

STATISTICAL ANALYSIS OF NEWFOUNDLAND DRINKING WATER SOURCES CONTAINING ARSENIC

Osama M. Rageh, Cynthia A. Coles, and Leonard M. Lye
Memorial University of Newfoundland, Faculty of Engineering and Applied Science, St. John's, Newfoundland, Canada



ABSTRACT

Arsenic (As) is a toxic element that is released to the environment by natural processes and anthropogenic activities. Canada and the United States recently lowered their recommended maximum acceptable concentration for As in drinking water to 10 µg/l. However, As contents exceeding this level have been detected in many wells and some small surface water bodies in the eastern, central and western regions of Newfoundland. Of 52 sources surveyed 49 had As concentrations exceeding the 10 µg/l level. The primary purpose of this paper is to obtain a better understanding of the factors contributing to the high levels of As in ground and surface water supplies in Newfoundland. Water sample data for the 52 sources were statistically analyzed to identify significant correlations among 32 different parameters. Principal component analysis revealed some differences from water sources in the eastern region of Newfoundland where the main geological formations were different than in the central and western Newfoundland regions.

RÉSUMÉ

L'arsenic (As) est un élément toxique dégagé dans l'environnement par des processus naturels ainsi que par des activités anthropiques. Le Canada et les États-Unis ont récemment baissé leur niveau de concentration maximal recommandé pour l'As dans l'eau potable à 10 µg/l. Toutefois, des niveaux d'As dépassant ce seuil ont été détectés dans de nombreux puits et certains plans d'eaux des régions orientale, centrale et occidentale de Terre-Neuve. Des 52 sites étudiés, 49 avaient des concentrations d'As supérieures à la limite de 10 µg/l. Le but principal de cette communication est d'arriver à une meilleure compréhension des facteurs contribuant aux niveaux élevés de l'As dans les eaux souterraines et de surface à Terre-Neuve. Les données sur les échantillons d'eau provenant des 52 sites ont été soumises à une analyse statistique afin d'identifier des corrélations significatives parmi 32 paramètres. L'analyse des composantes principales a révélé certaines différences dans les eaux provenant de sites de la région orientale de Terre-Neuve, où les formations géologiques étaient différentes de celles des régions centrale et orientale.

1 INTRODUCTION

For many rural Newfoundland communities ground water provides the main source of water for drinking and domestic purposes. However, high arsenic (As) contents have been detected in some wells, requiring that the well water receive special treatment or another source of water is found. The current cost of digging a new well or treating the water in the existing well is almost equal. However, in digging a new well there is the risk that the new source will also be contaminated.

Data obtained from the Newfoundland and Labrador Department of Environment and Conservation revealed that only 3 out of 52 sources now have As concentrations below the 10 µg/l recommended limit in Canada, while the other 49 sources were exceeding the 10 µg/l limit. The eastern part of the province known as the Avalon Peninsula is where the majority of the population resides and is having more contaminated wells and higher concentrations of As.

Arsenic is approximately the 20th most abundant element occurring naturally in the earth's crust. It is a component of more than about 300 minerals and is a constituent of some ores, especially nonferrous ores containing Cu, Pb, Zn, Au, and Ur (Lorenzen et al., 1995). In 2003 the USEPA set the maximum acceptable concentrations for As at 10 µg/l (Chuang, 2005), requiring more stringent regulations for industrial effluents. Conventional practices for removing As include coagulation with iron and aluminum salts, lime precipitation, ion exchange, selective membrane techniques, and adsorption on metal oxides and hydroxides (Lorenzen et al., 1995).

The four oxidation states for As are +3, +5, 0 and -3, however, it is stable in aqueous solution in moderately acidic media as Arsenate or As (V) and in moderately alkaline media as Arsenite or As (III). Toxicity of As depends on its speciation and oxidation state since As (III) is more soluble, mobile and toxic than As (V). Arsenic bioaccumulates and is carcinogenic. It is released during the mining and processing of ores for

minerals (Lorenzen et al, 1995) and as a result of the oxidation of polymetallic sulfide ores (Pokonova, 1998). The more complex the ores, the higher the levels of impurities such as As that may be present and may contaminate water bodies (Lorenzen et al., 1995).

Sources of As are organic or inorganic, and natural or anthropogenic. Arsenic is released from volcanoes, weathered rocks, pesticides, herbicides and wood preservatives, and during zinc production and forest fires. Urban runoff is estimated to be the largest source of As to surface water (Piver, 1983).

Since As exists naturally in sediments and rocks, weathering of these geologic formations contributes to As release to the environment. In Newfoundland, the two main types of rocks are igneous and sedimentary. Igneous rocks, such as granite have As concentrations ranging from 0.2-13.8 mg/kg while sedimentary rocks such as shale, limestone, and sandstone have higher As concentrations of 0.3-500, 0.1-20, and 0.6-120 mg/kg respectively (Allard, 1995).

Although the As concentration in the earth's crust is only about 1.7 mg/kg, most release of As is from natural sources. Sulfide minerals are the main As bearing formations and they are abundant in Newfoundland since they are abundant in mafic lavas and igneous rocks. Arsenic bearing minerals found in Newfoundland include arsenopyrite (FeAsS), realgar (As₂S₃), orpiment (As₂S₃), niccolite (NiAs) and cobbalite (CoAsS) (Swinden, 1988). Arsenic that occurs naturally or has accumulated in geological formations, sediments and soils may be released under reducing or harsh weathering conditions (Robinson et al., 2006).

Arsenic, nitrogen, phosphorus, antimony, and bismuth all belong to group 5A in the periodic table, they have an electron configuration of the outer shell of S² P³ and they tend to form trivalent and pentavalent compounds (Frank, 1978).

Arsenic exists in volatile, solid, and aqueous forms and the soluble forms are very mobile. Microorganisms in soil, sediments, and water can produce volatile organic arsenic, which enters the atmosphere and becomes transformed into an inorganic form. Soluble As (III) can be oxidized and transformed into the insoluble As (V), which can be adsorbed to sediments or soil (Environment Canada, 2002).

The primary purpose of this paper is to obtain a better understanding of the factors contributing to the high levels of As in ground and surface water supplies in Newfoundland.

2 MATERIALS AND METHODS

Water samples from ground and surface water supplies were collected from throughout Newfoundland by the Newfoundland and Labrador Department of

Environment and Conservation. From the 52 sources, 128 water samples were statistically analyzed in an effort to identify factors contributing to a high As content. A total of 28 samples were from surface waters and the remaining 100 samples were from ground water. Water supplies in the province were divided into eastern, western and central regions to conduct principal component analyses and account for the differences in practices, geological formations, and conditions in each region. The analysis included 87 samples from 26 sources in the eastern region, 25 samples from 16 sources in the western region and 16 samples from 10 sources in the central region.

To study the relationship between As and 31 other parameters, a correlation study was undertaken. Significant correlations were chosen according to the sample size, the Pearson's correlation (r) and the p-value. The p-value represents the probability of error when a correlation is considered to be significant so the smaller the p-value the less chance of error. Pearson's correlation value can be small but reflect a significant correlation if the sample size is large. The absolute value of r represents the strength of the relation between variables. The sign of the correlation indicates whether the concentrations of correlated variables are directly or inversely proportional (Vincent, 1996).

Minitab, used to find correlations between As and the other parameters, is a software package for statistical analysis of simple and complex functions (Zehna, 1992) developed in 1972 at Pennsylvania State University by Barbara Ryan, Thomas Ryan, Jr. and Brian Joiner (Wikipedia, 2006). The physical properties analyzed included alkalinity, conductivity, hardness, pH, total dissolved solids and turbidity. Boron, bromide (Br⁻), calcium, chloride (Cl⁻), fluoride, potassium, sodium, sulfate (SO₄²⁻), ammonia, nitrate, nitrite, phosphorus, aluminum, antimony (Sb), barium, cadmium, chromium, copper, iron (Fe), lead, magnesium, manganese (Mn), mercury, nickel, selenium, uranium, and zinc were the ions and metals analyzed.

Table 1 Significant values of the correlation coefficient (adapted from Vincent, 1996).

df	P-value		
	0.10	0.05	0.01
14	0.426	0.497	0.623
15	0.412	0.482	0.606
16	0.400	0.468	0.59
17	0.389	0.456	0.575
18	0.378	0.444	0.561
19	0.369	0.433	0.549
20	0.360	0.423	0.537
25	0.323	0.381	0.487
30	0.296	0.349	0.449
40	0.257	0.304	0.393
50	0.231	0.273	0.354
60	0.211	0.250	0.325
70	0.195	0.232	0.302
80	0.183	0.217	0.283
90	0.173	0.205	0.267

As the p-value and the number of samples decrease the accepted value for a significant correlation gets higher. Accepted correlations at p-values of 0.1, 0.05 and 0.01 for different degrees of freedom (df) are given in the Biometrika table (Table 1), which was the guideline followed in this paper to select significant correlations. The df is the number of samples in each region – 2, as a df is lost for each variable in a correlation (Vincent, 1996). In this paper a p-value of 0.05 was used.

3 RESULTS

Table 2 shows physical properties, ions and metals that were significantly correlated to As in the three different regions and in the combined regions excluding Labrador. These parameters are arranged in a descending order according to the value of their correlation with As in the eastern region, which contains more of the water sources that were studied.

Table 2 Significant correlations between As and the other parameters measured in water sources in Newfoundland.

	Arsenic and	Pearson's Correlation (r) P-value			
		Eastern (87)	Western (25)	Central (16)	Provincial
1	Bromide	0.660 0.000			0.386 0.000
2	Hardness	0.589 0.000			0.250 0.013
3	Antimony	0.509 0.000	-0.499 0.172		0.249 0.005
4	Chloride	0.494 0.000	-0.630 0.001		
5	Sulfate	0.476 0.000	-0.670 0.001		
6	Zinc	0.474 0.000			
7	Magnesium	0.418 0.000		-0.690 0.003	0.175 0.048
8	Chromium	0.407 0.000			0.308 0.001
9	Calcium	0.381 0.000	-0.442 0.027		
10	Color	0.377 0.001	0.634 0.001	0.689 0.003	0.504 0.000
11	Total Divalent ions	0.372 0.000	-0.423 0.035		
12	Total Dissolved solids	0.355 0.001	-0.728 0.000	-0.532 0.034	-0.159 0.000
13	Cadmium	0.352 0.001			
14	Conductivity	0.331 0.003	-0.727 0.000	-0.538 0.031	-0.174 0.055
15	Flouride	-0.322 0.003	-0.611 0.001		-0.305 0.001
16	pH level	-0.309 0.005	-0.692 0.000	-0.661 0.005	-0.403 0.000
17	Aluminum	-0.301 0.006	0.514 0.009		0.249 0.005
18	Potassium	-0.264 0.017	-0.769 0.000	-0.678 0.004	-0.313 0.000
19	Sodium	0.242 0.028	-0.616 0.001	-0.568 0.022	
20	Alkalinity	-0.192 0.085	-0.769 0.000	-0.776 0.000	-0.423 0.000
21	Lead		0.415 0.039		
22	Total Phosphorus		-0.567 0.003		

Globally, most of the areas suffering from high As concentrations are characterized by reducing conditions which promote As release. Vietnam, India, Bangladesh, Mongolia, Argentina, and United States have As toxicity problems and the conditions in most of these affected regions are alkaline (Katsyiannis and Katsyiannis, 2006; Anawara et al., 2003). Therefore in these areas correlations were found between As and pH or As and alkalinity or both. As (III) is the dominant species at high pH. It has high mobility and usually exists in aqueous forms. Both As (III) and As (V) tend to desorb at higher pHs from oxide surfaces and clay minerals. Reductive dissolution of Fe and Mn oxyhydroxides are important processes for mobilizing As in West Bengal, Bangladesh, and some parts of the U.S., and Argentina. In these regions As concentrations are positively correlated with Fe and Mn, and dissolved organic carbon (DOC) (Anawara et al., 2003). The correlations between As and different ions and parameter in different regions in the world are listed in Table 3.

Of the water sources that were analyzed in Newfoundland, 37 were alkaline, 15 were acidic and the As concentration was found to be negatively correlated with the pH. In the sources tested, Fe and Mn had very low concentrations and were not correlated with As. DOC was negatively correlated with As. Accordingly, reductive dissolution of Fe and Mn does not appear to be controlling As release in Newfoundland, and the conditions in Newfoundland, especially in the Avalon Peninsula, appear to be quite different from conditions shown in Table 3.

Table 3 Main parameters correlated with As in other parts of the world.

(r)	Ions and Parameters	Regions	References
-ve	SO ₄ ²⁻	Bangladesh (Nawabganj)	Ohno et al, 2005; Anawara et al., 2003.
+ve	Fe, Mn, & Al	Bangladesh U.S. (Florida)	Ohno et al, 2005; Cai et al, 2002; Anawara et al. , 2003.
+ve	pH	Argentina, U.S., India, Botswana Bangladesh	Mapila et al, 2006, P.L.; Smedley et al., 2002.
+ve	Alkalinity	Areas in Bangladesh, U.S., Argentina	Smedley et al., 2002.
+ve	DOC	Bangladesh,	Anawara et al. , 2003.
+ve	NH ₄ ⁺	Bangladesh	Anawara et al. , 2003.

The correlation between SO₄²⁻ and As in the eastern region was significant and positively correlated. However, the correlation was negative for both central and western regions. A negative correlation between SO₄²⁻ and As in ground water in central and western regions could mean that reducing conditions are responsible for As dissolution (Ohno et al., 2005). However, the negative correlations between As and pH and low concentrations of Fe and Mn indicate that the conditions may not be reducing (Anawara et al., 2003).

Oxidation of sulfide phases may be the reason for As release in the eastern regions as both SO₄²⁻ and As are positively correlated and the SO₄²⁻ concentration is high (4-50 mg/l). Newfoundland is a coastal area characterized by heavy precipitation throughout the year, and this can contribute to the presence of ions and metals in both ground and surface water. Rainfall supplying oxygen can promote oxidation of the sulfide minerals producing sulfates (Bohn et al., 1985) and releasing As. Rainfall may also cause the entrained salts in air from the ocean surface to become dissolved and fall in the form of wet precipitation, transporting Cl⁻ and Br⁻ to the ground water (Davis et al, 1998). This may help explain why, for the Avalon Peninsula or the eastern region, As is highly correlated with Br⁻, Cl⁻, and SO₄²⁻. Other metals and ions may also be leached and eluted with water from precipitation during infiltration before reaching the ground water (Ohno et al., 2005).

Most of the Fe sulfide bearing minerals can act both as a source and as a sink for As depending on the geochemical characteristics of the aquifer. Under oxidizing conditions Fe (II) will be oxidized to Fe (III) oxide (FeOOH) (Bohn et al., 1985), which will tend to adsorb rather than release As since Fe oxides are one of the main adsorbents for As. In addition the soluble Fe (II) when oxidized to Fe (III) may also co-precipitate with As and reduce its concentration in water. Accordingly, Fe bearing sulfides such as arsenopyrite (FeAsS) cannot be sources of As in water under oxidizing conditions although other sulfide minerals might be responsible for high As concentrations in water under such conditions (Anawara et al., 2003).

The presence of other anions such as sulfates (SO₄²⁻), phosphates (PO₄³⁻) and antimonates (SbO₄³⁻) might contribute to a high As concentration since they compete for the same sites on solid surfaces, sediments, and rocks. Positive correlations between As and SO₄²⁻, and As and Sb in the eastern region support the competition on sorption sites hypothesis (Katsyiannis and Katsyiannis, 2006).

The geological formations of the eastern region consist mainly of sandstone with some volcanic rocks. Most of the samples taken from water sources in the eastern region were located within sandstone rocks. On the other hand, samples from central and western regions are taken from areas with more volcanic and metamorphic rocks and fewer limestone and sandstone formations. The differences in the mineralogical

compositions may be the reason for the different correlations between As and the other parameters in the eastern region compared to central and western regions (Mining and Geology, 1991). However, there was no correlation between mineral-bound arsenic and dissolved arsenic. In other words, areas having geological formations with high As concentration were not necessarily the ones having higher As concentrations in the water. Sandstone and shale typically have higher As concentrations than volcanic and metamorphic rocks, although there were still areas with the latter geological formations that had the highest As concentrations and ones with sandstone that had lower As concentrations (Mining and Geology, 1991).

4 CONCLUSIONS

Principal component analyses revealed that the eastern region of Newfoundland is having different water characteristics than most of the areas in the world suffering from elevated As concentrations. This might be due to the oxidizing conditions created by the heavy precipitation in the area. Further studies must be done in this area and more water samples should be analyzed at different times of the year to systematically investigate the effect of seasonal variation on As release. Moreover, wells of high As concentration should be monitored for longer periods to detect the effect over time on As concentration. In addition, samples from different geological formations within the province should be studied and tested under different conditions such as reducing, oxidizing, acidic and alkaline. In this way detailed information can be obtained about the mechanisms of As release and the conditions that contribute to high As concentrations.

ACKNOWLEDGEMENTS

The authors would like to thank the NSERC for their funding towards this project and Mr. Keith Guzzwell, Groundwater Resources Manager, Department of Environment and Conservation, Government of Newfoundland and Labrador, for providing water sample data for the analysis.

REFERENCES

- Allard, B. 1995. Trace elements in natural water, B. Shalby and E. Steinnes (EDs.), Fl:CRC Press Inc.: 151-176.
- Anawara, H. M., Akaib, J., Komakic, K., Teraod, H., Yoshiokae T., Ishizukaf. T., Safiullahg S., and Kato K. 2003. Journal of Geochemical Exploration. 77: 109–131.
- Bohn, H., McNeal, B., and O'Connor, G. 1985. Soil Chemistry, 2nd ed., Wiley-Interscience, NewYork, USA. (p267)
- Cai, Y , Cabrer, J. C., Georgiadis, M., Jayachandranb, K. 2002. Assessment of arsenic mobility in the soils of some golf courses in South Florida. The Science of the Total Environment, 291: 123–134.
- Chuang, C.L., Fan, M., Xu, M., Brown, R. C., Sung, S., Saha, B., and Huang, C.P. 2005. Adsorption of arsenic (V) by activated carbon prepared from oat hulls, Chemosphere 61: 478-483.
- Davis, S. N., Whittemore, D. O., and Fabryka-Martin, J. 1998. Uses of chloride/bromide ratios in studies of potable water. Groundwater 36 (2): 338–350.
- Environment Canada, 2002, retrieved in July 2006 from www.ns.ec.gc.ca/epb/envfacts/arsenic.html
- Frank, B. 1978. Chemistry: A Modern Introduction, 2nd Ed., Philadelphia, PA, W. B.,Saunders Company.
- Lorenzen, L., van Deventer, J. S. J. and Landi, W. M. 1995. Factors affecting the mechanism of adsorption of arsenic species on activated carbon. Minerals Engineering, 8 (4/5): 557-569.
- Katsoyiannis, I. A., and Katsoyiannis, A. A. 2006. Arsenic and other metals contamination of groundwaters in the industrial areas of Thessaloniki, Northern Greece. Environmental Monitoring and Assessment, 123: 393–406.
- Mapila, P. H., Mapila, T., Letshwenyo, M., Wolski, P., Hemond, C. 2006. Characterization of arsenic occurrence in the water and sediments of the Okavango Delta, NW Botswana. Applied Geochemistry, 21: 1376–1391.
- Mining and Geology. 1991. In McManus, G.E., and Wood, C.F. (EDS.), Atlas of Newfoundland and Labrador (plate 19). Newfoundland, Canada: MUNCL.
- Ohno, K., Furukawa, A., Hayashi, K., Kamei, T. and Magara, Y. 2005. Arsenic contamination of groundwater in Nawabganj, Bangladesh, focusing on the relationship with other metals and ions. Water Science & Technology, 52 (8): 87–94.
- Piver, W. T., 1983, Biological and environmental effects of arsenic, Top Environ. Health, NY, Elsevier.
- Pokonova, Y. V. 1998. Carbon adsorbents for the sorption of arsenic. Carbon, 36 (4): 457-471.
- Robinson, G. R., Jr., and Ayotte, Joseph D. 2006. The influence of geology and land use on arsenic in stream sediments and ground waters in New England USA. Applied Geochemistry, 21 (9): 1482-1497.
- Smedleya, P.L., Nicollib, H.B., Macdonald, D.M.J., Barrosb, A.J., and Tullioc, J.O. 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Applied Geochemistry,7: 259–284.
- Swinden, H, 1988, The Volcanogenic sulfide district of central Newfoundland, Edited by H. Swinden and B. Kean, Department of Energy, Mines, and Resources, Government of Canada.
- Vincent, W. J. , 1996, Statistics in Kinesiology 3rd Ed., Human kinetics, U.S.
- Wikipedia, the Free Encyclopedia, Retrieved from <http://en.wikipedia.org/wiki/Minitab> in June 2007.
- Zehna, W. P. 1992. A Minitab comparison with Macros. Addison-Wesley Publishing Company, USA.