ELEVATED FLUORIDE AND BORON LEVELS IN GROUNDWATER FROM THE NANAIMO GROUP, VANCOUVER ISLAND, CANADA

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ABSTRACT
Groundwater geochemical data from a sand- and mudstone aquifer system on eastern Vancouver Island are described. As in many similar geological situations around the world, some of the samples have significantly elevated fluoride levels. We show that this can be largely attributed to the very high pH resulting from base-exchange softening, and that this process appears to be most effective in parts of the aquifer that have better-developed intergranular flow. We also see a strong correlation between boron and fluoride, and we propose that boron is also being controlled by base-exchange softening and pH. Both fluoride and boron lead to significant health implications at high concentrations, and the geochemical relationships established in our study can be used to predict potential risks.

RÉSUMÉ
Des données sur la nappe phréatique géochimique du système aquifère consistant de la grès et d'argile sur la côte est de l'Île de Vancouver sont décrites. Tout comme plusieurs cas semblables, certains échantillons contiennent des niveaux de fluoride plutôt élevés. Nous démontrons que ceci peut être attribué en grande partie au niveau très élevé de pH résultant de l'échange d'ion de calcium et de sodium. De plus, ce processus semble être très efficace dans certaines parties d'aquifères démontrant un écoulement intergranulaire plus développé. Nous remarquons aussi une importante corrélation entre le bore et le fluoride, et nous suggérons que le bore est aussi contrôlé par l'échange d'ion et de pH. Lorsque la teneur de fluoride et de bore est plus concentrée, ceci peut causer de sérieux problèmes de santé. Les liens géochimiques établis lors de notre étude démontrent la possibilité d'un tel risque.

1. INTRODUCTION

Although most ground and surface waters have fluoride concentrations well below 0.5 mg/L, there are numerous situations, worldwide, where levels exceed the World Health Organization maximum acceptable concentration of 1.5 mg/L (WHO 2004). In a few cases elevated fluoride levels can be attributed to groundwater contact with rocks that have particularly high fluorine contents (e.g., in the granitic terrain of northern Ghana, Apambire et al. 1997), but most fluoride-rich waters are found in sandy aquifers where the rocks have fluorine levels that are typical of background—a few hundred ppm at most. Some examples include the Cretaceous and Tertiary clastic sedimentary rocks of Alberta (Hitchon et al. 2001), the Carboniferous fluvial sandstones of New Brunswick (Boyle 1992), the Cretaceous Potomac sands of Virginia (Cederstrom 1946), the Cretaceous Dakota sandstone aquifer in Kansas (Macfarlane et al. 1992), the Permian-Triassic Karoo sandstone in Zimbabwe (Larsen et al. 2001), the Cretaceous Emscher-Mergel marls in Germany (Queste et al. 2001), and the recent loess deposits in the Buenos Aires area of Argentina (Kruse and Ainchil 2003).

We have studied the geochemistry of groundwater samples from 177 domestic water wells completed in clastic sedimentary aquifers on eastern Vancouver Island (Canada) and the adjacent Gulf Islands (Figure 1). Previous work in this region has shown that some Nanaimo Group wells have fluoride levels above 1.5 mg/L (Kohut and Hodge 1985). Fluoride and boron levels in our samples range up to 10 mg/L and 3860 µg/L

respectively. In this paper we describe the aquifers, present a model for the geochemical evolution of the groundwater, and discuss why some wells have high fluoride and boron levels, while others do not. Our results have important implications for understanding elevated groundwater fluoride and boron levels in this and other regions of the world.

1.1 Study area

The eastern coast of Vancouver Island, including the adjacent Gulf Islands, is largely underlain by the terrestrial and marine mudstone, sandstone and conglomerate of the Upper Cretaceous Nanaimo Group (Figures 1 and 2). Most residents of the Gulf Islands and of some rural parts of eastern Vancouver Island depend on private wells, and much of that groundwater is derived from Nanaimo Group aquifers.

The present study was confined to two rural areas near to the City of Nanaimo, including Gabriola Island and the Yellow Point region on Vancouver Island (Figure 3). The Late Cretaceous (ca. 94 to 65 Ma) Nanaimo Group is exposed along much of the eastern coast of Vancouver Island, on most of the adjacent Gulf Islands, and at a few locations on the British Columbia mainland (Figure 1). The group has an aggregate thickness of approximately 5000 m, and is divided into 11 formations, as summarized on Figure 2 (Mustard 1994). The upper six of those formations are exposed in the Yellow Point and Gabriola Island areas, and these strata are comprised of clastic

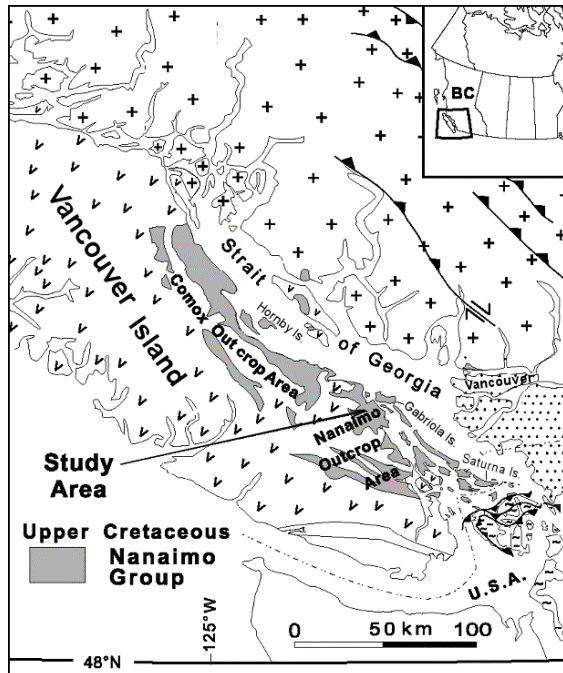sediments of submarine-fan origin. Lithological information for these 6 formations is included in Table 1.

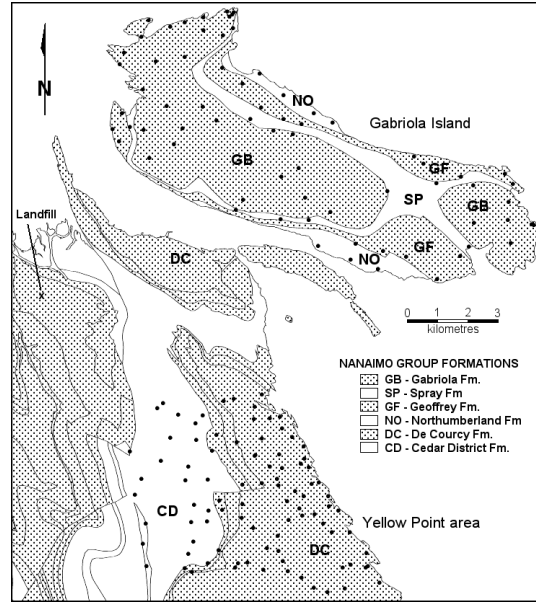Figure 1. Location and geology of the study area (after Mustard 1994).

Figure 2. Stratigraphy of the Nanaimo Group (after Mustard 1994).

Figure 3 Geology of the study area and locations of well-water samples (after Cathyl-Bickford and Hoffman 1998; England 1990).
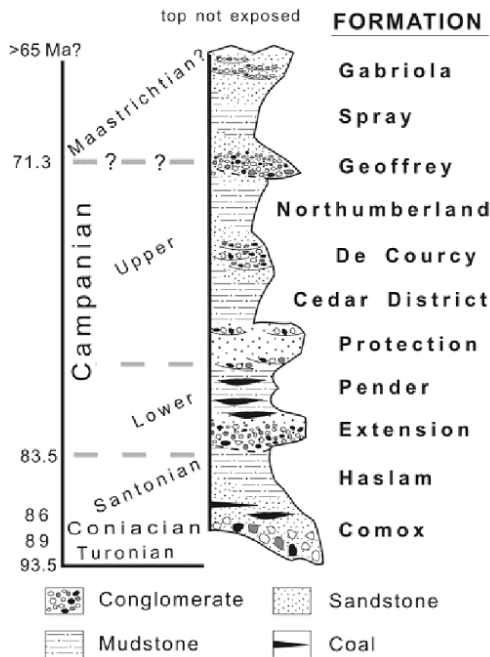
Table 1. Lithologies of the upper six formations of the Nanaimo Group.

Formation	Lithology
Gabriola	Medium- to coarse-grained submarine fan feldspathic sandstone (average 15% matrix), with mudstone interbeds
Spray	Submarine fan mudstone and siltstone with turbidites, and with sandstone interbeds
Geoffrey	Medium- to coarse-grained submarine fan feldspathic sandstone (average 15% matrix) interbedded with conglomerate
Northum-berland	Submarine fan mudstone and siltstone with sandstone interbeds
De Courcy	Medium- to coarse-grained submarine fan feldspathic sandstone (average 15% matrix), with mudstone interbeds
Cedar District	Submarine fan mudstone and siltstone with turbidites, and with sandstone interbeds

Post-glacial eustatic sea-level rise resulted in complete inundation of the study area at the end of the last glaciation. Maximum sea level was approximately 200 m above the current level at around 12,000 y B.P. (James et al. 2000). The maximum elevation in the study area is 160 m on Gabriola Island. Isostatic rebound led to the current shore line being established by around 6000 y B.P.

2. METHODS

Water samples were collected from domestic wells at an average density of 1 sample per km^2 (Figure 3). In all cases the water was allowed to flow for approximately 10 minutes before sampling to ensure that pipes were flushed. Water treatment devices of any kind were avoided. Samples were filtered on site using 1.2 µm glass-fibre filters. One sub-sample was treated with 0.5 mL preservative-grade HNO_3 acid, while the other was untreated. Samples were refrigerated at 4ºC from the time of collection until completion of all analysis.

Water temperature, pH and conductivity were determined on site at the time of sample collection. Temperature and pH were determined using a Fisher Accumet AP62 pH meter. Conductivity was measured using a Fisher AP65 conductivity meter.

Laboratory chemical analyses were carried out according to accepted methods as outlined in Standard Methods (1998). Fluoride was determined by ion-selective electrode using a combination electrode (Fisher 13-620-528) or a half cell electrode (Fisher 13-620-523) against silver/silver chloride reference, after adding total ionic strength adjustment buffer (SM 4500-F).

Sulphate was measured using the $BaCl_2$ turbidimetric method. Bicarbonate was determined from the original sample pH and the total alkalinity determined volumetrically to a pH = 4.50 +/- 0.05 endpoint (Fisher AR25 pH meter), according to (SM 2320). Chloride ion was measured by the argentometric titration method (SM 4500-Cl). Calcium, magnesium, potassium and sodium were determined by flame atomic absorption spectrophotometry (SM 3111) using a Perkin Elmer 703 AAS. Boron was determined by ICP-MS on acid preserved samples.

Charge balances were calculated using equation 1:

$$CB = ((\Sigma z M_c - \Sigma z M_a) / (\Sigma z M_c + \Sigma z M_a)) * 100 \qquad [1]$$

Where z is the ion charge and M the molarity, and the subscripts c and a refer to cations and anions, respectively.

Most of the 177 samples have CB values of less than 5%, but a significant number (56) have CB values between 5 and 10%, and some (32) have CB values of greater than 10%. All samples with CB values of greater than 10% have been excluded from further consideration.

Field blanks and replicate samples were collected periodically and subjected to full chemical analysis. In all cases, field blanks returned analytical results at or below our method detection limits. Results of sample replicates generally agree within 5%.

Rock samples were collected from 52 sites distributed throughout the study area. Samples were acquired using a 2 cm-diameter diamond core drill to access unweathered material approx-imately 8 cm from the rock surface. The samples were crushed and ground. For boron analysis a sub-sample was fused with sodium-peroxide and dissolved in nitric and hydrochloric acids and then analyzed by ICP-MS. For fluorine analysis sub-samples were fused with sodium-hydroxide at 580ºC, and then taken up in a weak solution of sulphuric acid and ammonium citrate prior to analysis by ion-specific electrode.

3. RESULTS

3.1 Major element water geochemistry

As shown on Figure 4a, the majority of the groundwaters that we sampled are dominated by bicarbonate, although a few have chloride as the major anion. Sulphate levels are very low in most of the samples from sandstone aquifers, but are elevated in some samples. Sodium and calcium are the major cations (Figure 4b). Some of the samples are strongly dominated by sodium.

Most samples have calcium levels ranging up to 60 mg/L and sodium levels ranging up to 250 mg/L, and there is a weak negative correlation between these variables (Figure 5).

There is a positive correlation between pH and sodium (Figure 6). Most of the samples with sodium levels above 100 mg/L have pH greater than 7.5, while almost all samples with sodium levels below 50 have pH less than 7.5. There is a negative correlation between pH and calcium (Figure 7). Most of the samples with pH above 7.5 have calcium levels below 20 mg/L.

The major-element characteristics of the Yellow Point and Gabriola groundwaters, as described above, are generally very similar to those of the groundwaters studied by Allen and Suchy (2001) on Saturna Island (situated to the southeast of this region) and by Allen and Matsuo (2002) on Hornby Island (situated to the northwest of this region) (see Figure 1 for locations).

3.2 Trace element water geochemistry

There is a strong correlation between pH and fluoride (Figure 8). A positive pH-fluoride relationship has been observed in many other areas with elevated groundwater fluoride levels, especially areas with sandy aquifers. See for example: Boyle (1992), Macfarlane et al. (1992), Queste et al. (2001), Saxena and Ahmed (2001). Most of the fluoride-rich samples are from sandstone aquifers; of the 19 samples with more than 1.5 mg/L fluoride, 17 are from sandstone aquifers.
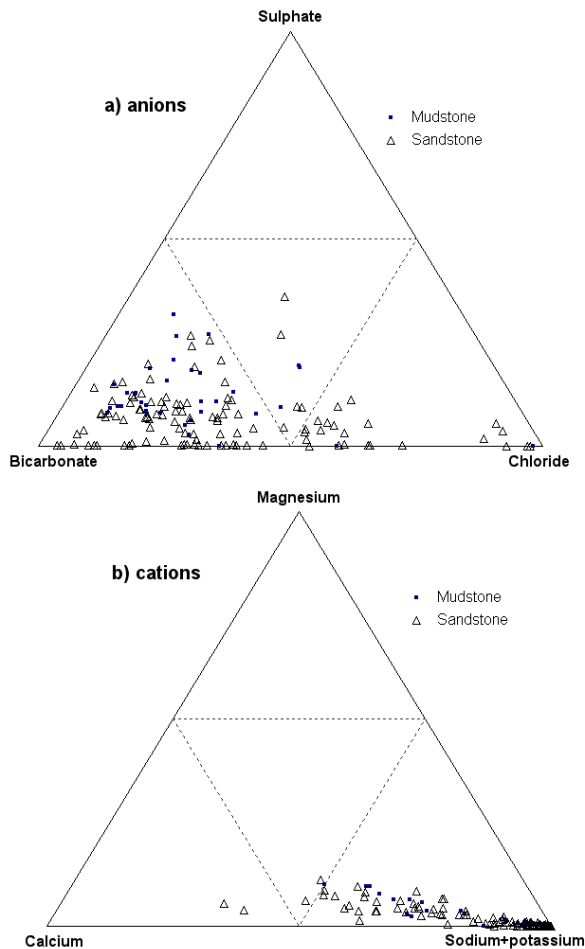
Figure 4. Anion and cation molar concentration ternary diagrams for Yellow Point and Gabriola groundwater samples.
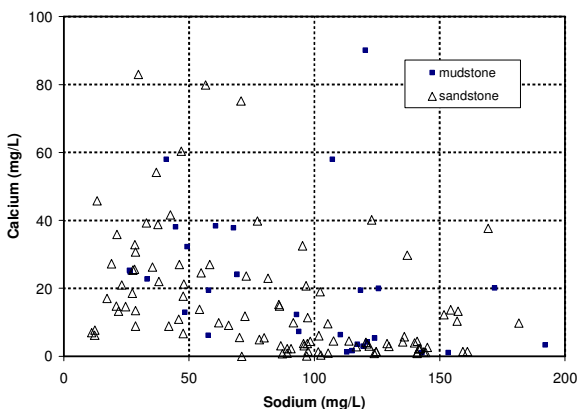

Figure 5. Calcium versus sodium in Yellow Point and Gabriola groundwater samples.
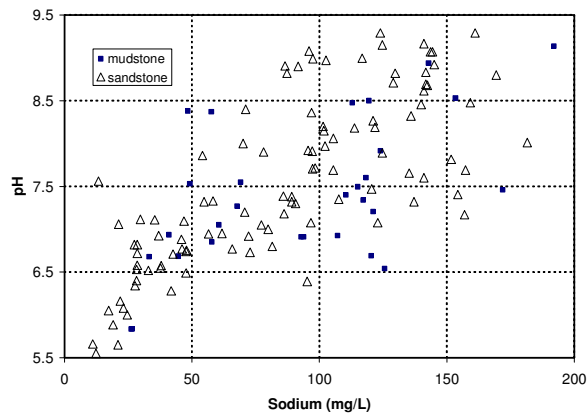

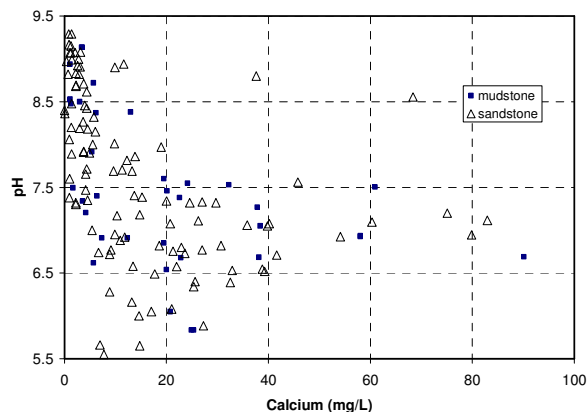Figure 6. pH versus sodium in Yellow Point and Gabriola groundwater samples.

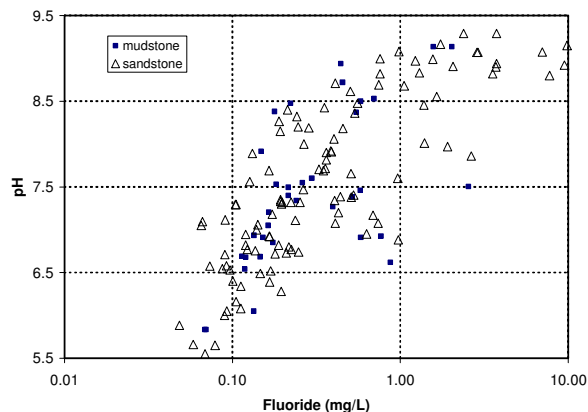Figure 7. pH versus calcium in Yellow Point and Gabriola groundwater samples.

Figure 8. pH versus fluoride in Yellow Point and Gabriola groundwater samples.

There is a strong correlation between fluoride and boron (Figure 9). Queste et al. (2001) also observed a positive boron-fluoride relationship in the Muenster area in Germany. As with fluoride, most of the boron-rich samples are from sandstone aquifers; of the 25 samples with more than 500 µg/L boron, 20 are from sandstone aquifers. Boron is also positively correlated with pH (Figure 10) and with sodium (Figure 11).

Fluoride and boron enrichment appear to be largely restricted to two regions, one in the northeastern part of the Yellow Point area, and the other in the northern part of Gabriola Island (Figures 12 and 13). Apart from the fact that both of these areas are underlain by sandstone (De Courcy and Gabriola Formations respectively) we do not have any specific geological explanation for the apparent localization of the fluoride and boron enrichment.
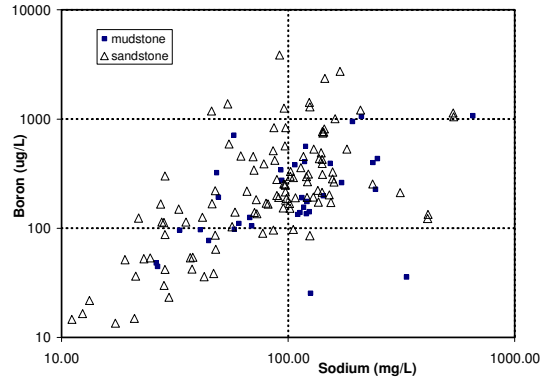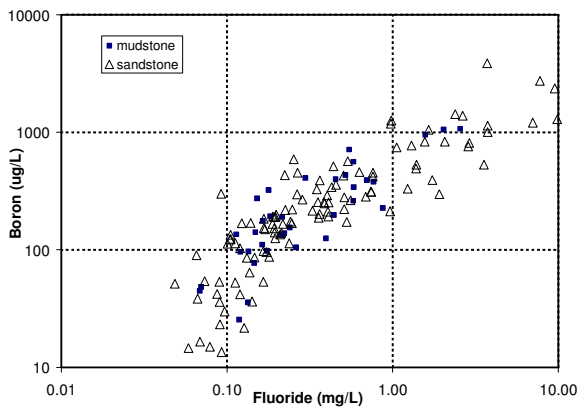

Figure 9. Boron versus fluoride in Yellow Point and Gabriola groundwater samples.

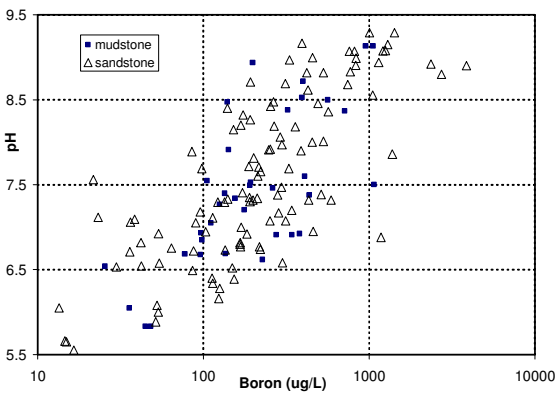Figure 10. pH versus boron in Yellow Point and Gabriola groundwater samples.

Figure 11. Boron versus sodium in Yellow Point and Gabriola groundwater samples.
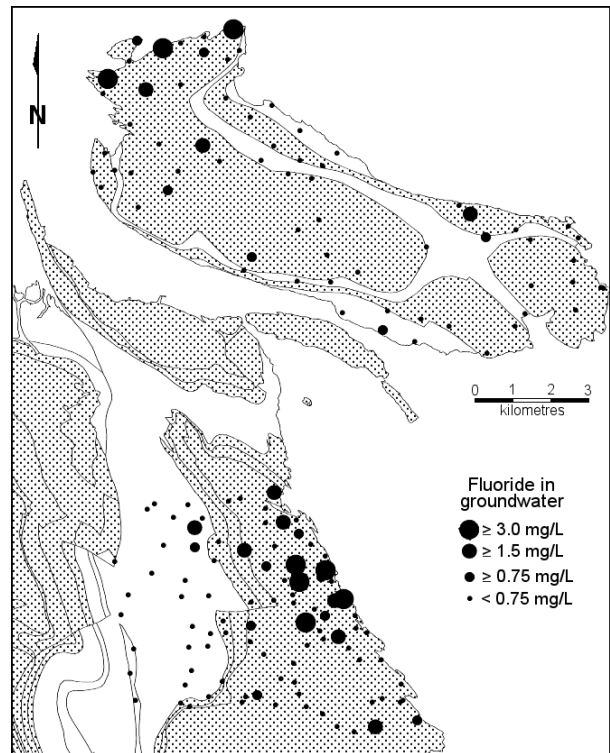

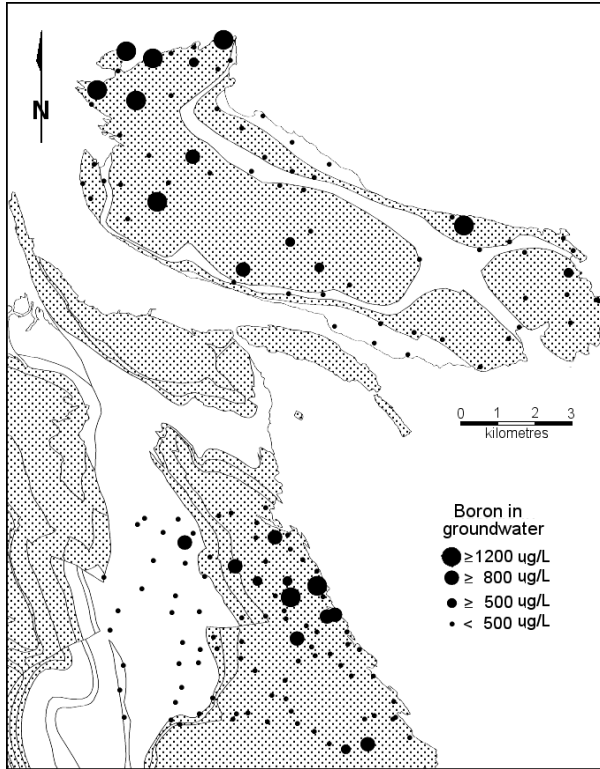Figure 12. Distribution of fluoride in Yellow Point and Gabriola Island well samples.

Figure 13. Distribution of boron in Yellow Point and Gabriola Island well samples.

3.3 Rock geochemistry

Fluorine levels in the rock samples range from 230 to 1340 ppm. The average fluorine level in mudstone samples is 523 ppm, while the average in sandstone samples is 380 ppm. Boron levels range from 6.2 to 85.4 ppm, with an average of 44.8 ppm in the mudstones and 12.5 ppm in the sandstones (see Table 2). The relationship between fluorine and boron in the rock samples is shown in Figure 14.
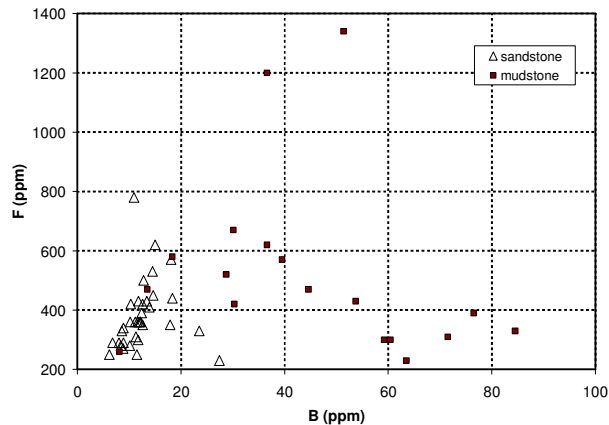

Figure 14. Fluorine versus boron in Yellow Point and Gabriola rock samples.

Global data for sandstones and mudstones, as reported by Rose et al. (1979), are consistent with our observation that mudstones tend to have higher levels of both fluorine and boron than do sandstones (Table 2). They also report considerably higher levels of fluorine, but lower levels of boron, in granites, compared with sandstones and mudstones.

Table 2. Average fluorine and boron levels in rock samples from the Yellow Point and Gabriola areas.

Rock type	F (ppm)	B (ppm)
Sandstone (this study)	380	12.5
Sandstone (global)*	280	35
Mudstone (this study)	523	44.8
Mudstone (global)*	680	100
Granite (global)*	810	10

* global data are from Rose et al. (1979)

4. DISCUSSION

The data presented here are consistent with the proposition of Allen and Suchy (2001) and Allen and Matsuo (2002) that base-exchange softening is important in controlling groundwater chemical evolution in the Nanaimo Group aquifers. As is typical with base-exchange softening, we observe that pH levels increase with increasing sodium levels and decreasing calcium levels.

There is clear evidence of base-exchange softening in the data from a series of nested monitoring wells completed in Nanaimo Group rocks around a landfill northwest of the Yellow Point area[1]. As summarized in Table 3, the water samples collected from the lower levels in these nested wells (average depth 18 m) have con-sistently higher pH, generally lower calcium levels and generally higher sodium levels than the samples collected at the upper levels (average depth 11 m). Of the 11 nested wells, pH is higher at depth in all 11, calcium is lower at depth in 8 out of 11, and sodium is higher at depth in 9 out of 11.

Since groundwater fluoride levels are consistently higher in the sandstone aquifers than in the mudstone aquifers, even though the sandstone has generally lower fluorine contents than the mudstone, we conclude that groundwater fluoride levels in the Nanaimo Group aquifers are not directly related to the bulk fluorine contents of the aquifer rocks. In fact, like most other clastic aquifers, neither the sandstone nor the mudstone has particularly high fluorine contents compared with most granitic rocks.

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[1] The landfill location is given in Figure 3. None of the wells included on Table 3 shows any indication of landfill contamination.

Table 3. pH, calcium and sodium data for nested wells (data provided by the Regional District of Nanaimo).

Variable	mean		ratio
	Upper*	Lower*	upper/lower
pH	7.5	8.0	0.95
Ca	24.0	15.3	1.6
Na	82.3	103.5	0.80
Variable	number of wells	
	upper>lower	lower>upper
pH	0	11
Ca	3	8
Na	9	2

* "Upper" refers to the upper well in each nested pair (avg. depth 11 m). "Lower" refers to the lower well in each nested pair (avg. depth 18 m).

As was suggested by Boyle (1992) for the sandstone aquifers of New Brunswick, it is our interpretation that, fluoride levels are elevated because of base-exchange softening. Base-exchange softening results in reduced calcium levels and elevated sodium, carbonate and pH. The competition of hydroxyl ions at high pH results in the release of fluoride from exchange sites (via ligand exchange) into solution (cf. Stumm and Morgan 1996). This hypothesis is supported by the strong correlation between pH and fluoride. Furthermore, because fluoride levels are limited by the low solubility of CaF_2, fluoride solubility is enhanced at the low calcium concentrations produced by base-exchange softening.

Boron is present as boric acid and borate ion in aqueous solution. The strong correlation observed between fluoride and boron suggests that a ligand exchange mechanism may also control boron levels. Alternatively, Ravenscroft and McArthur (2004) propose that equilibration of an aquifer with sea water (which has 4200 µg/L boron), will result in exchange sites being loaded with borate ion. The removal of that boron, by flushing with fresh water, coincident with the process of base-exchange softening, accounts for the observed relationships of boron with sodium, pH and fluoride. This is consistent with the evidence that the Nanaimo Group aquifer was in equilibrium with sea water between 12,000 and 6000 y B.P.

Base-exchange softening and the consequent enhanced fluoride and boron desorption can take place in aquifers where there are sufficient exchange surfaces (e.g., clay minerals) to permit base-exchange, and sufficient water-rock interaction to allow that process to significantly change the calcium and sodium contents and, consequently, the pH. This should include any clay-bearing sandy aquifer, providing that there is enough intergranular flow for significant water-rock interaction.

We propose that enrichment of fluoride and boron are favoured in waters from the sandstone units of the Nanaimo Group—which have better- developed intergranular flow than the mud-stones—because intergranular flow facilitates both base-exchange softening and freshwater flushing. These processes do not take place to the same extent in the mudstone aquifers because most of the water flows quickly along fractures; there is almost no intergranular flow, and there is little opportunity for exchange processes on clay minerals.

Fluoride levels in excess of the WHO limit of 1.5 mg/L represent a serious risk to the dental and skeletal health of millions of people around the world (WHO 2004). Because much more groundwater is extracted from fluorine-poor sedimentary rocks than fluorine-rich granitic rocks, it is likely that more instances of elevated fluoride levels are related to base-exchange softening, than to high fluorine levels in rocks.

Boron levels above the WHO provisional limit of 500 µg/L constitute a risk to the male repro-ductive system (WHO 2004). Boron levels above 1000 µg/L can also be toxic to crops (Ayers and Westcot 1989). Relatively little is known about the boron chemistry of groundwater, but it appears that base-exchange softening and freshwater flushing may be important factors in its enrichment.

5. CONCLUSIONS

Elevated levels of fluoride in groundwaters from a sandstone and mudstone aquifer system on eastern Vancouver Island are largely a result of base-exchange softening and the consequent high pH levels. It is evident that this process may be responsible for elevated fluoride levels in sandy aquifers around the world.

Boron enrichment in the same waters may be the product of base-exchange softening, but could also be a consequence of freshwater flushing of an aquifer that was in equilibrium with boron-rich marine water as recently as 6000 years ago.

In view of the close correlations of both fluoride and boron with pH—here and elsewhere—we recommend the use of pH as a screening method for delineation of areas that have the potential for elevated levels of these elements. 30 of our samples have pH greater than 8.5. Of these 30 samples, 17 have fluoride levels greater than 1.5 mg/L. Only 2 out of the remaining 115 samples have fluoride greater than 1.5. Similarly, 21 of the 30 high-pH samples have boron greater than 500 µg/L. Only 4 of the remaining 115 samples have boron greater than 500 µg/L. We propose that a pH of 8.5 be used a rapid screening threshold to predict water-quality risks associated with fluoride and boron in groundwater.

6. ACKNOWLEDGEMENTS

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