

## 3 Groundwater geochemistry

In this section we will look at the general chemical characteristics of groundwaters, and at some of the geochemical processes that are important in the chemical evolution of water that flows through the ground – including carbonate equilibrium, oxidation-reduction reactions and adsorption-desorption processes. We will also examine some groundwater geochemical data from the Nanaimo Group in order to understand its characteristics and evolution.

### 3.1 Dissolved constituents in groundwater

Dissolved  
constituents

A wide range of different elements can become dissolved in groundwater as a result of interactions with the atmosphere, the surficial environment, soil and bedrock. Groundwaters tend to have much higher concentrations of most constituents than do surface waters, and deep groundwaters that have been in contact with rock for a long time tend to have higher concentrations than shallow and or young waters.

It is convenient to divide dissolved constituents into major components (the predominant cations and anions), and trace elements.

Dissolved constituents are typically expressed in **mg/L** for the major components and **µg/L** for the trace elements. Some rare elements are expressed in **ng/L** (nanograms/litre). Since 1 mg is 0.001 g and 1 litre of water is very close to 1000 g, mg/L is equivalent to parts per million (ppm), while µg/L is equivalent to parts per billion (ppb).

Units of  
concentration  
and molality

We can also express concentrations in **molality** terms (moles per litre of water). For example for a solution with 34.1 mg/L of Ca the molality of calcium is:

$$34.1/40.08 = 0.851 \text{ millimoles/litre (mM/L)}$$

(The atomic weight of Ca is 40.08 g/mole.)

It is also common to express concentrations of ions as molar **equivalents**, which is similar to molality, except that the charge on the ion is taken into consideration. If a solution has a calcium ion molality of 0.851 mM/L, it has 1.702 milliequivalents per litre (mEq/L) of  $\text{Ca}^{2+}$  because the calcium ion is divalent. A solution with 0.56 mM/L  $\text{Na}^+$  will have 0.56 mEq/L of  $\text{Na}^+$  because the sodium ion is monovalent.

Equivalents

Equivalents are not used for dissolved species that do not form charged ions – such as silica, and they cannot necessarily be used for ions that might have more than one valence state, such as iron ( $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ).

## Major components

Major components

The major dissolved components of groundwaters include the anions bicarbonate, chloride and sulphate, and the cations sodium, calcium, magnesium and potassium. These constituents are typically present at concentrations in the range of a few mg/L to several hundred mg/L.

The concentrations of these major cations and anions for some groundwater samples from the Nanaimo Group are shown below by way of example:

| Sample number | K <sup>+</sup> (mg/l) | Na <sup>+</sup> (mg/l) | Ca <sup>2+</sup> (mg/l) | Mg <sup>2+</sup> (mg/l) | Cl <sup>-</sup> (mg/l) | HCO <sub>3</sub> <sup>-</sup> mg/L | SO <sub>4</sub> <sup>2-</sup> (mg/l) | pH   | Cond. ms/cm |
|---------------|-----------------------|------------------------|-------------------------|-------------------------|------------------------|------------------------------------|--------------------------------------|------|-------------|
| 1             | 0.62                  | 121.1                  | 4.2                     | 0.62                    | 8.7                    | 123.6                              | 22                                   | 7.21 | 429         |
| 2             | 1.55                  | 37.0                   | 54.1                    | 13.13                   | 16.5                   | 93.6                               | 70                                   | 6.93 | 441         |
| 3             | 0.19                  | 122.9                  | 40.2                    | 6.12                    | 97.7                   | 115.8                              | 24                                   | 7.08 | 721         |
| 4             | 0.23                  | 106.5                  | 4.2                     | 0.59                    | 12.3                   | 104.2                              | 4                                    | 7.87 | 372         |
| 5             | 0.69                  | 537.2                  | 68.4                    | 0.76                    | 900.2                  | 47.5                               | 2                                    | 8.56 | 3010        |
| 6             | 0.26                  | 181.6                  | 9.8                     | 0.09                    | 126.0                  | 112.3                              | 1                                    | 8.01 | 808         |
| 7             | 0.16                  | 135.2                  | 4.2                     | 0.11                    | 10.0                   | 143.2                              | 22                                   | 7.66 | 497         |
| 8             | 0.18                  | 129.7                  | 2.9                     | 0.08                    | 15.8                   | 131.9                              | 1                                    | 8.82 | 490         |
| 9             | 1.07                  | 36.7                   | 27.9                    | 4.36                    | 9.6                    | 63.2                               | 1                                    | 6.63 | 254         |
| 10            | 0.95                  | 157.0                  | 10.3                    | 2.44                    | 74.9                   | 135.9                              | 20                                   | 7.17 | 734         |

Example major-component data

The major cations in these particular samples are Na<sup>+</sup> and Ca<sup>2+</sup> and the major anions are Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup>.

Another very important characteristic of groundwater is the hydrogen ion concentration or **pH**. Hydrogen ion activities (similar to molality) typically range from about 10<sup>-4</sup> to about 10<sup>-10</sup> for natural waters, and we express these in pH units, where the pH is the negative of the log of the hydrogen ion activity. (In other words, the pH of natural water generally ranges between 4 and 10.) pH is considered to be neutral when the activity of H<sup>+</sup> ions is equal to that of OH<sup>-</sup> ions, and that is at pH=7. Waters with excess of H<sup>+</sup> ions are acidic, and have pH of less than 7. Waters with excess of OH<sup>-</sup> ions are alkaline, and have pH of greater than 7.

pH

pH levels are given above for some Nanaimo Gp. samples.

The sum of the concentrations of all of the dissolved constituents in a water sample is known as the **total dissolved solids** or TDS. TDS can be estimated by adding up the concentrations of all of the analyzed constituents, or by measuring the electrical conductivity of the water using a probe that measures the conductivity of the water between two electrodes a fixed distance apart. The conductivity is expressed in siemens/cm. You can see from the table above how conductivity correlates with the concentrations of the various ions.

TDS

## Trace elements

Trace elements

All of the elements in the periodic table are present at some concentration in most water samples, but only a fraction of these are important to us. Some example concentrations (in mg/L and µg/L) for the same ten samples listed above are given in the table below.

Si and F<sup>-</sup> are the most abundant of the trace elements in these samples, followed by B, Sr, Ba and Fe. In fact the concentrations of some of the trace constituents in these samples (esp. Si) are higher than those for some of the so-called major components. Some of the values are listed as undetected (ud), indicating not that there isn't any there, but that the concentrations are below the detection limit for the analytical method used.

| Sample number | F <sup>-</sup> (mg/L) | Si (mg/L) | Li (µg/L) | B (µg/L) | Al (µg/L) | Sc (µg/L) | Mn (µg/L) | Fe (µg/L) | Cu (µg/L) | Zn (µg/L) | As (µg/L) | Sr (µg/L) | Ba (µg/L) |
|---------------|-----------------------|-----------|-----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1             | 0.16                  | 6.29      | 19.0      | 176      | 20        | 1.197     | 7.8       | ud        | 6.64      | 27.76     | 0.316     | 74        | 77.8      |
| 2             | 0.17                  | 12.41     | 11.0      | 54       | 5         | 2.482     | 888.8     | 1968      | 3.67      | 54.17     | 2.706     | 684       | 296.4     |
| 3             | 0.74                  | 5.08      | 24.8      | 314      | 3         | 0.973     | 41.1      | 99        | 17.33     | 18.42     | 0.626     | 467       | 65.8      |
| 4             | 1.45                  | 4.87      | 17.8      | 352      | 226       | 0.983     | 3.4       | 137       | 13.50     | 19.95     | 0.782     | 70        | 27.9      |
| 5             | 1.65                  | 2.76      | 114.5     | 1049     | 10        | 0.632     | 31.7      | 178       | ud        | 6.06      | 3.894     | 904       | 55.4      |
| 6             | 1.39                  | 4.87      | 29.8      | 529      | 18        | 1.034     | 6.7       | ud        | ud        | 5.28      | 1.068     | 177       | 40.5      |
| 7             | 0.51                  | 8.07      | 19.4      | 222      | 24        | 1.626     | 2.7       | ud        | 14.00     | 48.60     | 0.212     | 82        | 36.3      |
| 8             | 3.56                  | 4.54      | 20.2      | 530      | 20        | 0.935     | 3.5       | ud        | 0.85      | 11.91     | 0.080     | 66        | 20.1      |
| 9             | 0.16                  | 6.58      | 3.7       | 45       | 49        | 1.382     | 460.3     | 718       | 80.08     | 13.24     | 0.949     | 150       | 21.4      |
| 10            | 0.69                  | 6.66      | 25.5      | 284      | 15        | 1.348     | 40.4      | 92        | ud        | 7.75      | 0.360     | 164       | 48.5      |

Example trace-element data

(ud = undetected)

## 3.2 Groundwater geochemical processes

Geochemical processes

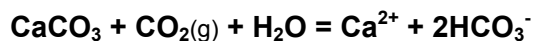
Water moving through the ground will react to varying degrees with the surrounding minerals (and other components), and it is these rock-water interactions that give the water its characteristic chemistry. As already noted, the silicate minerals that comprise most rocks do not react readily with most groundwaters. On the other hand, carbonate minerals do react quite readily with water, and they play an important role in the evolution of many groundwaters.

### Carbonate reactions

Carbonate reactions

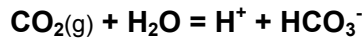
Since carbonates are present in many different types of rock, including most sedimentary rocks, and even some igneous and metamorphic rocks, carbonate chemistry is relevant to the evolution of most groundwaters.

The main mechanism for the dissolution of calcite is as follows:

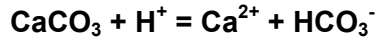


Carbon dioxide and hydrogen ions

This reaction includes the following step:



which is the reaction of carbon dioxide with water, to produce the hydrogen ions (acidic conditions) that promote the dissolution of calcite by the following reaction:



From the first reaction we can see that calcite solubility is controlled by the amount of carbon dioxide available – the more  $\text{CO}_2$  the more calcite will dissolve. From the last reaction we can see that calcite solubility is also controlled by pH – the lower the pH (more hydrogen ions) the more calcite will dissolve. Other processes – such as oxidation of sulphide minerals, or reactions of sulphur pollutants in the air – can also produce hydrogen ions that will promote dissolution of calcite.

There is enough  $\text{CO}_2$  in the air to provide for some calcite solubility, but there is typically much more  $\text{CO}_2$  within the soil and overburden because biological activity in the soil produces  $\text{CO}_2$ . Water percolating through the soil becomes enriched in  $\text{CO}_2$  and will then dissolve calcite quite readily. As this water reacts with calcite the  $\text{CO}_2$  gets used up, and, if there is no additional source of  $\text{CO}_2$  the water will eventually become saturated with respect to calcite and will no longer be able to dissolve the rock.

Calcite saturation

Where groundwater seeps into an opening in a karst (limestone cave) environment it equilibrates with the cave air (which has a  $\text{CO}_2$  level close to atmospheric), and this results in some loss of  $\text{CO}_2$  to the air. The same thing happens where carbonate-bearing groundwater comes to surface.



Speleothems and travertine

When  $\text{CO}_2$  is lost, the solubility of calcite drops, and calcite crystallizes from the water. This is the mechanism by which speleothems (stalactites etc.) grow within caves, or travertine (calcite crusts) are formed at surface - as shown above at Travertine Falls in the Grand Canyon.

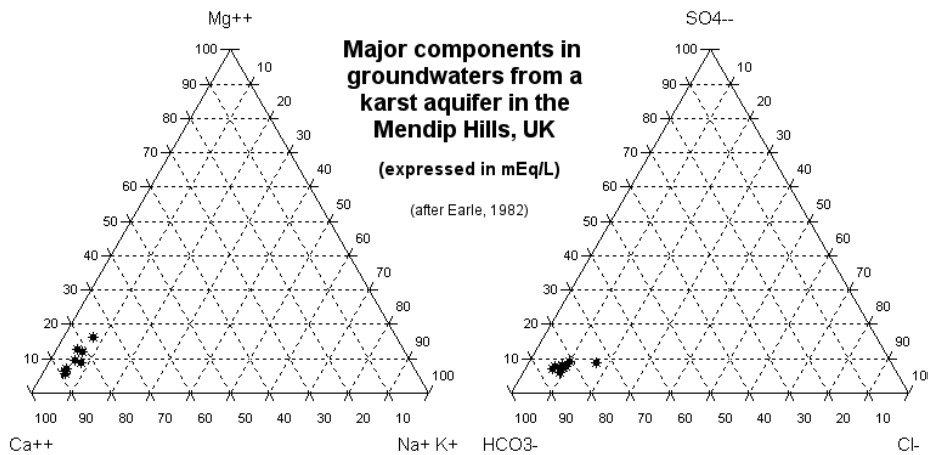
Groundwaters that are primarily controlled by carbonate reactions will have relatively high calcium and bicarbonate contents, and, if the rock includes some dolomite, could also have quite high magnesium levels.

Characteristics of "carbonate" waters

Data from a carbonate (karst) aquifer in the Mendip Hills (England) are shown on the following table and diagram.

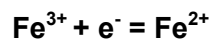
Mendip Hills  
carbonate  
groundwater  
data

| site | Ca <sup>2+</sup><br>mg/L | Mg <sup>2+</sup><br>mg/L | Na <sup>+</sup><br>mg/L | K <sup>+</sup><br>mg/L | HCO <sub>3</sub> <sup>-</sup><br>mg/L | Cl <sup>-</sup><br>mg/L | SO <sub>4</sub> <sup>2-</sup><br>mg/L | pH  |
|------|--------------------------|--------------------------|-------------------------|------------------------|---------------------------------------|-------------------------|---------------------------------------|-----|
| 5    | 104                      | 6.8                      | 7.0                     | 2.8                    | 280                                   | 14                      | 25                                    | 6.9 |
| 7    | 138                      | 6.6                      | 7.6                     | 2.8                    | 304                                   | 14                      | 18                                    | 7.0 |
| 14   | 82                       | 5.2                      | 6.8                     | 3.6                    | 195                                   | 13                      | 35                                    | 7.0 |
| 18   | 112                      | 10.4                     | 7.2                     | 1.2                    | 287                                   | 11                      | 24                                    | 7.1 |
| 21   | 93                       | 3.5                      | 5.7                     | 1.5                    | 240                                   | 12                      | 16                                    | 6.9 |
| 23   | 86                       | 10.8                     | 8.4                     | 1.9                    | 283                                   | 18                      | 28                                    | 7.0 |
| 25   | 100                      | 8.8                      | 8.6                     | 1.7                    | 249                                   | 13                      | 23                                    | 7.1 |
| 27   | 110                      | 4.6                      | 6.2                     | 1.9                    | 272                                   | 15                      | 22                                    | 6.9 |
| avg: | 103.1                    | 7.1                      | 7.2                     | 2.2                    | 263.8                                 | 13.8                    | 23.9                                  | 7.0 |



## Oxidation-reduction reactions

Chemical reactions that involve the transfer of electrons from one ion to another are called oxidation-reduction reactions (or *redox* reactions). An example is:



This shows the “reduction” of ferric iron to ferrous iron. Redox reaction rates and directions are controlled by the oxidation state of the surrounding environment – for example of the water.

Oxygen is the ultimate oxidant in the natural environment. Water in equilibrium with the atmosphere will be oxidizing

Organic matter is the ultimate reductant in the natural environment. Organic matter will consume oxygen, and the conditions will lead to bacterial reduction of carbon species to methane. Sulphide minerals and reduced forms of iron are also reductants.

When water infiltrates into the ground it becomes isolated from atmospheric oxygen. It starts to become more reduced as it reacts with reducing agents such as organic matter and sulphide minerals.

Oxidation-  
reduction  
reactions

Oxygen and  
organic matter

Many elements can exist in more than one oxidation state, and the different oxidation states are likely to have different solubilities under natural conditions. The best-known example is iron. Ferrous iron ( $\text{Fe}^{2+}$ ) is readily soluble in water, while ferric iron ( $\text{Fe}^{3+}$ ) is quite insoluble. Ferrous iron will dissolve in groundwater that is sufficiently reducing, but when that water comes to surface (at a spring or a well) the iron will oxidize to the ferric state and will precipitate as an iron mineral – such as ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ). Arsenic, which can exist as  $\text{As}^{3+}$  and  $\text{As}^{5+}$ , is also more soluble under reducing conditions than oxidizing conditions.

Oxidations states and solubility

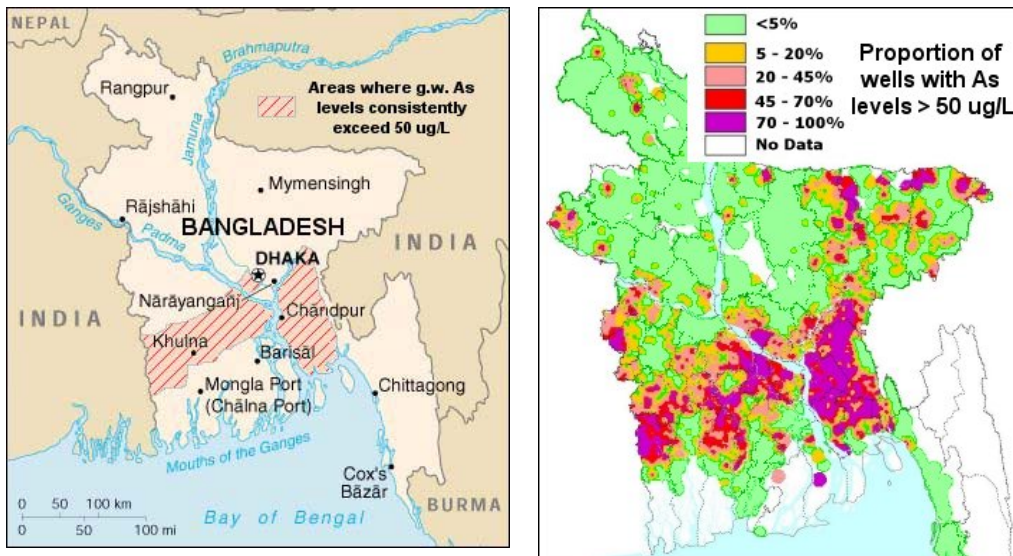
For many other elements the oxidized form is more soluble than the reduced form. Examples are copper, zinc, cadmium, lead and uranium, which are soluble under oxidizing conditions and tend to be insoluble under reducing conditions.

Trace elements

A good example of the role of redox processes in groundwater chemistry comes from the floodplain area of the Ganges and Brahmaputra Rivers in Bangladesh. In this region over 100 million residents extract shallow groundwater from small “tube wells” (wells with diameters of less than about 10 cm). About 8 million such wells were installed in Bangladesh between 1960 and 1990, many with assistance from UNICEF. Prior to that time most Bangladeshi’s did not have access to “clean” drinking water.

Arsenic in Bangladesh groundwater

In the mid 1990s it was discovered that many of the wells have As levels above 50  $\mu\text{g/L}$  (see maps), and as many as 20 million Bangladeshi’s are at risk of As poisoning (outcomes include cancer, diabetes, thickening of the skin, liver disease and problems with the digestive system). The current (1998) WHO guideline for drinking water arsenic levels is 10  $\mu\text{g/L}$ .



According to McArthur et al. (2001) the high levels of As are directly related to the oxidation state of the water in the aquifer. Most of the wells are completed in unconsolidated sand and gravel river sediments (dominated by quartz, feldspar and mica) that include extensive peat deposits. The organic matter generates the reducing conditions that result in the reduction and dissolution of the mineral limonite ( $\text{FeOOH}$ ) to soluble ferrous iron, and release of the As that was adsorbed

Reduction of limonite



onto the limonite. These same reducing conditions ensure that the As remains in the more soluble arsenite state ( $\text{As}^{3+}$ ).

## Ion exchange processes

Ion exchange processes

Because of their electrical charge, the ions in water have a tendency to be attracted onto solid surfaces. Such surfaces include ordinary mineral grains (eg. feldspar or quartz) but these are much less efficient than the surfaces of minerals such as iron oxides and clay minerals. Both anions and cations take part in ion exchange processes. Clays are particularly effective at adsorbing cations because their surfaces are consistently negatively charged.

The ions of different elements have different tendencies to be adsorbed or desorbed<sup>1</sup>. The tendency for adsorption amongst the major cations in natural waters is as follows:

Adsorption tendencies of major ions

(strongly adsorbed)  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$  (weakly adsorbed)

which means that calcium ions are much more likely to be adsorbed onto surfaces than are sodium ions.

A water softener works because of this relationship. As the “hard” water is passed through the system calcium and magnesium ions in solution are preferentially adsorbed onto a substrate (ion-exchange resin). After some time most of the exchange sites are occupied by calcium and magnesium and the system ceases to function effectively. A NaCl brine is then passed through the system, and because of the overwhelming amount of sodium in the solution the calcium and magnesium on the exchange sites are replaced by sodium – thus “recharging” the ion exchange resin.

Water softening

This process, which is known as **base-exchange softening**, also works well in nature. Providing that there is a reservoir of sodium ions adsorbed onto clay minerals, calcium and/or magnesium ions in the water will preferentially attach to the exchange sites and the sodium will be ejected and transferred into the water.

Base-exchange softening

Ion exchange is also an important process for trace elements, especially those that behave as cations. Clay-mineral bearing rocks and sediments will naturally adsorb heavy-metal cations from contaminated water. Engineered clay barriers, such as those at the landfill, are based on this principal. As described above, other minerals, including iron-oxides, can also be effective at adsorbing trace elements.

Trace elements

## 3.3 Geochemistry of the Nanaimo Group aquifers

Nanaimo Gp. groundwater geochemistry

In 2000 and 2001 the Geology and Chemistry Departments at Malaspina collected and analyzed about 175 groundwater samples from wells in the Yellow

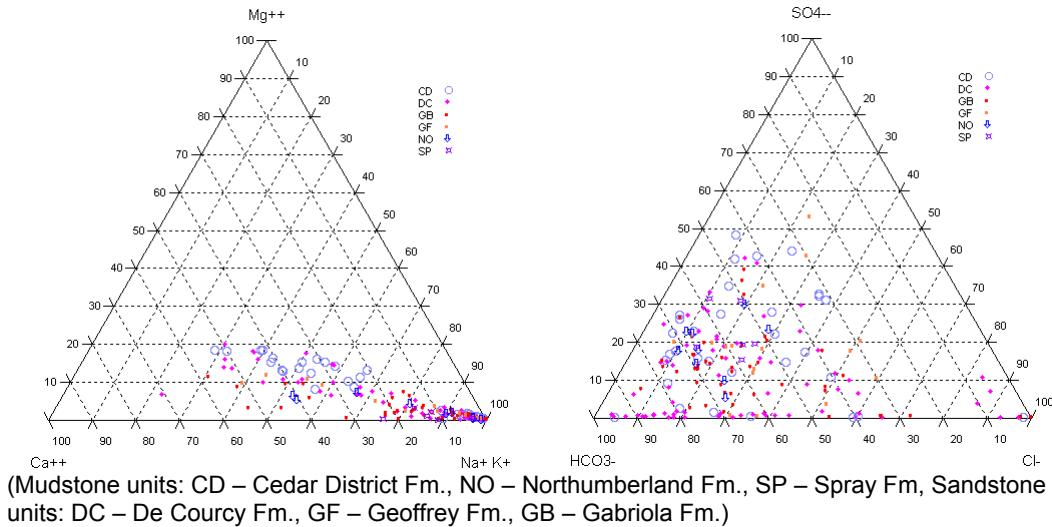
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<sup>1</sup> Note that the word is adsorb not absorb. Adsorption means being attached onto a surface. Absorption means being incorporated into a solid. Water is absorbed into a sponge, but ions are adsorbed onto the surfaces of minerals.

Point and Gabriola Island areas. The primary objective of this work was to understand the origin and extent of elevated fluoride levels in some Nanaimo Group samples.

The major element characteristics of these samples are shown below. The waters are dominated by sodium (with lesser amounts of calcium) and by bicarbonate.

Major element data

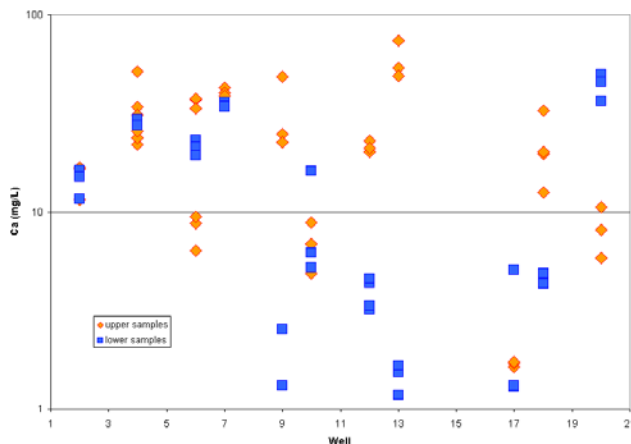


A few of these samples have anomalously high levels of sodium and chloride, and these are probably the result of contamination with seawater in near-shore regions.

The trend between Ca-rich and Na+K-rich groundwater has been observed in many locations around the world (including elsewhere in the Nanaimo Gp. cf. Allen and Suchy, 2001), and is generally ascribed to an ion exchange process where calcium in solution is exchanged for sodium on clay minerals. This is base-exchange softening (as described above).

Base-exchange softening

We have evidence from the RDN landfill data set that this process is taking place here. At sites where there are multi-depth peizometers calcium levels are consistently lower in the deeper sample than in the shallower sample (see below)

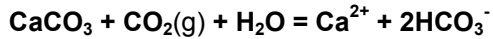


Calcium data (left) from 3 or 4 sampling dates in 2000 for monitoring wells at the RDN landfill. At all locations except holes 10, 17 and 20 the calcium levels are lower in the deeper holes.

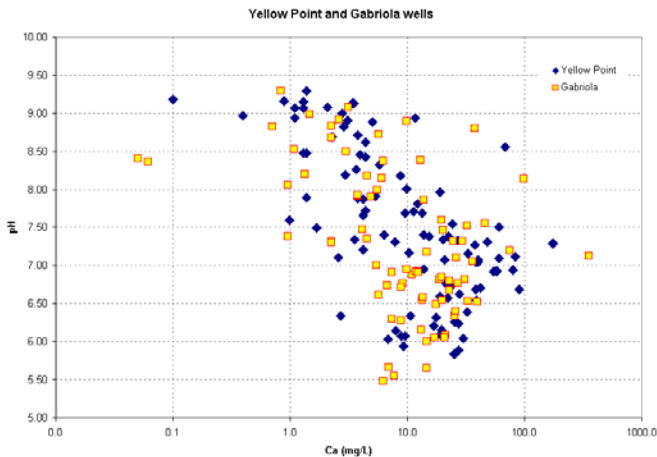
Evidence for base-exchange softening at the RDN landfill



Replacement of  $\text{Ca}^{2+}$  by  $\text{Na}^+$  in solution results in a change in pH because the removal of calcium leads to a change in equilibrium of the reaction:



driving it further to the right, increasing the bicarbonate level and the pH.

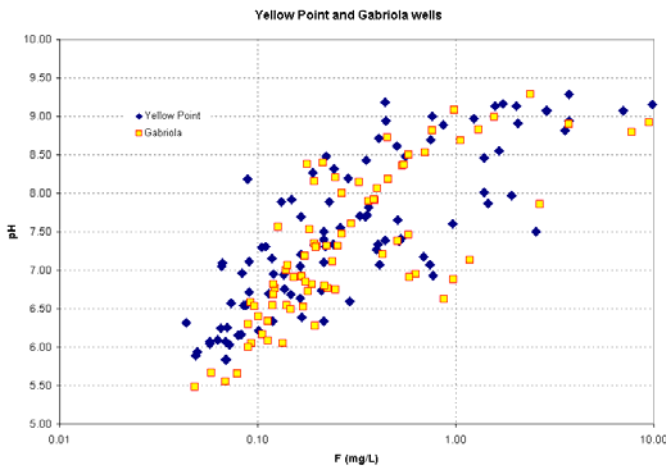


As shown on the diagram to the left, there is a consistent relationship between pH and calcium in Yellow Point and Gabriola waters, with pH increasing as calcium levels drop.

Base-exchange softening and pH in Nanaimo Gp. waters

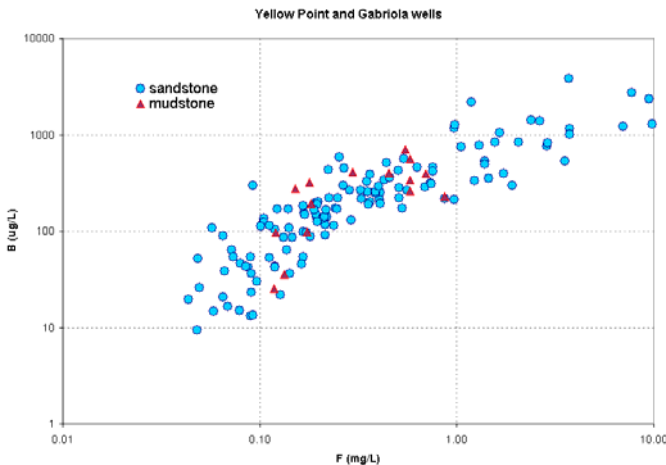
Fluoride solubility is controlled by pH and by the calcium

content. Fluoride is most soluble at high pH and also at low calcium levels, because at high levels of calcium the insoluble mineral  $\text{CaF}_2$  (fluorite) will form.



We observe a strong correlation between pH and fluoride (as shown to the left) and a negative correlation between calcium and fluoride (not shown). Most of the water samples with more than 1 mg/L fluoride have pH above 8.5, and many have pH above 9.0.

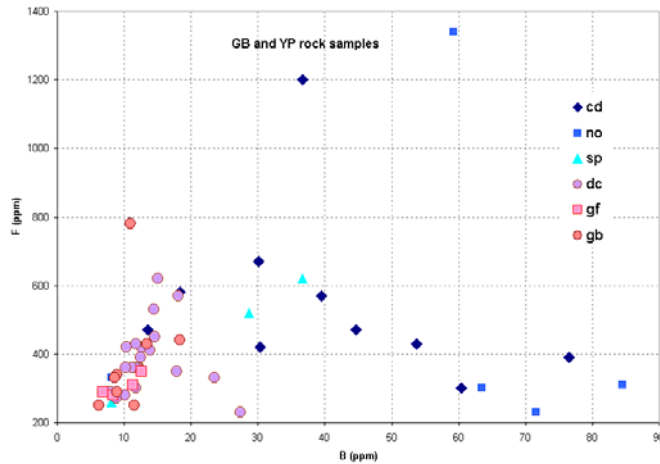
pH and fluoride in Nanaimo Gp. waters



We have also noted a very strong correlation between fluoride and boron in these samples (see diagram), a trend that has been observed elsewhere. The wells that have high B and F levels are exclusively located in sandstone units, as opposed to mudstone.

Fluoride and boron in Nanaimo Gp. waters

The two possible explanations for the strong B-F relationship are: 1) that boron and fluorine levels are closely correlated in the rocks themselves, or 2) that boron and fluoride behave similarly in solution in this hydrogeological environment.



In order to answer the first part of that question we have collected and analyzed 51 Nanaimo Gp. outcrop samples from the two study areas. Our results (left) show firstly that the B and F levels are close to typical levels for these types of rocks. Secondly, we observe no significant

Fluoride and boron in Nanaimo Gp. rocks

correlation between these two elements in the rocks. Finally, while the mudstone samples show the highest levels of these constituents (esp. for boron), the water samples from sandstone units are most strongly enriched in both of these elements.

We conclude that the elevated levels of B and F in groundwaters from the Nanaimo Group are primarily related to the base-exchange softening process, which results in very high pH levels and relatively low calcium levels. Evidence that this process is taking place has been observed in sandstone aquifers from around the world, and fluoride is similarly enriched in many such cases.

Importance of base-exchange softening

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