heavy metals (Hooker and Nathanail, 2006). The method facilitates quantification of spatial features of minerals and enables its spatial interpolation within the environment, *i.e.*, the variables are linked to locations (Hinkle and Polette, 1999). Observations in space are linked to their co-ordinates and each observation has its specific place in space. Geostatistics are based on the theory of a regionalized variable, which is distributed in space and shows spatial auto-correlation with the samples that are closest in the space than those that are farther apart (Burnham and Anderson, 1998). This is carried out in three main steps (Kumi-Boateng, 2007):

- Exploring the dataset
- Calculating the experimental variogram
- Kriging interpolation and determination of a probability map taking into account values exceeding the MAC.

All statistical analysis in this study was performed on categorical or rank-transformed data; these transformations are not sensitive to differences in the concentrations depicted by the interpolation process versus actual values. Logarithmic transformation was performed to remove a second-order trend. Trend analysis was analyzed using the Geostatistical Analyst Tool of ArcMap software. Ordinary spherical models were used and a neighbourhood search was used with preferably 5 neighbours, and a minimum of 2 for most cases (Figure 13).

When using ordinary kriging (Welhan and Merrick, 2004), there was no ability to account for anisotropy for almost all interpolations. The search ranges were circular, so no weighting was given to any particular direction. Although not taking anisotropy into consideration provides the best predictive surface (Cochran, 2004), anisotropy had to be considered for till samples to improve the interpolation of the data from Gander Bay area.

Figure 14 shows the correlation between observed and predicted values. The solid line shows a line of best fit throught the scatter plot.

Results of these kriging interpolations can be seen in Figures 15, 16 and 17.

DISCUSSION

The data for arsenic concentrations in bedrock, lake-sediment and till were grouped according to bedrock lithology. The arsenic distribution map obtained from lake-sediment samples shows that Fogo Island, Ladle Cove, Aspen Cove, and Gander Bay through to the area south of Glenwood, and in the areas of Baytona up to the area north of Comfort Cove–Newstead all contain elevated concentrations of arsenic. These areas are mainly composed of sedimentary rocks from Davidsville, Gander and Botwood groups, and plutonic rocks from the Mount Peyton intrusive suite and Fogo Batholith. Arsenic concentrations from till samples have better resolution. Elevated arsenic concentrations are localized in sedimentary and metasedimentary rocks of the Davidsville and Gander groups, respectively.

Bedrock sample data covers only a small area (mostly the area of the Mount Peyton Intrusive Suite), but the distribution map shows that elevated arsenic concentrations occur in, and south of, the Mount Peyton Intrusive Suite, and in sedimentary rocks of the Davidsville and Botwood groups.

Arsenic data from groundwater samples were also grouped reflecting the bedrock lithology in which each well was located. The GIS and map analysis identified 12 lithostratigraphic units that were represented by groundwater samples from the Botwood Group, Loon Bay Batholith, Davidsville Group, Fogo Batholith, Mount Peyton Intrusive Suite, Twillingate Pluton, Gander River Complex, Exploits Group, Badger Group, Gander Group, Indian Island Group and Hamilton Sound Group. The groundwater arsenic concentrations had a distribution ranging from below the detection limit to 0.790 mg/L over the Gander Bay area. The mapping of groundwater arsenic concentrations indicates in general that arsenic concentrations tend to be more elevated in the western part of the study area (Table 5).

Table 6 shows that the distribution of arsenic concentrations in the Gander Bay area for till samples sorted by

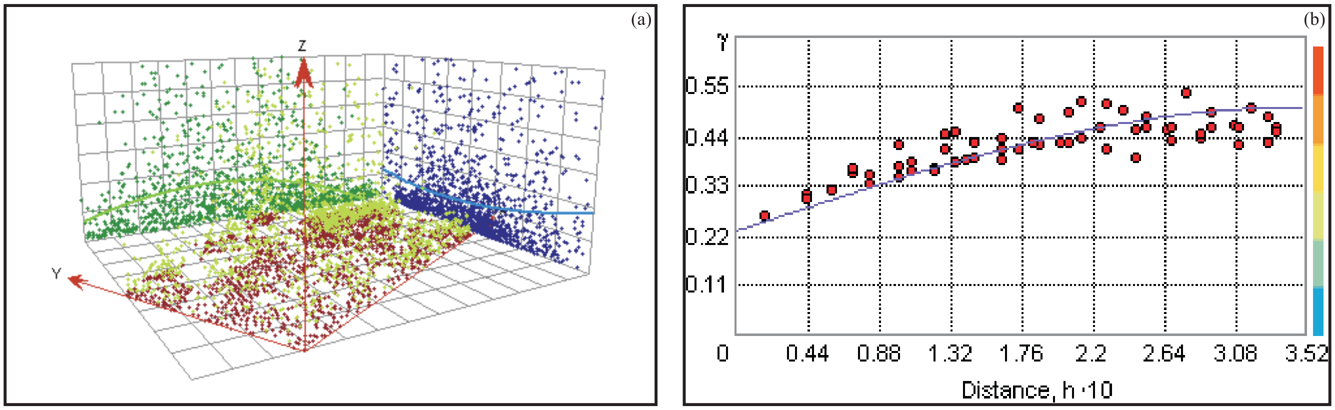
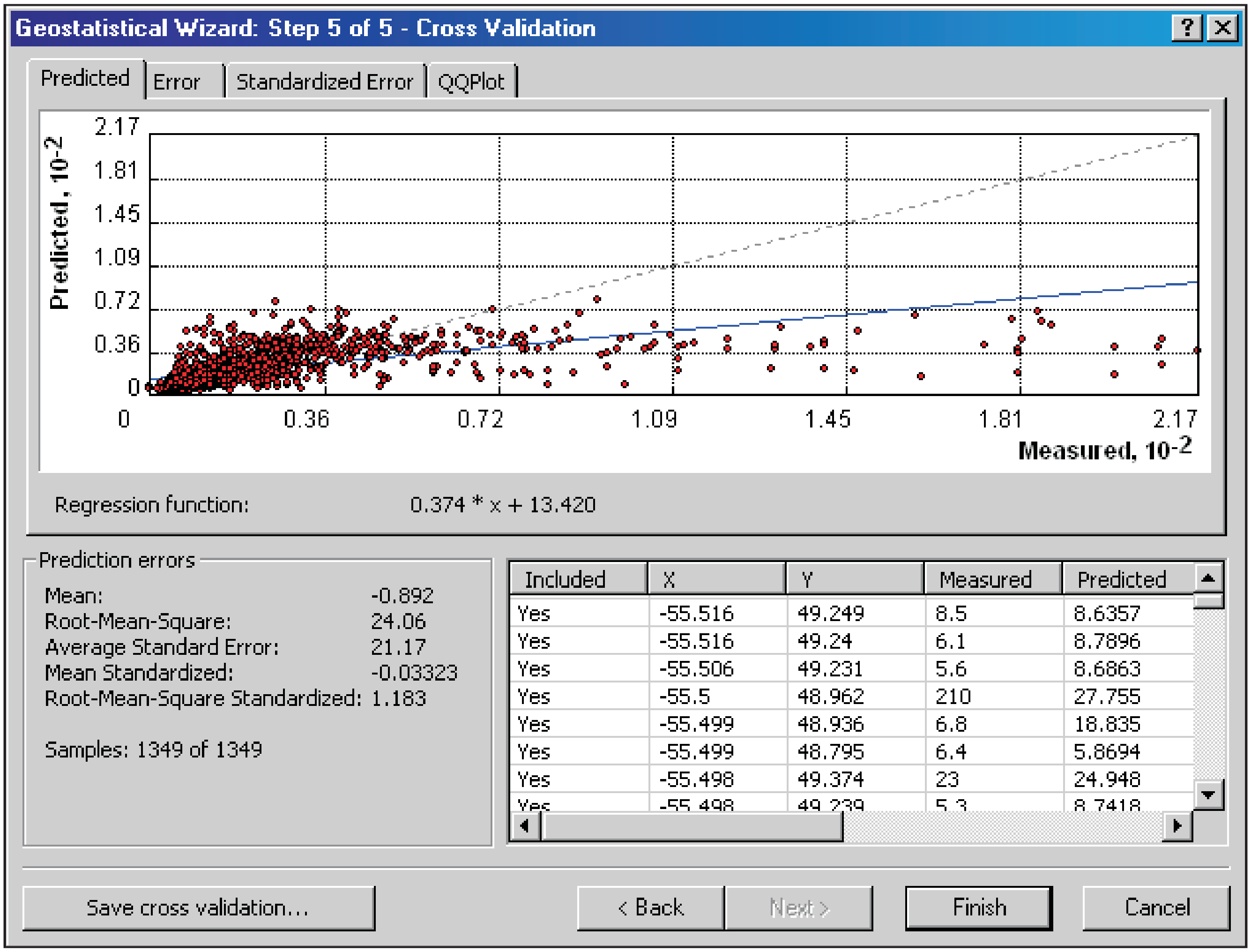


Figure 13. *(a) A second-order polynomial trend given by the U-shaped curve projected on the x and y walls; (b) semi-variogram showing the best model for till samples in the Gander Bay area.*



Regression function: 0.374 * x + 13.420

Prediction errors

Mean: -0.892
Root-Mean-Square: 24.06
Average Standard Error: 21.17
Mean Standardized: -0.03323
Root-Mean-Square Standardized: 1.183

Samples: 1349 of 1349

Included	X	Y	Measured	Predicted
Yes	-55.516	49.249	8.5	8.6357
Yes	-55.516	49.24	6.1	8.7896
Yes	-55.506	49.231	5.6	8.6863
Yes	-55.5	48.962	210	27.755
Yes	-55.499	48.936	6.8	18.835
Yes	-55.499	48.795	6.4	5.8694
Yes	-55.498	49.374	23	24.948
Yes	-55.498	49.239	5.3	8.7418

Figure 14. *Cross-validation table depicting scatter of points that shows the correlation between observed and predicted values. The solid line shows a line of best fit through the scatter plot.*

lithology; the samples show greater median and mean arsenic concentrations in sedimentary rocks relative to the other bedrock groups in that area.

The apparent relationship of arsenic occurrence to lithology shown by the arsenic distribution maps was confirmed with the statistical contingency table (Robinson and

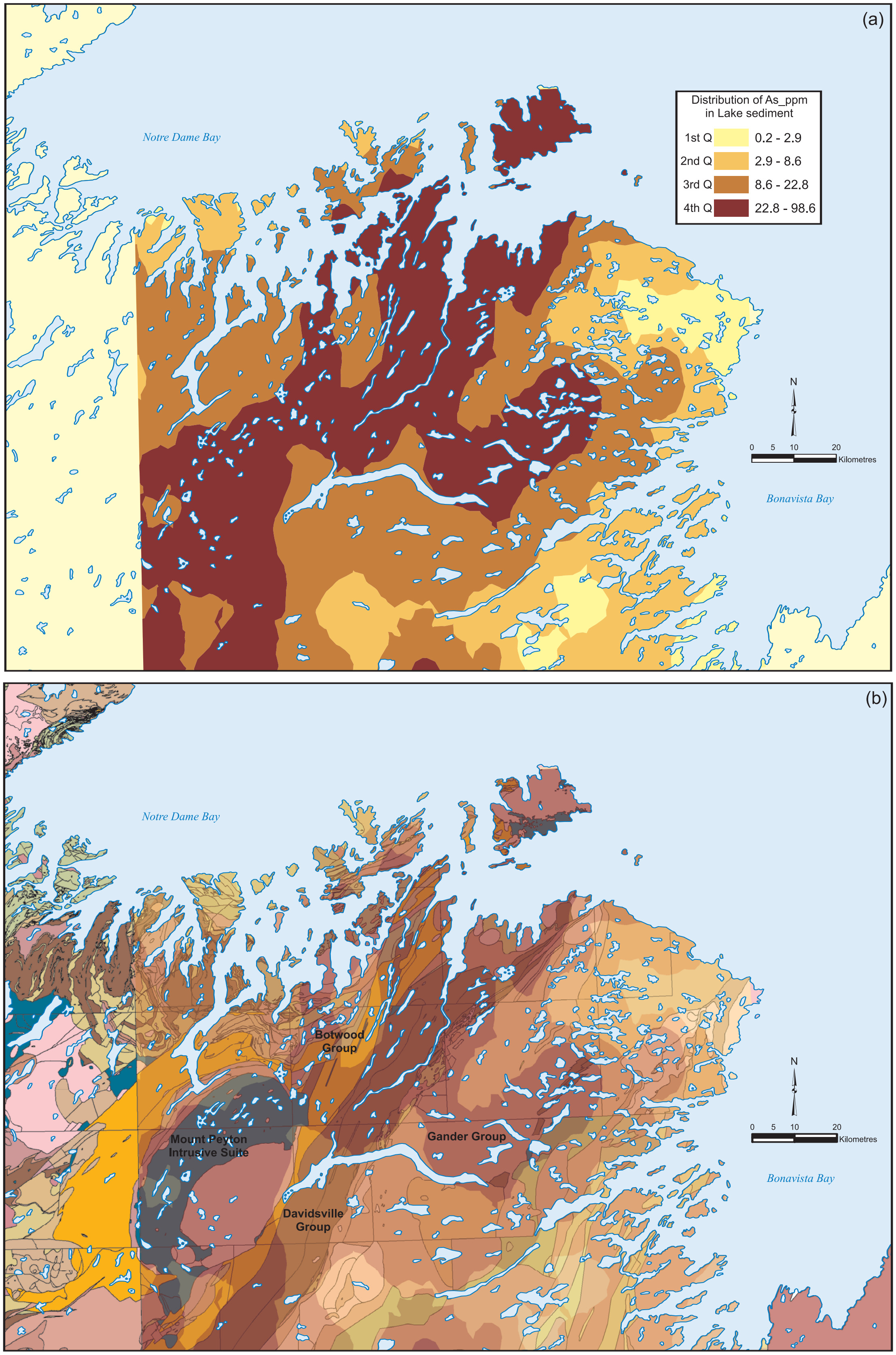


Figure 15. *(a) As distribution (kriging interpolation) in lake-sediment samples in the Gander Bay area, and (b) As distribution overlying bedrock geology map.*

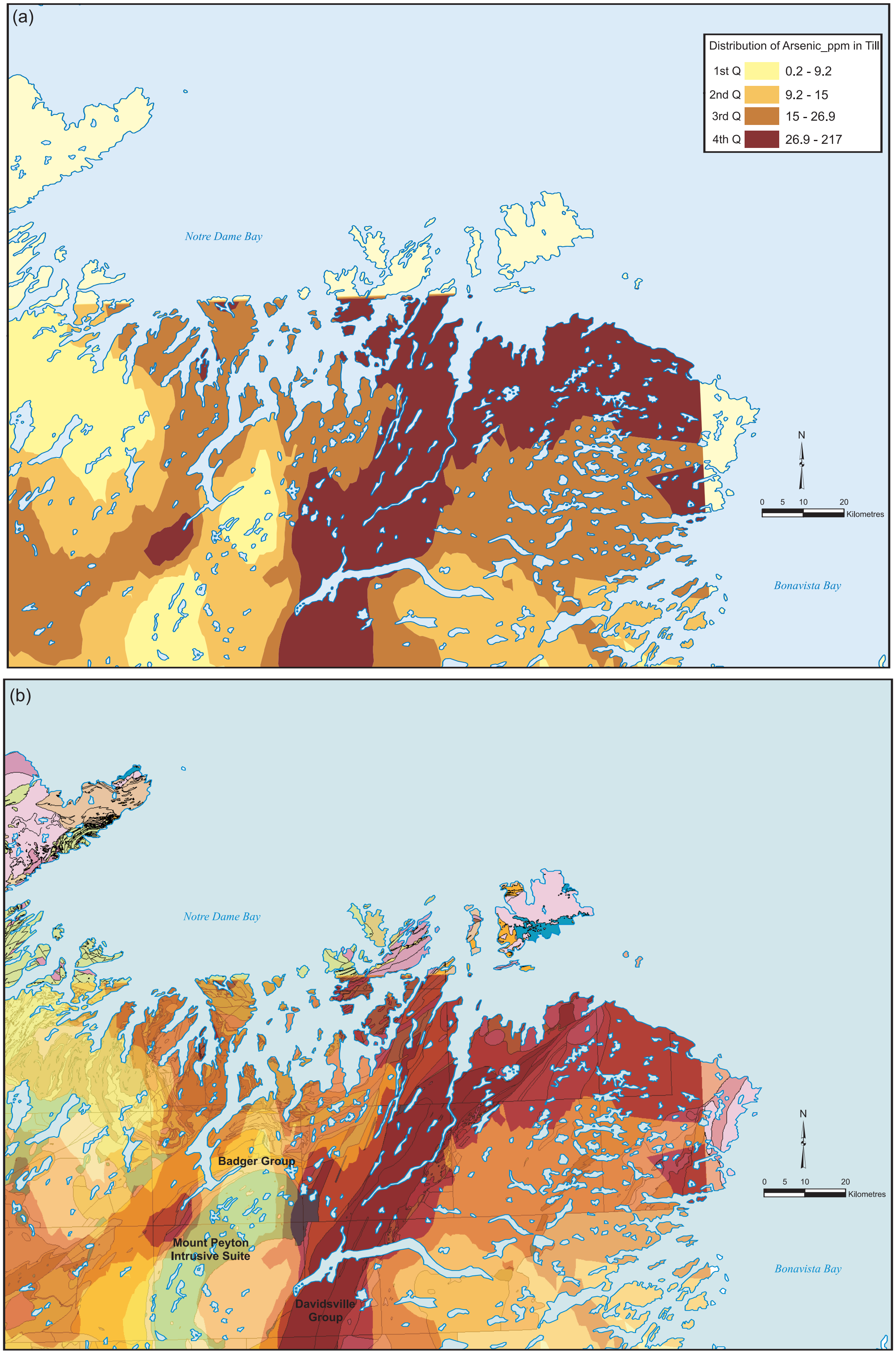


Figure 16. *(a) As distribution (kriging interpolation) in till samples in the Gander Bay area, and (b) As distribution overlain on the bedrock geology.*

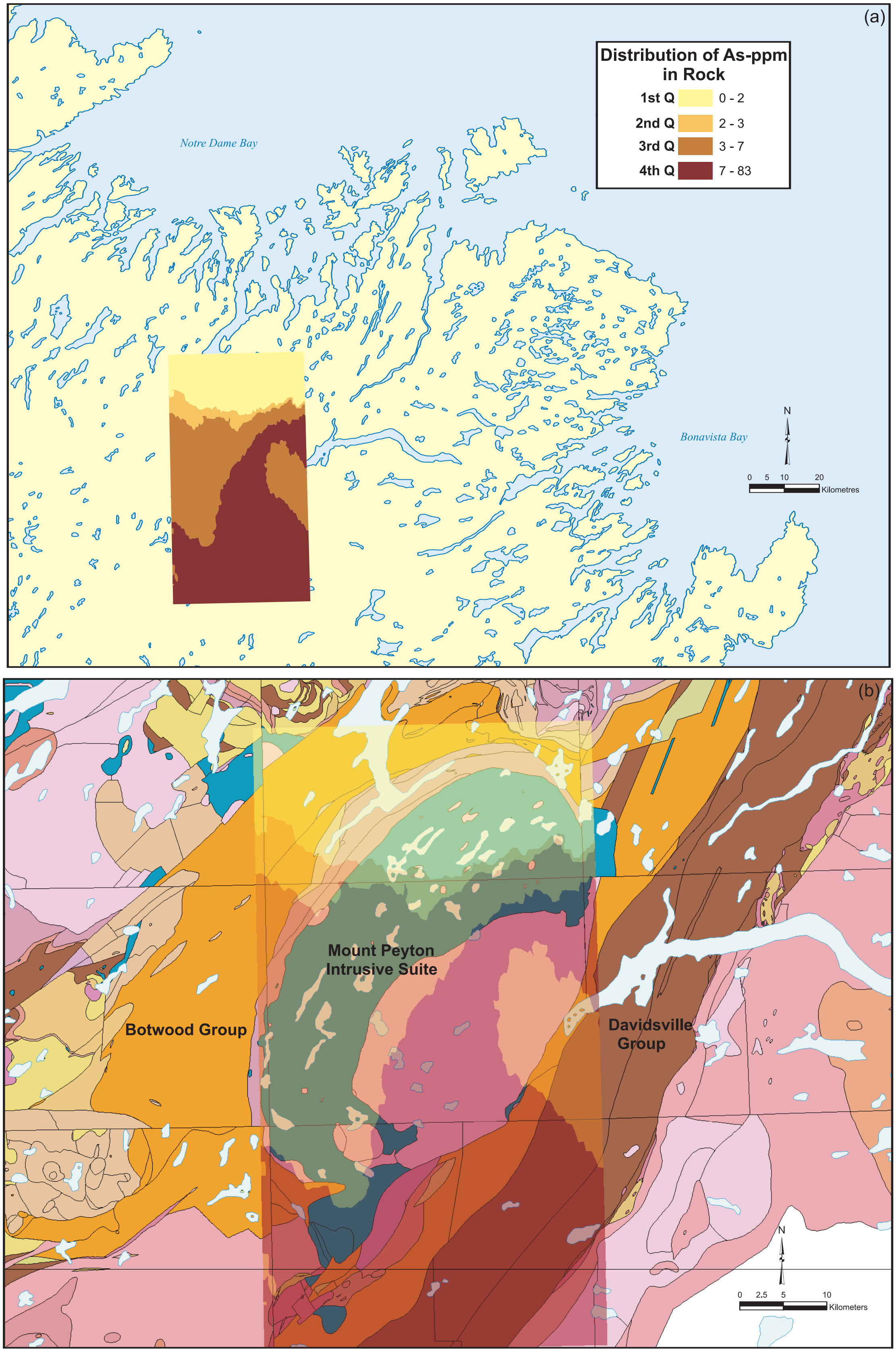


Figure 17. *(a) As distribution (kriging interpolation) in rock samples in the Gander Bay area, and (b) As distribution overlain on bedrock geology map.*

Ayotte, 2006) that records and analyzes the relationship between the variables (igneous, sedimentary and metamorphic rocks). The mapping of the different bedrock types of Gander Bay area showed that the probability of elevated arsenic concentrations is higher in sedimentary bedrock types than in the igneous rocks. However, according to the groundwater well data, groundwater well supplies having elevated arsenic concentrations are found in plutonic rocks (Table 6; Bright, 2006; Sullivan, 2007). Therefore, it can be implied that not only does the bedrock contribute to the elevated arsenic concentrations in the Gander Bay area, but mineralization also appears to play a very important role.

Table 2 indicates that pathfinders in bedrock for As in the Gander Bay area are mainly gold and antimony. Arsenic is a by-product of mining for arsenopyrite, copper and/or gold. Gold and copper occurrences are widely found in central Newfoundland (Figure 3), and are also associated with arsenopyrite. These occurrences are mainly associated with volcanic terranes of the Cambro-Ordovician ophiolitic rocks of the Dunnage Zone and Cambro-Ordovician metasedimentary rocks of the Gander Zone. The ores are grouped into ophiolitic volcanic-hosted and arc volcanic-hosted environments of the Dunnage Zone and associated with relatively deeply formed late orogenic quartz veins and low sulphidation epithermal deposits in the Gander Zone. Antimony occurrence in the Gander Bay area takes place in monomineralic veins and carbonate or quartz-carbonate-bearing vugs, and also shows textures of a low sulphidation epithermal environment (Squires, 2005) throughout this area.

ARSENIC CONTAMINATION MAP

A statistical model has been developed to predict the probability of elevated arsenic concentrations in drinking-water wells in bedrock by geographic area in the Gander Bay area (Figure 18). For drinking-water purposes, a 'safe' threshold is defined by the Health Canada maximum acceptable concentration at 0.010 mg/L. This value was used for the arsenic occurrence map and was based on the spatial distribution map using Ordinary Kriging: Probability Map. The raw dataset was classified into two parts (*i.e.*, high and low). Higher values are indicated by the darker colour, with the number 1 representing 100% probability of finding arsenic concentrations greater than 0.010 mg/L. Lower values are indicated by a lighter colour, with 0 corresponding to the 0% probability of finding elevated arsenic concentrations.

The probability map also shows a strong correlation between elevated arsenic concentrations in groundwater wells, and copper and gold occurrences (Figure 18). This can be explained because arsenic, in its most recoverable form, is found in various types of metalliferous minerals (Mandal and Suzuki, 2002), such as pyrite and chalcopyrite (arsenical-pyritic-copper deposits), and arsenopyrite, realgar and orpiment (arsenic sulphide and arsenic-sulphide gold deposits). Pyrite, chalcopyrite and arsenopyrite are by far the most common ore and gangue minerals in the area. Thus, due to the lowering of the water table below the deposits, 'pyrites' oxidized in the vadose zone release arsenic as arsenic adsorbed on iron hydroxide (Madhaven and Subramanium, 2000). During the subsequent recharge period, iron hydroxide releases arsenic into the groundwater (Fazal and Kawachi, 2001).

CONCLUSIONS

Groundwater wells located in the Silurian and Devonian granite and gabbro intrusions have the highest arsenic concentrations. However, arsenic levels that have elevated concentrations were also found in till- and lake-sediment samples overlying sedimentary bedrock. In lake sediments, when arsenic is exposed to water and soil, it moves downhill into bodies of water. As the arsenic collects on the floor of the bodies of water, it would be trapped in the sediments and would eventually become part of the sedimentary sequence, while in till, glacial erosion and dispersal transport arsenic-rich sediment from its source in bedrock to areas that are underlain by bedrock with low arsenic concentrations. Thus, a combination of bedrock geology (Peters *et al.*, 2006) and surficial and chemical process are responsible for elevated arsenic concentrations within the Gander Bay area. Since igneous rocks come from deep underground, they are mostly unaffected by variation in arsenic levels on the surface.

Table 7 indicates that elevated arsenic contamination was found in mafic plutonic rocks associated with alkaline waters (ph greater than 7). Also, gold and copper deposits in the Gander Bay area commonly occur in close association with sulphide mineralization especially pyrite, arsenopyrite and chalcopyrite (O'Driscoll and Wilton, 2005). Moreover, water samples show associations between zinc, lead and iron concentrations, confirming the presence of a sulphide mineralization at depth. Thus, groundwater in the gold-copper belt zone of the area is potentially vulnerable to the presence of elevated concentrations of dissolved arsenic as a result of the oxidation of the sulphide minerals. Furthermore, deposits of arsenic were found in the study area, such as Foot Pond, Brink's Pond and Rat Pond Southeast. Groundwater flowing through these deposits can dissolve arsenic from the minerals and thus increase arsenic concentration in the well water.

RECOMMENDATIONS

The results of this project have provided a clearer

Table 5. Summary of arsenic in groundwater from communities in the Gander Bay area

Group	Communities	# of Samp.	Arsenic Concentrations (mg/L) Min	Max	Mean	% of samp As > 0.01 mg/L
Fogo Batholith	Seldom-Little Seldom	43	0.002	0.790	0.100	60
	Joe Batt's Arm	6	0.001	0.036	0.017	
	Barr'd Island	2	0.001	0.003	0.002	
	Deep Bay	2	0.001	0.002	0.002	
	Man O'War Cove	1	0.003	0.003	0.003	
	Stag Harbour	2	0.004	0.015	0.01	
Loon Bay Batholith	Baytona	2	0.013	0.025	0.019	67
	Birchy Bay	2	0.002	0.023	0.013	
	Boyd's Cove	2	0.002	0.013	0.008	
Mount Peyton	Notre Dame Junct.	1	0.031	0.031	0.031	100
Twillingate P	Black Duck Cove	1	0.002	0.002	0.002	0
Gander River	Greenspond	1	0.030	0.030	0.030	100
Botwood	Change Islands	7	0.001	0.014	0.007	36
	Island Harbour	2	0.001	0.01	0.006	
	Stanhope	3	0.001	0.011	0.005	
	Stag Harbour	1	0.070	0.070	0.070	
	Laurenceton East	2	0.014	0.019	0.017	
Davidsville	Glenwood	2	0.0002	0.001	0.0006	0
	Clarke's Head	1	0.005	0.005	0.005	
	Wings Point	2	<0.002	0.005	0.003	
	Gander Bay N	1	0.004	0.004	0.004	
	Lumsden	2	<0.002	<0.002	<0.002	
Exploits	Michael's Harb.	2	0.012	0.012	0.012	100
Badger	Campbellton	6	0.013	0.019	0.014	67
	Twillingate	1	<0.002	<0.002	<0.002	
	Frederickton	1	0.008	0.008	0.008	
	Newville	1	0.003	0.003	0.003	
Gander	Gander Bay Road	2	0.013	0.025	0.019	67
	Gander	1	<0.002	<0.002	<0.002	
	Hare Bay	1	<0.002	<0.002	<0.002	
Indian Island	Horwood	2	0.009	0.025	0.017	33
	Victoria Cove	1	0.001	0.001	0.001	
Hamilton Sound	Main Point	2	0.020	0.066	0.043	70
	Noggin Cove	2	0.02	0.03	0.025	
	Aspen Cove	1	0.035	0.035	0.035	
	Aspen Brook	1	0.036	0.036	0.036	
	Carmanville	2	<0.002	<0.002	<0.002	
	Frederickton	1	0.01	0.01	0.01	
	Victoria Cove	1	<0.002	<0.002	<0.002	

Table 6. Summary statistics for bedrock arsenic data grouped by lithology; concentration units are in ppm

	Rocks							
	Igneous				Sedimentary		Metamorphic	
Sample	Intrusive		Volcanic					
Type	Mean	Median	Mean	Median	Mean	Median	Mean	Median
Lake Sed.	17.06	7.00	10.08	4.50	19.28	11.00	17.23	9.00
Till	12.89	9.00	22.29	17.00	38.80	28.80		
Rock	8.31	3.00	2.60	0.00				
Gw	0.018	0.012	0.007	0.007	0.011	0.005		

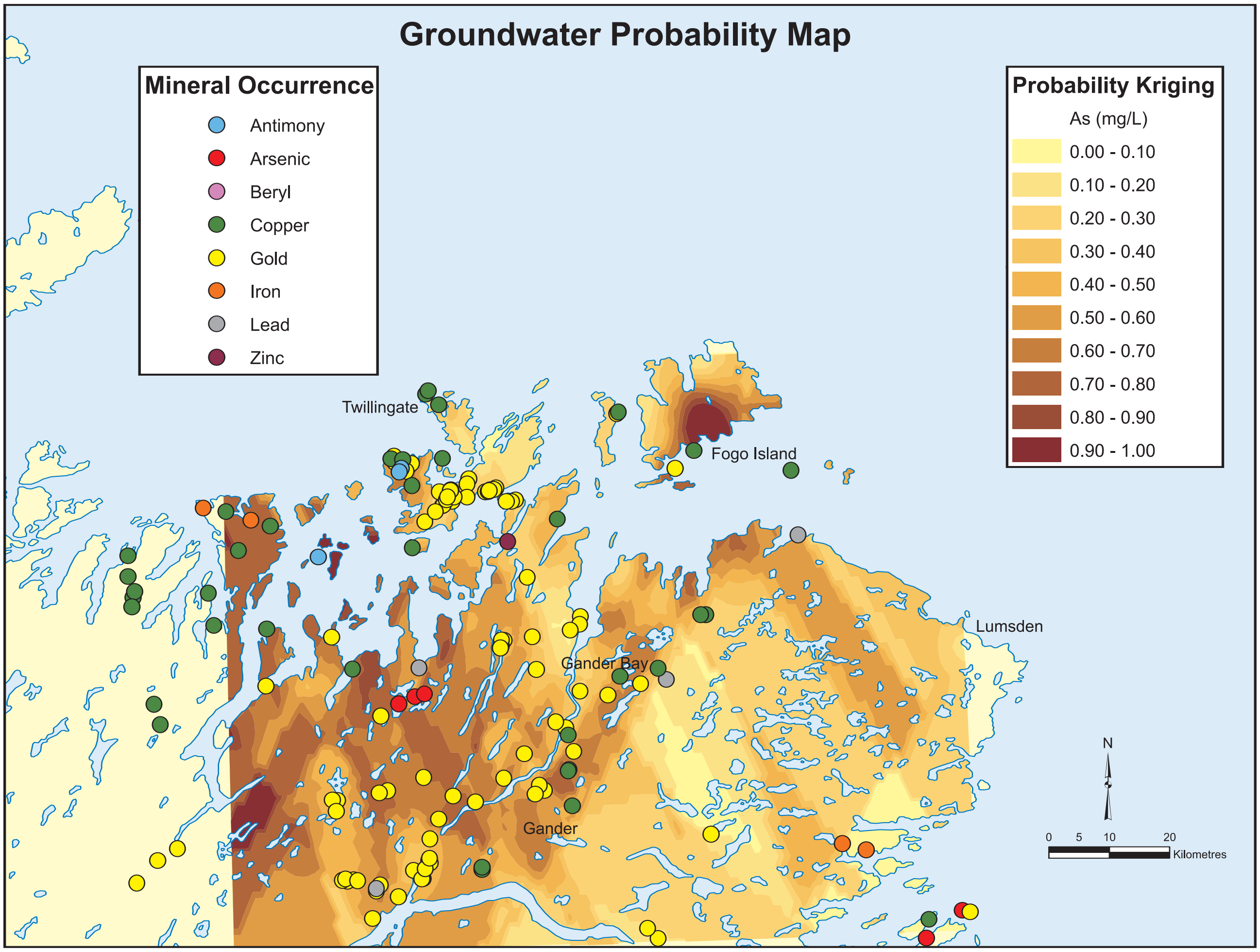


Figure 18. *Arsenic probability map–Mineral Occurrence.*

understanding of the causes for there being elevated arsenic concentrations in groundwater in the Gander Bay, Fogo and Bonavista north area. Hypotheses have been offered to satisfactorily explain the observed patterns of elevated arsenic concentrations. In any future ongoing studies, it is recommended that both, soil and vegetation samples be collected and analyzed for arsenic in order to examine any biological activity that may be influencing arsenic mobilization from sediment to water. Unfortunately, no biogeochemical experiments were performed during this study to directly support this hypothesis.

To safeguard Newfoundland's public and private groundwater supplies, future work should entail additional comprehensive studies of other elements, such as uranium, fluoride, lead, copper, zinc, and iron, which can pose a health risk. Elevated concentrations of uranium and fluoride already have been detected in some Newfoundland commu-

Table 7. Summary statistics for As content in felsic and mafic intrusive rocks

	N. of Samples	Mean (ppm)	Median (ppm)
Intrusive Felsic	19	0.009	0.007
Intrusive Mafic	46	0.04	0.03

nities through well-water testing of public and randomly selected private water supplies.

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