

## 10. Faryab: Groundwater Chemistry

### 10.1 Introduction

We have already examined, in Chapters 8 and 9, the topics of groundwater salinity, major ion hydrochemical types and possible groundwater hydrochemical evolution.

We will now examine some of the other components in groundwater, based on the 132 samples collected from the Kohistan, Gurziwan, Bilchiragh, Qaysar and northern (Andkhoy, Qaramqol, Khani Chahar Bagh and Qurgan) districts of Faryab in 2013. Of these samples, 40 were from springs, 91 from dug wells and 1 from a drilled borehole.

The data will typically be presented either as hydrochemical maps, or as **boxplots**.

#### Boxplots

In boxplots, the central “box” represents the interquartile range with a horizontal line at the median. The “whiskers” represent the non-outlying extraquartile range, with outliers shown as small squares (near outliers) or crosses (far outliers). Parentheses around the median represent a robust 95% confidence interval on the median. The #numbers along the top represent the number of data in each subset.

In the discussion of the presented parameters, the drinking water significance of the element will be commented in the light of:

- the WHO Drinking Water Guidelines: 4<sup>th</sup> Edition (WHO 2011)
- the European Drinking Water Directive 98/83/EC of November 1998

while recognising that neither of these documents has any legal authority within Afghanistan.

A large number of parameters were analysed, mostly either by ion chromatography (IC) or inductively coupled plasma mass spectrometry (ICP-MS) techniques at the laboratories of the British Geological Survey (BGS), Keyworth, UK. Only a relatively small number of parameters are discussed in this section. Those parameters selected for discussion are:

- those with health significance
- those where the large majority of samples returned values over the detection limit.

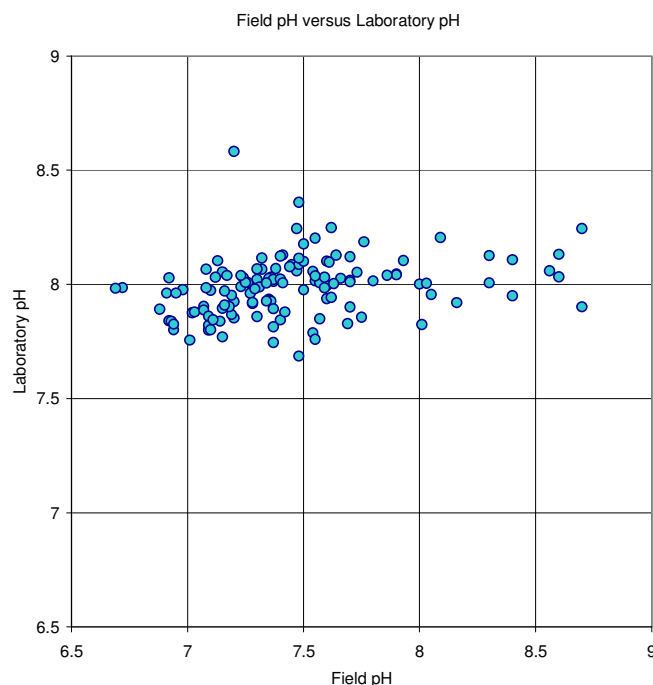
Where samples returned analytical values below the detection limit, we have elected to set the concentration to a value of half the lowest detection limit for the purposes of plotting diagrams (the reader should note that detection limit depends on salinity for many parameters and this arbitrary practice can be misleading in cases where large numbers of samples return values below detection limit).

### 10.2 pH

During 2013 and early 2014, pH was measured in the field (after pumping for c. 5 minutes to obtain fresh groundwater) at 435 groundwater survey locations in Faryab. This is referred to as the N=435 data set.

At N=132 of these locations, groundwater samples were collected and return to BGS for analysis. pH was also measured in the laboratory at BGS. The field measurements are to

be preferred, as transport and storage typically result in the samples losing dissolved  $\text{CO}_2$ , resulting in a pH increase. In fact, it can be seen that the majority of the waters, by the time they have been returned to the laboratory, have equilibrated at a pH of around 8.



**Figure 10.1. Plot of laboratory pH (measured at BGS) versus field-determined pH (N=132).**

All the measured sources returned field pH values in the range 6.5 to 9, with vast majority between 7 and 8. The distribution of these according to district is shown in Figure 8.2. It will be observed that the generally higher pH values are observed in the southern districts, with pH generally decreasing slightly to the north. It is possible that this may be a temperature effect (the pH of pure water is 7.27 at 10°C, 7.08 at 20°C and 7.00 at 25°C), or it may represent some form of salinity-based interference.

#### pH

**EC 1998 Directive:** Indicator parameter. Should be between 6.5 and 9.5

**WHO (2011):** No guideline set. Not of health concern at levels found in drinking-water.

Field pH 25-percentile in Faryab = 7.18 (N=132) 7.23 (N=435)

Field pH 50-percentile in Faryab = 7.37 (N=132) 7.46 (N=435)

Field pH 90-percentile in Faryab = 8.01 (N=132) 8.00 (N=435)

For the N=435 data set, the relation between field pH, temperature (T, in °C) and electrical conductivity (EC, in  $\mu\text{S}/\text{cm}$ ) is described by the following best-fit linear trend-lines:

$$\text{pH} = (51.903 - T) / 4.6029 \quad r^2 = 0.2409$$

$$\text{pH} = (31859 - \text{EC}) / 3740.8 \quad r^2 = 0.2094$$

### 10.3 Arsenic (As)

#### Arsenic

**EC 1998 Directive:** < 10 µg/L

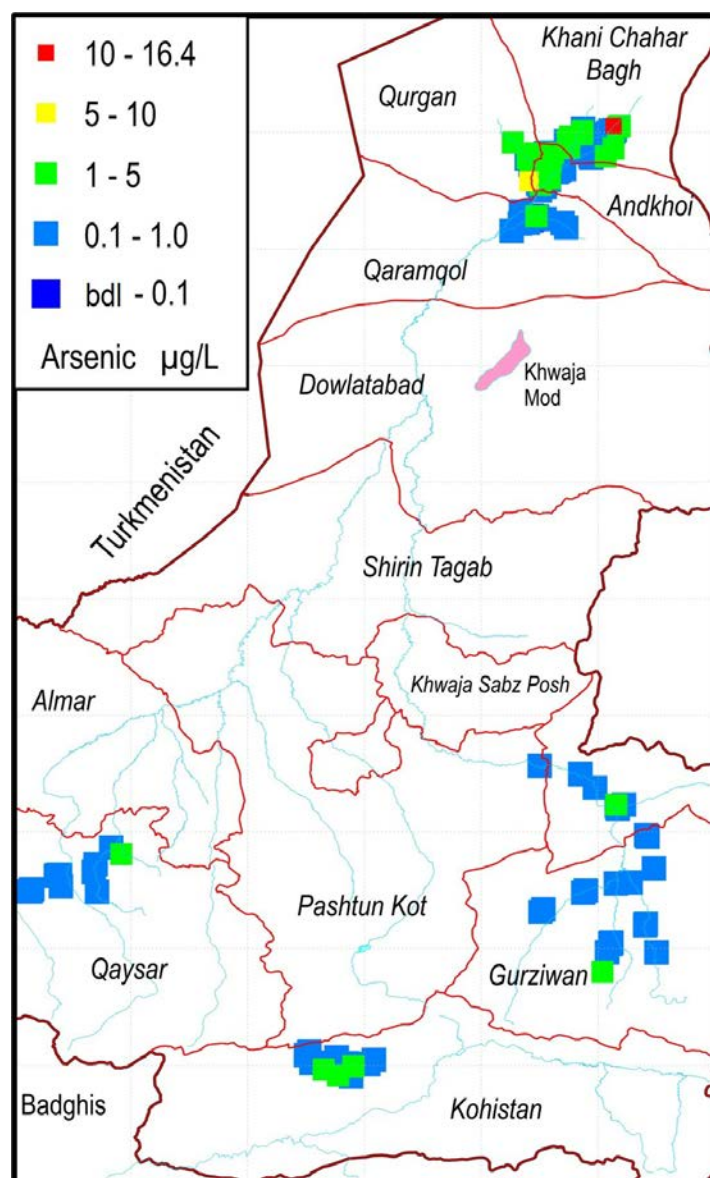
**WHO (2011):** Provisional guideline < 10 µg/L

25-percentile in Faryab = 0.46 µg/L (N=132)

50-percentile in Faryab = 0.70 µg/L (N=132)

90-percentile in Faryab = 1.31 µg/L (N=132)

Arsenic can be harmful to human health in high concentrations in drinking water. Its hydrochemistry is complex. It can be released from sulphide mineralisations and may also occur in geothermal waters. It is often sorbed onto iron (III) oxyhydroxide minerals and can be released under moderately reducing conditions by reductive dissolution of these minerals. In neutral-alkaline solutions it can be rather soluble and can be concentrated by evaporative processes.



**Figure 10.2. Distribution of As concentrations in groundwater in Faryab.** One sample of 132 is below detection limit (bdl).

Only a single sample from Faryab exceeded the WHO (2011) guideline of 10 µg/L, from Khani Chahar Bagh district. The next highest concentration is a single sample at 5.1 µg/L in Qurgan district.

There is a slight tendency to increasing concentrations of arsenic in groundwater to the north.

### 10.4 Antimony (Sb)

#### Antimony

**EC 1998 Directive:** < 5 µg/L

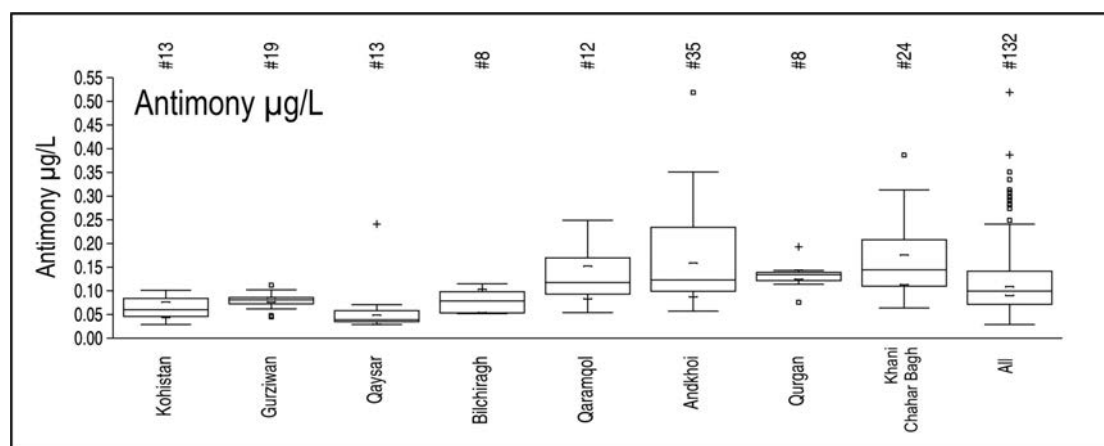
**WHO (2011):** Guideline < 20 µg/L

25-percentile in Faryab = 0.07 µg/L (N=132)

50-percentile in Faryab = 0.10 µg/L (N=132)

90-percentile in Faryab = 0.25 µg/L (N=132)

The antimony concentrations in the 132 groundwater samples from Faryab do not approach concentrations warranting health concern. The maximum recorded was 0.52 µg/L from a dug well in Andkhoy region. There is a weak tendency to increasing concentrations towards the north.



**Figure 10.3. Boxplot showing distribution of antimony (Sb) in N=132 groundwater samples from Faryab.** None of the 132 samples returned a value below the detection limit.

### 10.5 Barium (Ba)

#### Barium

**EC 1998 Directive:** No limit set

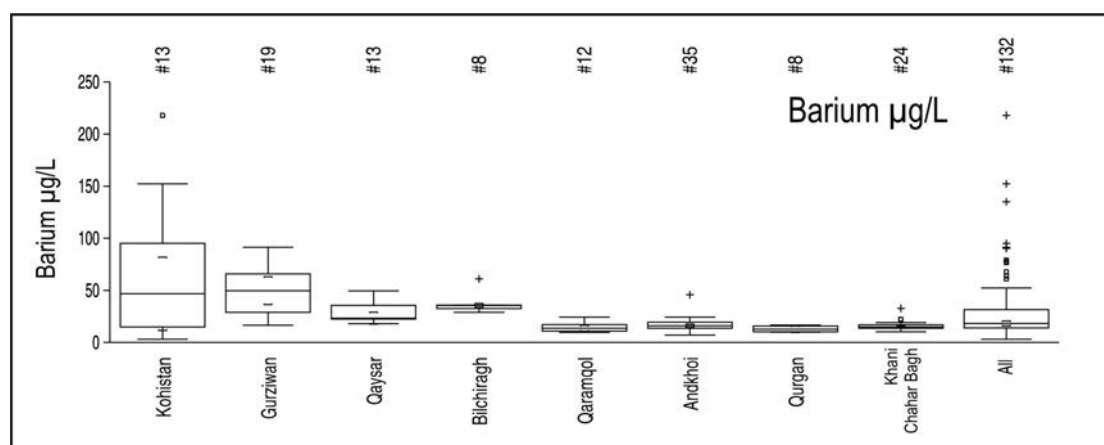
**WHO (2011):** Guideline < 700 µg/L

25-percentile in Faryab = 14 µg/L (N=132)

50-percentile in Faryab = 18 µg/L (N=132)

90-percentile in Faryab = 52 µg/L (N=132)

The highest recorded barium concentration in Faryab is 218 µg/L, in a dug well in Kohistan, well below the WHO Guideline level.



**Figure 10.4. Boxplot showing distribution of barium (Ba) in N=132 groundwater samples from Faryab.** None of the 132 samples returned a value below the detection limit.

There is a clear trend to decreasing concentrations of barium in groundwater to the north. It is believed that this is related to suppression of barium solubility by barite saturation, occasioned by high sulphate concentrations in groundwater of the northern areas. Barium exhibits a negative correlation with sulphate in the groundwaters.

## 10.6 Beryllium (Be)

Beryllium is a highly toxic element. The EU and WHO (2011) do not set drinking water guidelines for beryllium, but the USEPA (2009) sets a limit of 4 µg/L.

All of the 132 groundwater samples from Faryab returned concentrations below the detection limit, which varied from <0.01 µg/L to <0.05 µg/L. All samples were well below the USEPA limit, therefore.

## 10.7 Boron (B)

### Boron

**EC 1998 Directive:** < 1000 µg/L

**WHO (2011):** Guideline < 2400 µg/L

25-percentile in Faryab = 178 µg/L (N=132)

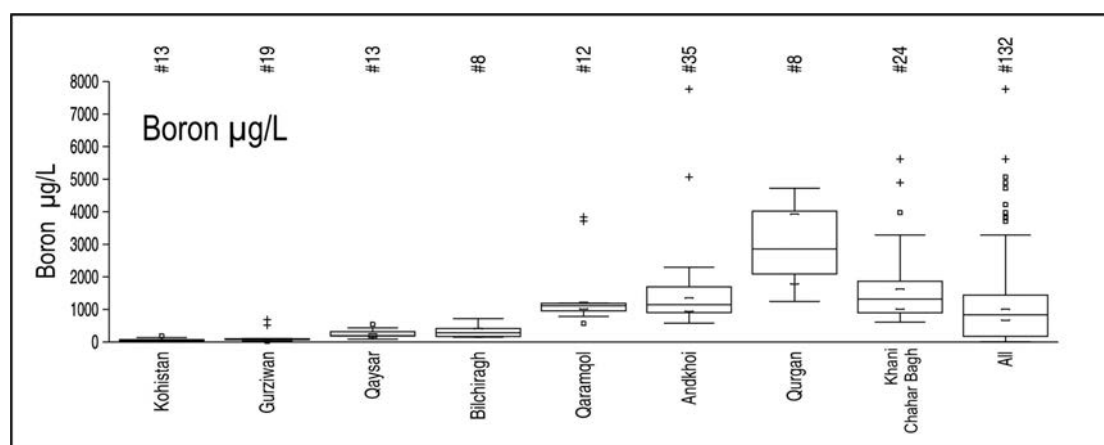
50-percentile in Faryab = 859 µg/L (N=132)

90-percentile in Faryab = 2474 µg/L (N=132)

14 of the 132 groundwaters sampled in Faryab exceed the recommended WHO (2011) Guideline value of 2400 µg/L, which is set from a human health perspective (possible effects on the male reproductive tract). The highest concentration of 7760 µg/L was from a groundwater from Andkhohi district.

It should be remembered that boron can be toxic to some plant species in smaller concentrations, making high-boron water unsuitable for irrigation of some species. For example, water containing more than 300 µg/L can be phytotoxic to sensitive plants such as avocado, bean or apple (Nable et al. 1997).



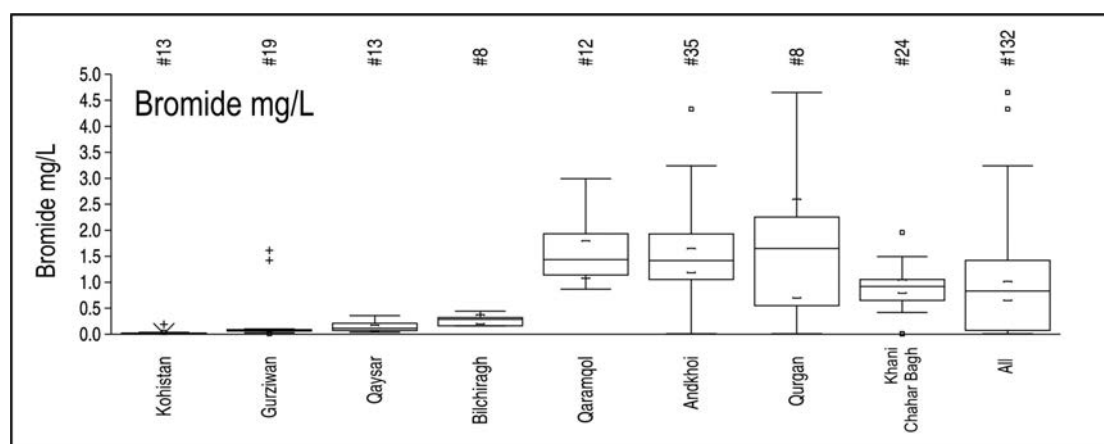


**Figure 10.5. Boxplot showing distribution of boron in N=132 groundwater samples from Faryab.** 1 of the 132 samples returned a value below the detection limit of <10 µg/L.

Boron concentrations exhibit a clear increasing trend from south to north. Boron typically occurs in alkaline groundwater in the form of a highly soluble borate anion and is susceptible to evapoconcentration.

### 10.8 Bromide (Br)

Bromide was measured as an anion on the ion chromatograph at BGS.



**Figure 10.6. Boxplot showing distribution of bromide in N=132 groundwater samples from Faryab.** 16 of the 132 samples returned a value below the detection limit and all 16 were arbitrarily set to 0.01 mg/L for the purposes of plotting, despite the fact that the detection limit varied from <0.02 to <1 mg/L depending on salinity. This erroneously give the impression of a few very low-bromide waters in the northern districts.

#### Chloride : Bromide mass ratios (Davis et al. 1998)

Atmospheric precipitation: 50 to 100

Shallow groundwater: 100 to 200

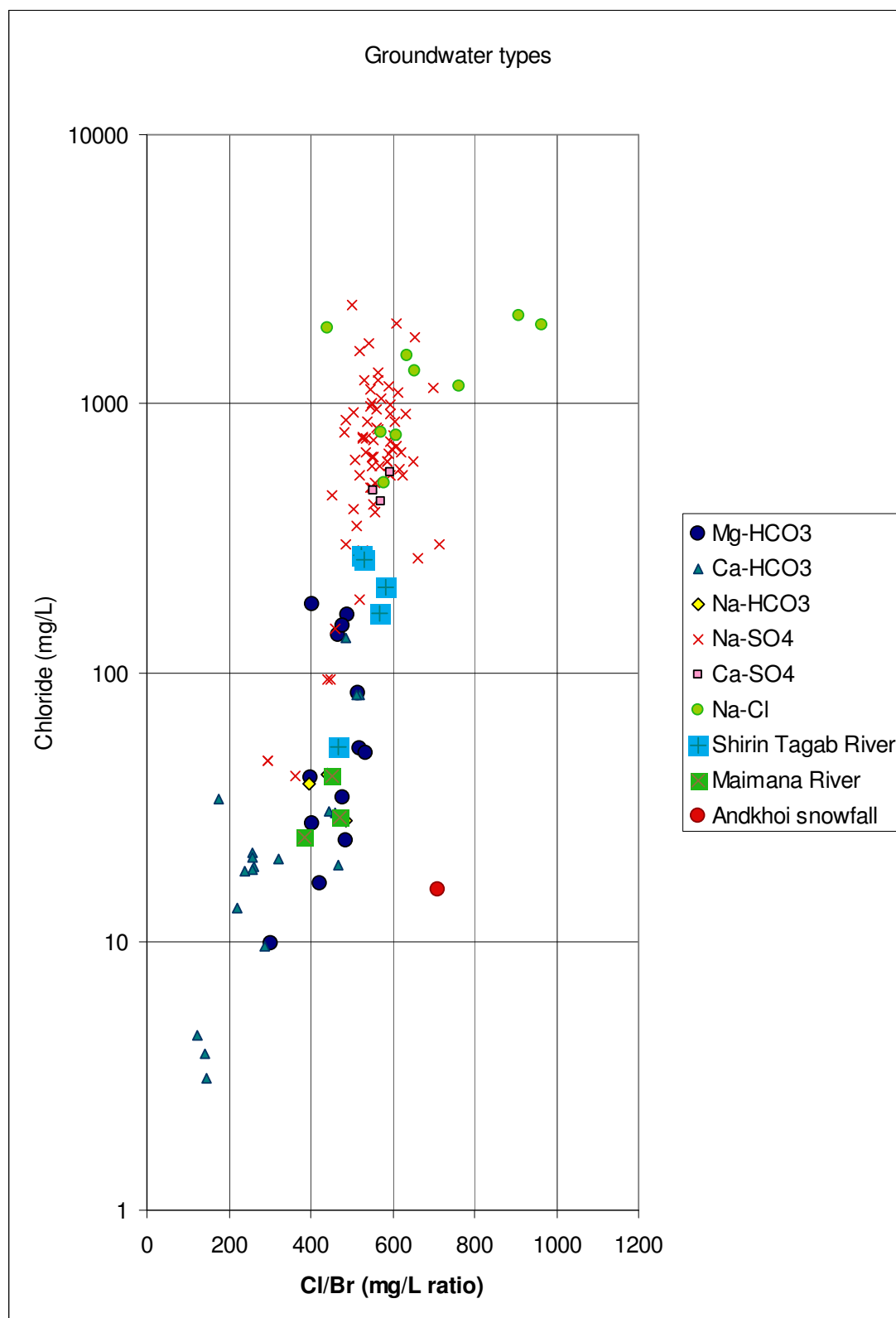
Seawater: 290

Domestic sewage: 300 to 600

Halite dissolution: 1000 to 10,000

Residual brine after halite precipitated: 50

The maximum concentration in groundwater was 4.65 mg/L in a dug well in Qurgan district. Bromide exhibits a strong correlation with salinity and the highest values clearly occur in the four northern districts.



**Figure 10.7.** Chloride to bromide mass ratios, plotted against chloride concentration, for groundwaters sampled in 2013 (samples where bromide < detection limit omitted), subdivided according to water type (see Chapter 9). The diagram also shows river waters (sampling discussed in Chapter 3) and a single snowfall sample from Andkhai where bromide was above detection limit.

**Bromide****EC 1998 Directive:** No guideline**WHO (2011):** No guideline

25-percentile in Faryab	=	0.16 mg/L (N=116 samples above dl)
50-percentile in Faryab	=	0.92 mg/L (N=116 samples above dl)
90-percentile in Faryab	=	2.1 mg/L (N=116 samples above dl)

Figure 10.7 clearly shows that chloride : bromide ratio increases from south to north in groundwater, as salinity increases. In the southern districts, ratios as low as 200 occur, whereas, in the northern districts the typical ratio is around 580. River waters fall on the same trajectory.

Davis et al. (1998) wrote a key paper on Cl<sup>-</sup>/Br<sup>-</sup> ratios, where they report characteristic ratios for different sources (see text box above). They argue that evaporation in itself does not affect the Cl<sup>-</sup>/Br<sup>-</sup> ratio (although without clear evidence for this) and that the main influence on Cl<sup>-</sup>/Br<sup>-</sup> ratios is halite precipitation (lowers ratio in groundwater), halite dissolution (increases ratio) and admixture with halite-dissolution brines (increases ratio).

Davis et al. (2004), in their later paper, acknowledge that bromide chemistry is rather complex and that fractionation takes place at the seawater interface. Bubble-bursting and microbial processes mobilise bromine preferentially into the aerosol phase and leave precipitation enriched in bromide.

Conventional wisdom (Alcalá & Custudio 2004) holds that evapoconcentration during recharge does not affect Cl<sup>-</sup>/Br<sup>-</sup> ratios. One can only speculate (see Vengosh et al. 1992) whether fractionation *could* possibly take place during intensive evaporation in arid environments, leaving small quantities of recharge water depleted in bromide (high Cl<sup>-</sup>/Br<sup>-</sup> ratio). This hypothesis is certainly recognised by Wood & Sanford (2007) for an Arabian sabkha environment, Smoydzin, L. & von Glasow, R. (2009) for the Dead Sea and Zhou & McLennan (2011) for Mars!

Thus, using conventional models, we would conclude that the increasing Cl<sup>-</sup>/Br<sup>-</sup> ratios from south to north reflect increasing degrees of dissolution of evaporite minerals (such as halite) - possibly with a component of sewage / latrine leakage. Newer research does not preclude, however, the alternative model that intense evaporation can also cause the increase in Cl<sup>-</sup>/Br<sup>-</sup> ratios.

The high Cl<sup>-</sup>/Br<sup>-</sup> ratio in the single snowfall sample from Andkhoi could simply reflect windblown halite-containing dust being entrained in the sample.

### 10.9 Chromium (Cr)

The highest recorded chromium concentration in Faryab is 37 µg/L, from a dug well in Bilchiragh, below the WHO provisional health-based Guideline level of 50 µg/L.

There is no clear geographical trend in the chromium concentrations, both Bilchiragh and Khani Chahar Bagh districts exhibit median chromium concentrations well above most other districts.

Four of 132 samples returned values below the analytical detection limit.

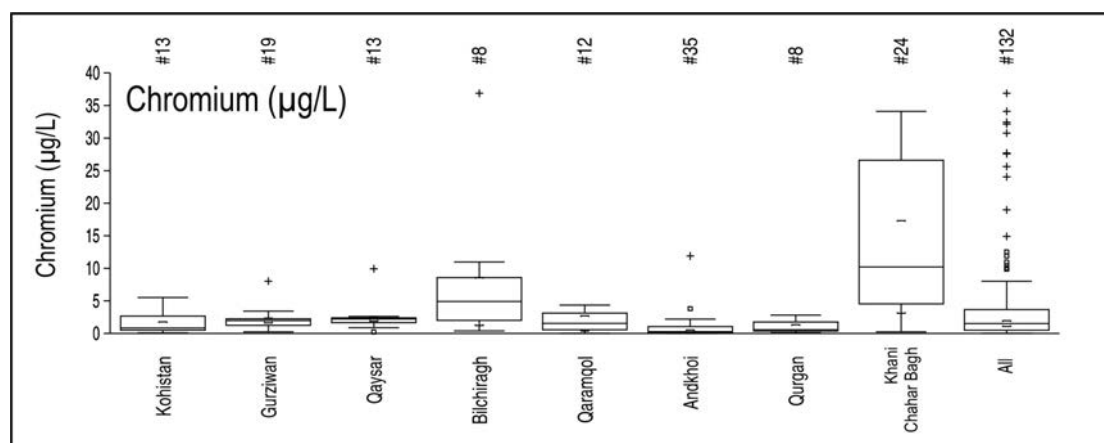


**Chromium****EC 1998 Directive:** < 50 µg/L**WHO (2011):** Provisional guideline < 50 µg/L

25-percentile in Faryab = 0.49 µg/L (N=132)

50-percentile in Faryab = 1.52 µg/L (N=132)

90-percentile in Faryab = 10.9 µg/L (N=132)



**Figure 10.8. Boxplot showing distribution of chromium (Cr) in N=132 groundwater samples from Faryab.** Four of the 132 samples returned a value below the detection limit (which varies between <0.05 and <0.3 µg/L) and these have been set to a value of 0.025 µg/L for plotting purposes.

### 10.10 Fluoride (F<sup>-</sup>)

Fluoride was measured as an anion on the ion chromatograph at BGS. Modest quantities of fluoride are beneficial for correct bone and tooth development. A deficiency in fluoride can lead to increased vulnerability to dental caries.

Excessive fluoride intake can lead to fluorosis of teeth and, in extreme cases, of bones, in livestock and humans. Children are especially vulnerable.

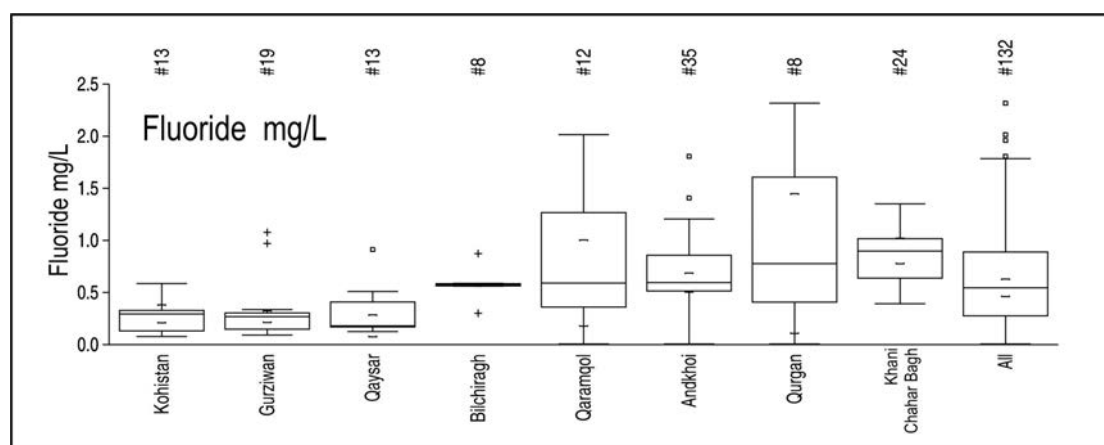
**Fluoride****EC 1998 Directive:** < 1.5 mg/L**WHO (2011):** Guideline < 1.5 mg/L

25-percentile in Faryab = 0.3 mg/L (N=127 samples above dl)

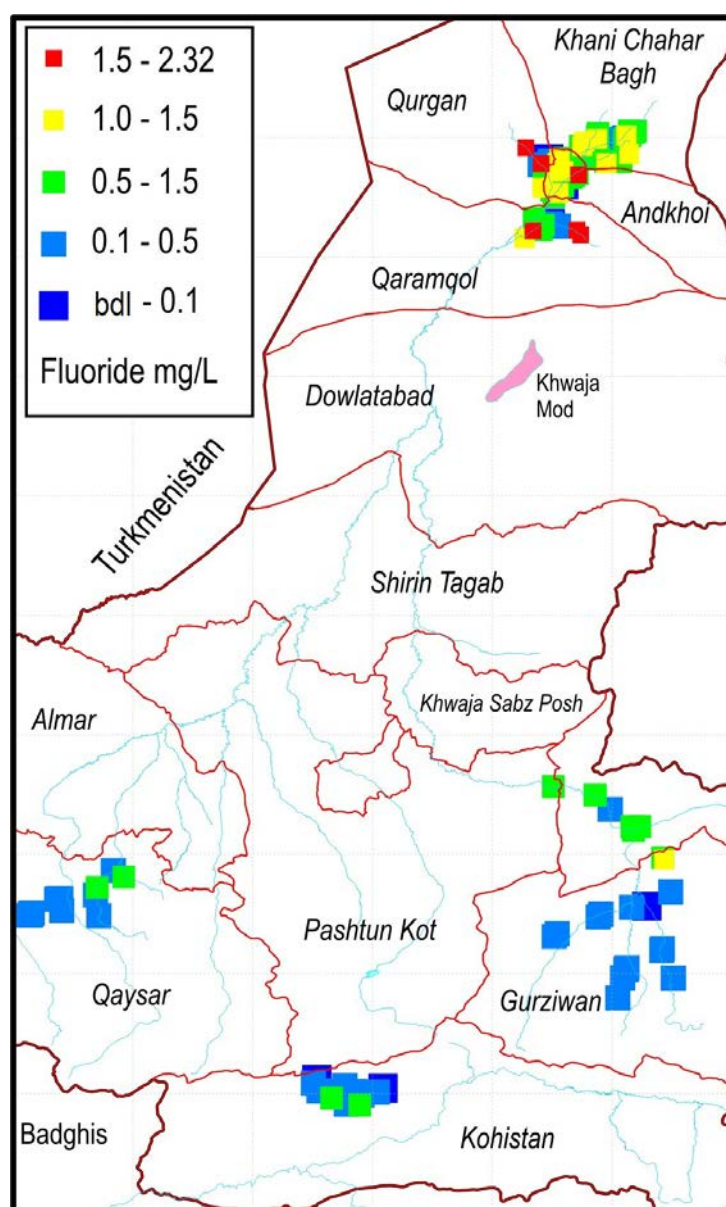
50-percentile in Faryab = 0.56 mg/L (N=127 samples above dl)

90-percentile in Faryab = 1.13 mg/L (N=127 samples above dl)

In Faryab, the range of fluoride concentrations in groundwater is largely within an optimum window. Only six of the 132 samples exceed the WHO Guideline concentration of 1.5 mg/L, with the highest value of 2.3 mg/L occurring in a dug well in Qurgan district.



**Figure 10.9. Boxplot showing distribution of fluoride (F<sup>-</sup>) in N=132 groundwater samples from Faryab.** Five of the 132 samples returned a value below the detection limit (which varies from <0.01 to <1 mg/L) and these have been set to a value of 0.005 mg/L for plotting purposes.



**Figure 10.10. Distribution of F<sup>-</sup> concentrations in groundwater in Faryab.** Five samples of 132 are below detection limit (bdl).

Fluoride can be affected by anion exchange and thus tends to be more mobile in alkaline waters. It can also be affected, up to a point, by evapo-concentration, as it is relatively soluble. However, the presence of calcium in the groundwater hinders the accumulation of excessively high concentrations of fluoride, due to fluorite saturation being attained ( $\text{CaF}_2$ ). Figures 10.9 and 10.10 confirm that the highest fluoride concentrations occur in the four northern districts.

### 10.11 Iron (Fe)

#### Iron

**EC 1998 Directive:** Indicator parameter <200 µg/L

**WHO (2011):** No guideline set. Not of health concern.

Only 31 of the 132 groundwater samples returned iron concentrations in excess of the detection limit (which varied from <1 to <12 µg/L). The highest iron concentration detected in the 132 Faryab groundwater samples was 11 µg/L, from a dug well in Andkhoi district.

Iron in drinking water is of aesthetic (colour, staining of sanitary ware) significance, rather than of health significance. It is typically found in reducing or acidic waters. The generally alkaline and oxidising nature of the sampled Faryab groundwaters is assumed to suppress iron solubility.

### 10.12 Lithium (Li)

Lithium belongs to the alkali metal group and is highly soluble in water. It thus tends to be evapoconcentrated along with potassium and sodium.

#### Lithium

**EC 1998 Directive:** No limit set

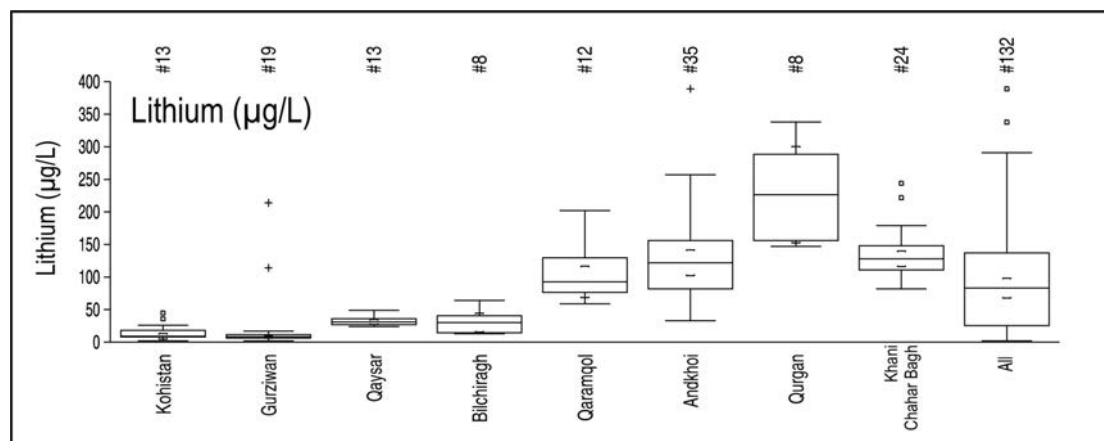
**WHO (2011):** No guideline set

25-percentile in Faryab = 26 µg/L (N=132)

50-percentile in Faryab = 83 µg/L (N=132)

90-percentile in Faryab = 211 µg/L (N=132)

The maximum lithium concentration was 389 µg/L from a dug well in Andkhoi. Figure 10.11 clearly shows that lithium accumulates in groundwater to the north, along with the other salinity-related components.



**Figure 10.11. Boxplot showing distribution of lithium (Li) in N=132 groundwater samples from Faryab.** None of the 132 samples returned a value below the detection limit.

### 10.13 Manganese (Mn)

#### Manganese

**EC 1998 Directive:** Indicator parameter <50 µg/L

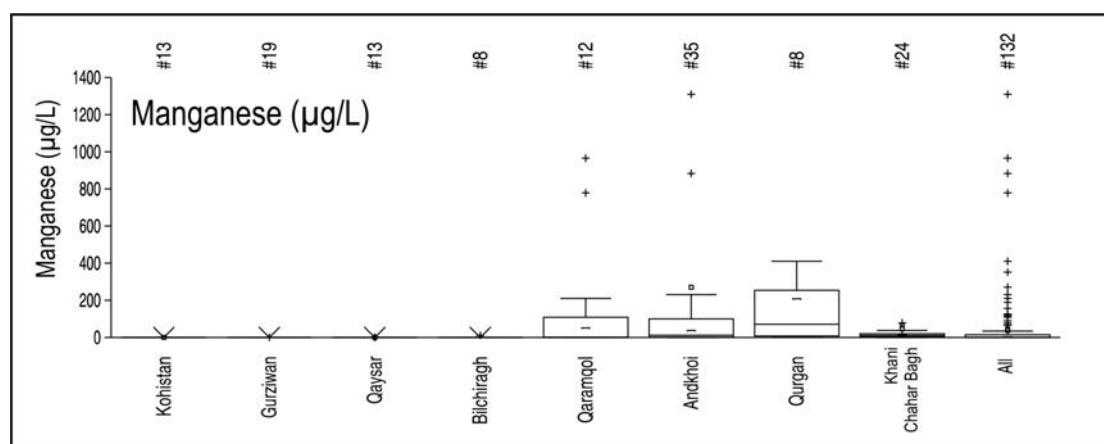
**WHO (2011):** No guideline set. Not of health concern.

25-percentile in Faryab = <0.2 µg/L (N=132)

50-percentile in Faryab = 0.9 µg/L (N=132)

90-percentile in Faryab = 120 µg/L (N=132)

Only 85 of the 132 groundwater samples returned iron concentrations in excess of the detection limit (which varied from <0.2 to <0.7 µg/L). 20 of the 132 samples exceeded the EC guideline value of 50 µg/L. The highest manganese concentration detected in the 132 Faryab groundwater samples was 1310 µg/L, from Andkhoi district. Manganese is only found in concentrations of any significance in the samples from the four northern districts (Figure 10.12). Manganese in drinking water is of aesthetic (staining of sanitary ware) significance, rather than of health significance.



**Figure 10.12. Boxplot showing distribution of manganese (Mn) in N=132 groundwater samples from Faryab.** 47 of the 132 samples returned a value below the detection limit and these have been set to a value of 0.1 µg/L for plotting purposes.

### 10.14 Nitrate (NO<sub>3</sub><sup>-</sup>)

Nitrate was measured as an anion on the ion chromatograph at BGS. It is one of very few of the analysed parameters that can degrade during storage and transport. While every effort was made to ensure cool and dark storage and swift transport, it cannot be excluded that some of laboratory analyses may underestimate the “as sampled” nitrate concentrations.

The WHO (2011) and EC limits of 50 mg/L nitrate as NO<sub>3</sub><sup>-</sup> (equivalent to 11 mg/L as N) are set to protect infants against the possibility of methaemoglobinaemia (“blue baby” syndrome).

Sources of nitrate include agricultural practices (ploughing, application of organic and mineral fertilisers), sewage and leachate from pit latrines. Modest quantities of nitrate in rainfall can also be derived from vehicle exhausts, industry and nitrification of atmospheric nitrogen by lightning. Banks et al. (2002) have demonstrated a correlation

between nitrate concentrations in groundwater and urban areas / pit latrines. As a highly soluble anion, nitrate is susceptible to evapoconcentrative effects.

### Nitrate

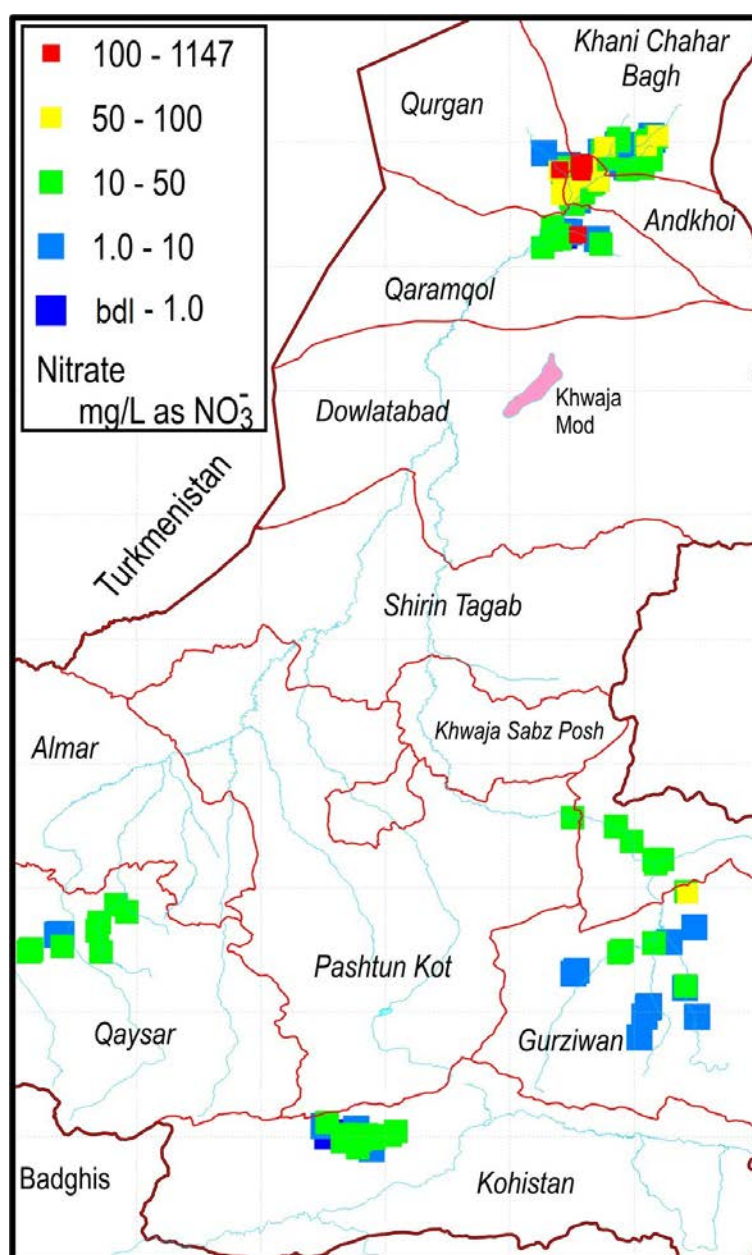
**EC 1998 Directive:** <50 mg/L (as  $\text{NO}_3^-$ )

**WHO (2011):** Guideline value <50 mg/L (as  $\text{NO}_3^-$ )

25-percentile in Faryab = 9.0 mg/L (N=132)

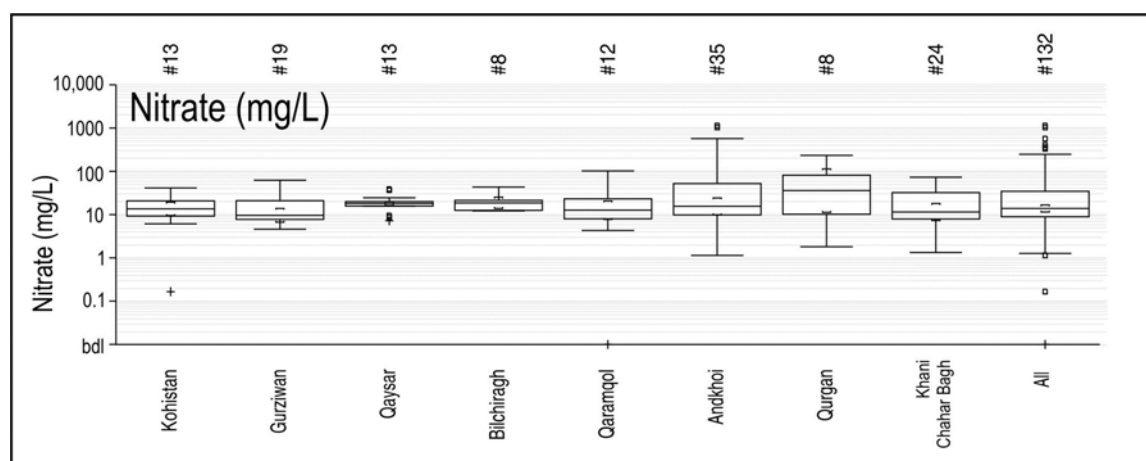
50-percentile in Faryab = 13.8 mg/L (N=132)

90-percentile in Faryab = 62 mg/L (N=132)



**Figure 10.13.** Distribution of nitrate (as mg/L  $\text{NO}_3^-$ ) concentrations in groundwater in Faryab. One sample of 132 is below detection limit (bdl).





**Figure 10.14. Boxplot showing distribution of nitrate (as mg/L  $\text{NO}_3^-$ ) in N=132 groundwater samples from Faryab.** 1 of the 132 samples returned a value below the detection limit (which varies between <0.02 and <1 mg/L) and this has been set to a value of 0.01 mg/L for plotting purposes.

20 of the 132 (15%) Faryab groundwater samples exhibited nitrate concentrations exceeding 50 mg/L. The highest value was an enormous 1147 mg/L from a dug well in Andkhoy, although a worrying 9 out of 132 samples exhibited nitrate concentrations in excess of 100 mg/L. The samples exceeding the WHO (2011) guideline value almost all came from the four northern districts around Andkhoy.

### 10.15 Potassium (K)

Potassium belongs to the alkali metal group and is highly soluble in water. It thus tends to be evapoconcentrated along with rubidium, lithium and sodium.

Potassium can be derived from hydrolysis of silicate rocks, but is also associated with organic matter and can be released from organic wastes (e.g. sewage effluents).

The maximum potassium concentration was 171 mg/L from a dug well in Andkhoy, which also exhibited a very high nitrate concentration of 1034 mg/L. Figure 10.15 clearly shows that potassium accumulates in groundwater to the north, along with the other salinity-related components.

#### Potassium

**EC 1998 Directive:** No guideline set

**WHO (2011):** Occurs at concentrations well below those of health concern

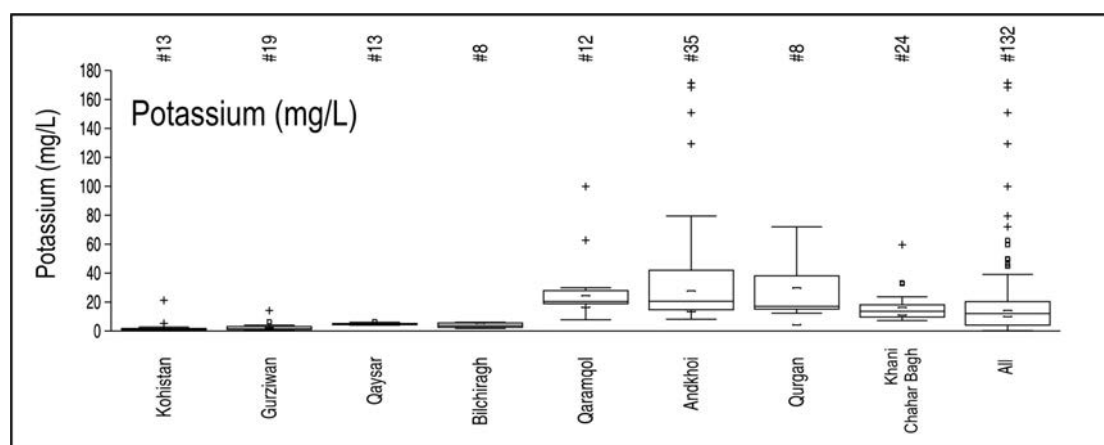
25-percentile in Faryab = 4.2 mg/L (N=132)

50-percentile in Faryab = 12.1 mg/L (N=132)

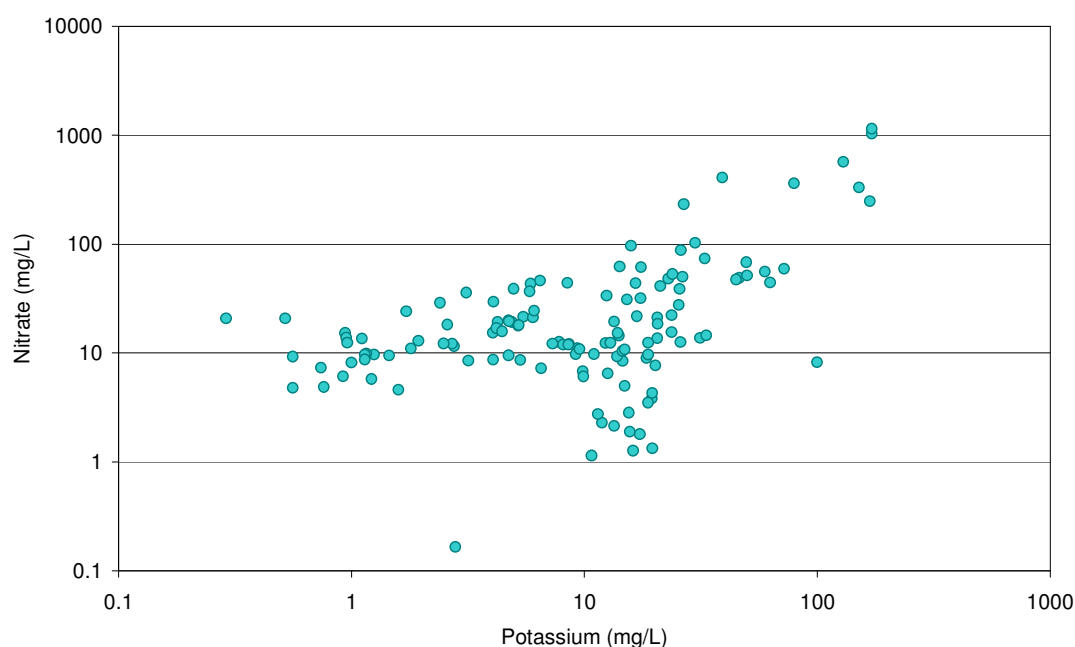
90-percentile in Faryab = 44 mg/L (N=132)

When potassium is plotted against nitrate, it is found that the highest potassium concentrations tend to coincide with the highest nitrate concentrations. It is unclear if this is simply a reflection of mutual evapoconcentrative effects or whether it is due to a common derivation in infiltrating sewage effluent (for example) - or, quite possibly, both.





**Figure 10.15. Boxplot showing distribution of potassium (K) in N=132 groundwater samples from Faryab.** None of the 132 samples returned a value below the detection limit.



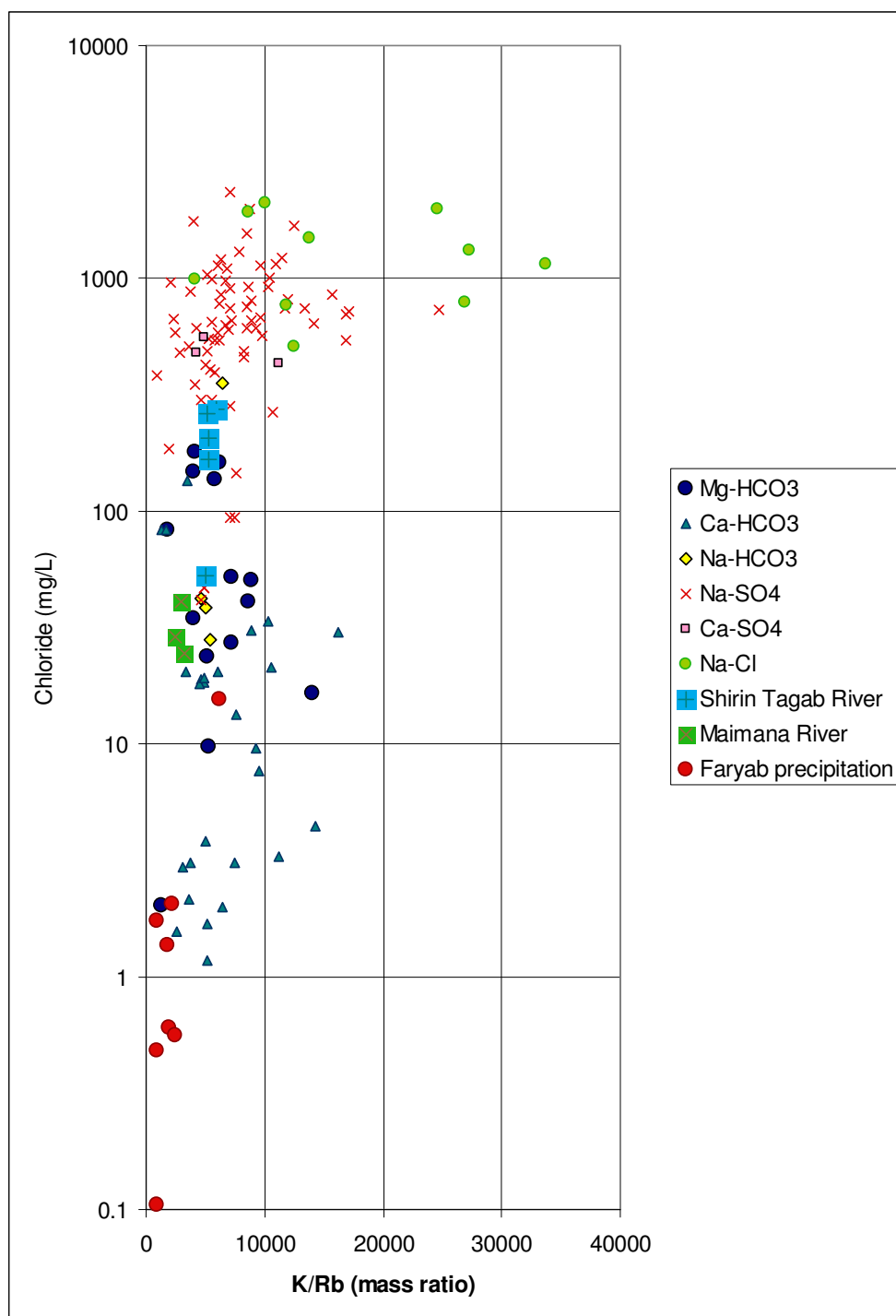
**Figure 10.16. Scatterplot of groundwater concentrations of nitrate (as mg/L NO<sub>3</sub><sup>-</sup>) versus potassium.** N = 131 (one sample with nitrate below detection limit omitted).

### 10.16 Rubidium (Rb)

Rubidium belongs to the alkali metal group and is highly soluble in water. It thus tends to be evapoconcentrated along with potassium, lithium and sodium.

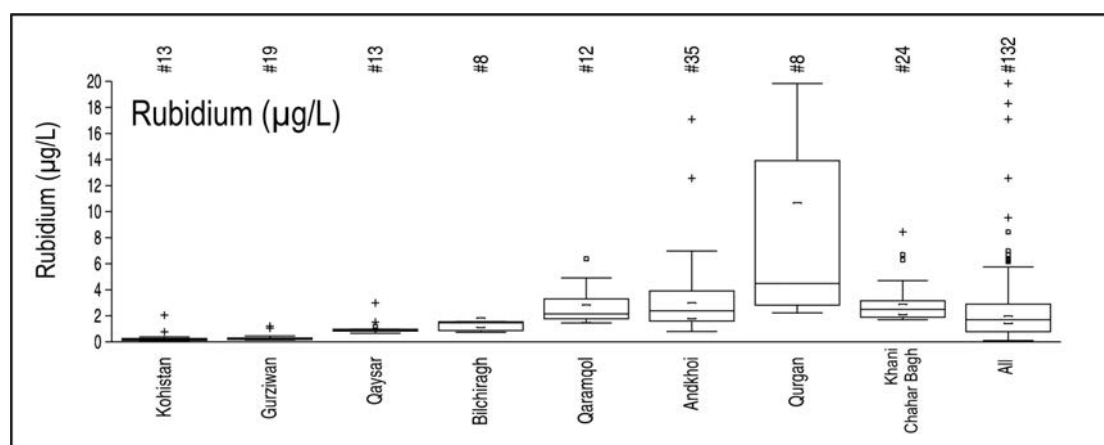
The maximum rubidium concentration was 19.8 µg/L from a dug well in Qurgan district. Figure 10.18 clearly shows that rubidium accumulates in groundwater to the north, along with the other salinity-related components. Especially high concentrations are observed in Qurgan district.

Rubidium is often regarded as a chemical analogue of potassium. Figure 10.17 shows a plot of the K/Rb mass ratio, plotted against chloride as a surrogate of salinity.



**Figure 10.17. Potassium to rubidium mass ratios, plotted against chloride concentration, for groundwaters sampled in 2013 subdivided according to water type (see Chapter 9). The diagram also shows river waters (sampling discussed in Chapter 3) and precipitation samples (Chapter 2)**

Figure 10.17 shows a fairly consistent K/Rb mass ratio of 3,000-10,000 for most groundwaters, with river waters lying on the groundwater trend. A significant proportion of the Na-Cl groundwater types (and some Na-SO<sub>4</sub>) groundwater types exhibit K/Rb ratios exceeding 10,000 and even exceeding 30,000 in one case.



**Figure 10.18. Boxplot showing distribution of rubidium (Rb) in N=132 groundwater samples from Faryab.** None of the 132 samples returned a value below the detection limit.

### Rubidium

**EC 1998 Directive:** No guideline set

**WHO (2011):** No guideline set

25-percentile in Faryab = 0.79 µg/L (N=132)

50-percentile in Faryab = 1.7 µg/L (N=132)

90-percentile in Faryab = 5.5 µg/L (N=132)

## 10.17 Selenium (Se)

Selenium is an essential trace element, with the WHO (2011) recommending an adult daily intake of 26-35 µg. However, in excess, selenium can be toxic, with WHO (2011) recommending a maximum daily intake of 400 µg.

### Selenium

**EC 1998 Directive:** <10 µg/L

**WHO (2011):** Provisional guideline <40 µg/L

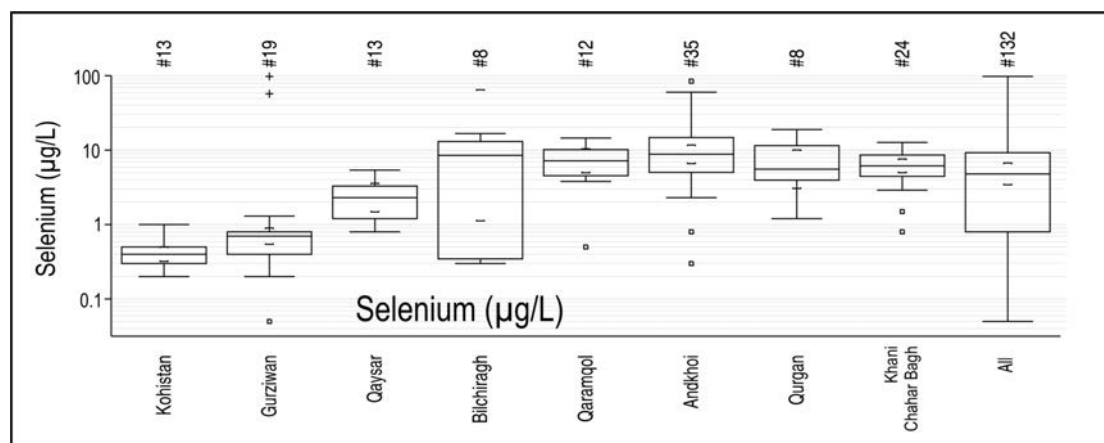
25-percentile in Faryab = 0.8 µg/L (N=132)

50-percentile in Faryab = 4.8 µg/L (N=132)

90-percentile in Faryab = 14.8 µg/L (N=132)

Of the 132 Faryab groundwater samples, four samples (3%) exceed the WHO (2011) provisional guideline of 40 µg/L, while 30 samples (23%) exceed the EC limit of 10 µg/L. The highest concentrations are typically from the four northern districts and also from Bilchiragh.

The highest individual value of 98 µg/L was, however, from a spring in Gurziwan district.

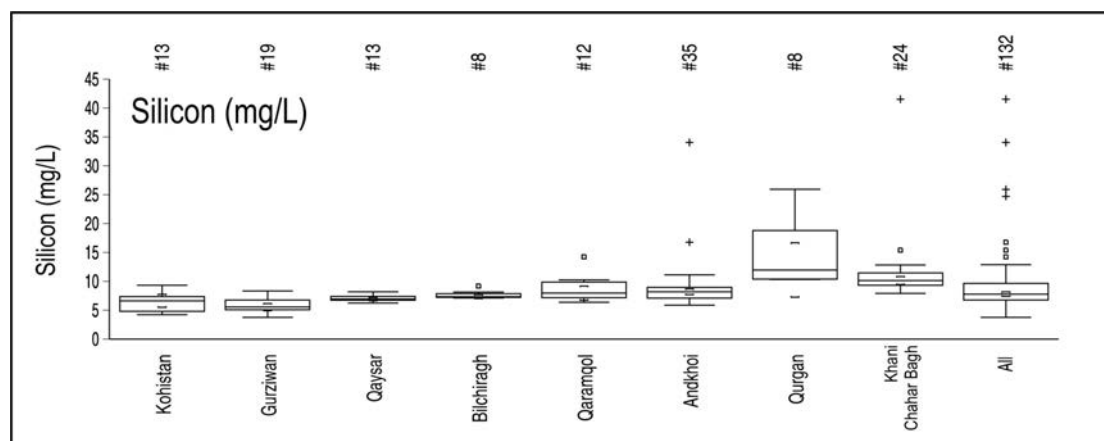


**Figure 10.19. Boxplot showing distribution of selenium (Se) in N=132 groundwater samples from Faryab.** 1 of the 132 samples returned a value below the detection limit (of  $<0.1 \mu\text{g/L}$ ) and this has been set to a value of  $0.05 \text{ mg/L}$  for plotting purposes.

### 10.18 Silicon (Si)

Groundwaters typically contain 5-10 mg/L of dissolved silicon. This is typically in the form of monosilicic acid ( $\text{H}_4\text{SiO}_4$ ) or, at higher pH, hydrogen silicate anions. The solubility of silicon increases with temperature; otherwise, groundwater dissolved silicon contents are seldom strongly affected by other aspects of the water's chemistry, typically being controlled by the solubility of cryptocrystalline silica (e.g. chalcedony or similar).

However, it has been found that (a) evapoconcentration can allow elevated concentrations of silicon to occur and for silica saturation to be exceeded, due to kinetic constraints on silica precipitation and (b) that other species in saline waters (e.g. sodium, by forming a  $\text{SiO}_2(\text{OH})_2\text{Na}^-$  complex ion) may be able to enhance silica solubility (Jones et al. 1967, Tanaka et al. 2004, Tanaka & Takahashi 2007).



**Figure 10.20. Boxplot showing distribution of silicon (as Si) in N=132 groundwater samples from Faryab.** None of the 132 samples returned a value below the detection limit.

Indeed, it is found that the Faryab samples typically contain 5-10 mg/L Si. Concentrations significantly in excess of 10 mg/L only occur in a few locations in the northern districts, especially in Qurgan and Khani Chahar Bagh.

Figures 10.21a,b show that there is a weak correlation between silicon concentration and temperature and a slightly stronger one with sodium concentration. There are, however, a number of high Si concentrations (> 15 mg/L) that are not clearly explained by either of these factors.

### Silicon

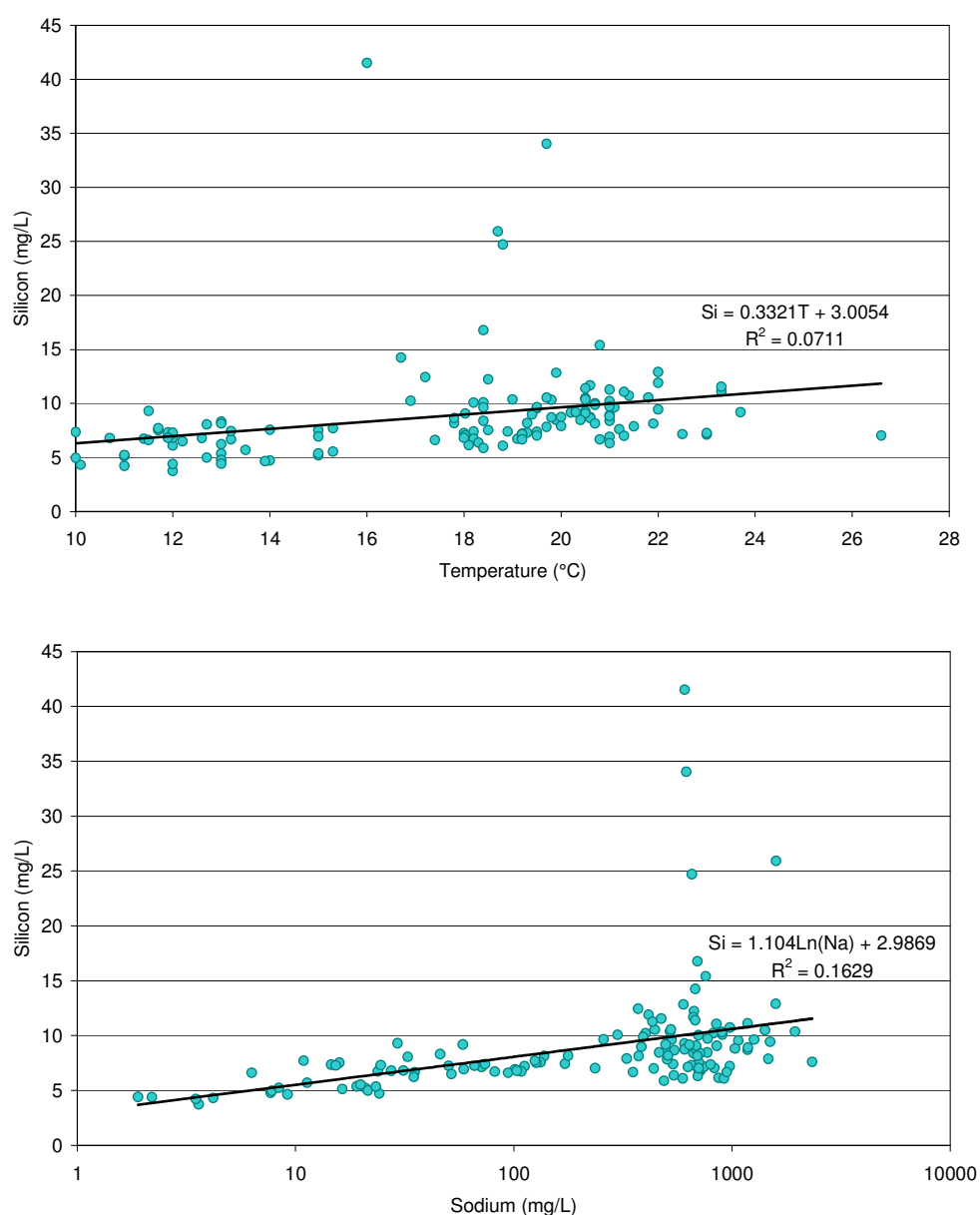
**EC 1998 Directive:** No guideline provided

**WHO (2011):** No guideline provided

25-percentile in Faryab = 6.8 mg/L (N=132)

50-percentile in Faryab = 7.8 mg/L (N=132)

90-percentile in Faryab = 11.5 mg/L (N=132)



**Figure 10.21. Scatterplots showing correlations of silicon in the 132 Faryab groundwater samples with (top) groundwater temperature and (bottom) sodium.**

### 10.19 Strontium (Sr)

Strontium is an alkaline earth element, chemically analogous to magnesium.

#### Strontium

**EC 1998 Directive:** No guideline provided

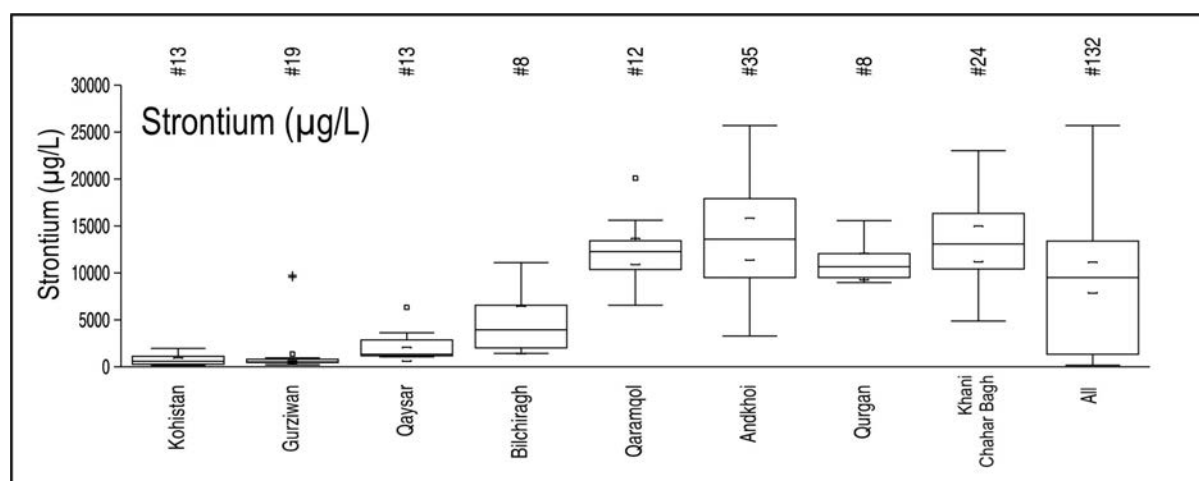
**WHO (2011):** No guideline provided

25-percentile in Faryab = 1.3 mg/L (N=132)

50-percentile in Faryab = 9.5 mg/L (N=132)

90-percentile in Faryab = 17.6 mg/L (N=132)

Concentrations of strontium in Faryab's groundwater are generally relatively high. The highest recorded concentration of 25.7 mg/L is from a dug well in Andkhoi. Like many other elements, strontium concentrations broadly reflect salinity, increasing towards the north.



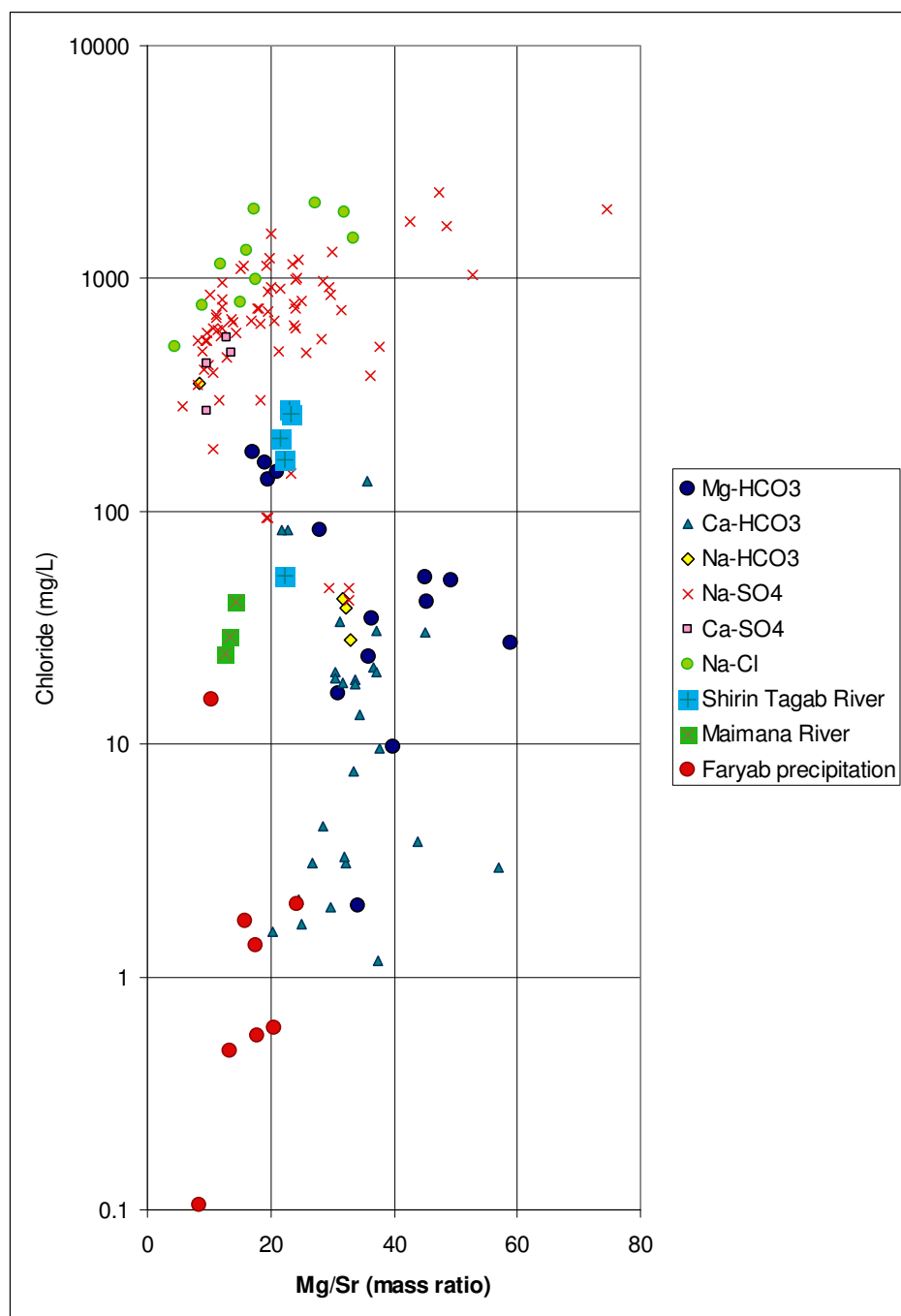
**Figure 10.22. Boxplot showing distribution of strontium (Sr) in N=132 groundwater samples from Faryab.** None of the 132 samples returned a value below the detection limit.

Figure 10.23 shows the mass ratio of Mg/Sr in groundwaters, river waters and precipitation in Faryab.

It will be seen that precipitation, river waters and many of the more saline groundwaters all exhibit a Mg/Sr ratio in the region of 10-20. The lower salinity groundwaters, however, exhibit a much higher Mg/Sr ratio in the region 20-60, together with some of the more saline groundwaters. For reference, the Mg/Sr ratio in modern abiotic marine calcite (Bahamas) is around 37. By contrast, modern biotic marine calcite has a much lower ratio 6-20 (Carpenter & Lohmann 1992). Seawater itself has a mass ratio of around 162 (Dickson & Goyet 1994).

As groundwater evolves and becomes saturated with calcite, one might expect the precipitation of abiotic calcite to remove magnesium preferentially from the groundwater, leaving groundwater enriched in Sr, and with a lower Mg/Sr ratio.





**Figure 10.23. Magnesium to strontium mass ratios, plotted against chloride concentration, for groundwaters sampled in 2013 subdivided according to water type (see Chapter 9). The diagram also shows river waters (sampling discussed in Chapter 3) and precipitation samples (Chapter 2)**

### 10.20 Thallium (Tl)

Thallium is a highly toxic element. The EU and WHO (2011) do not set drinking water guidelines for thallium, but the USEPA (2009) sets a limit of only 2 µg/L.

All but 7 of the 132 groundwater samples from Faryab returned concentrations below the detection limit, which varied from <0.01 µg/L to <0.2 µg/L. The highest recorded concentration was 0.05 µg/L. All samples were thus well below the USEPA limit.

### 10.21 Uranium (U)

Uranium is a mildly radioactive actinide element. Surprisingly, its chemotoxicity is regarded as being more important than its radiotoxicity, as discussed by Frengstad & Banks (2014).

#### Uranium

**EC 1998 Directive:** No guideline provided

**WHO (2011):** Provisional guideline <30 µg/L

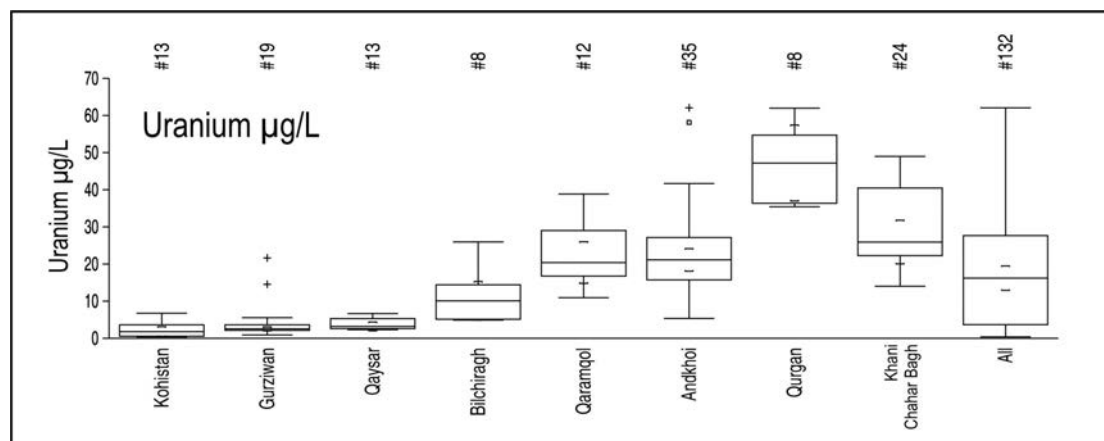
25-percentile in Faryab = 3.7 µg/L (N=132)

50-percentile in Faryab = 16.2 µg/L (N=132)

90-percentile in Faryab = 41 µg/L (N=132)

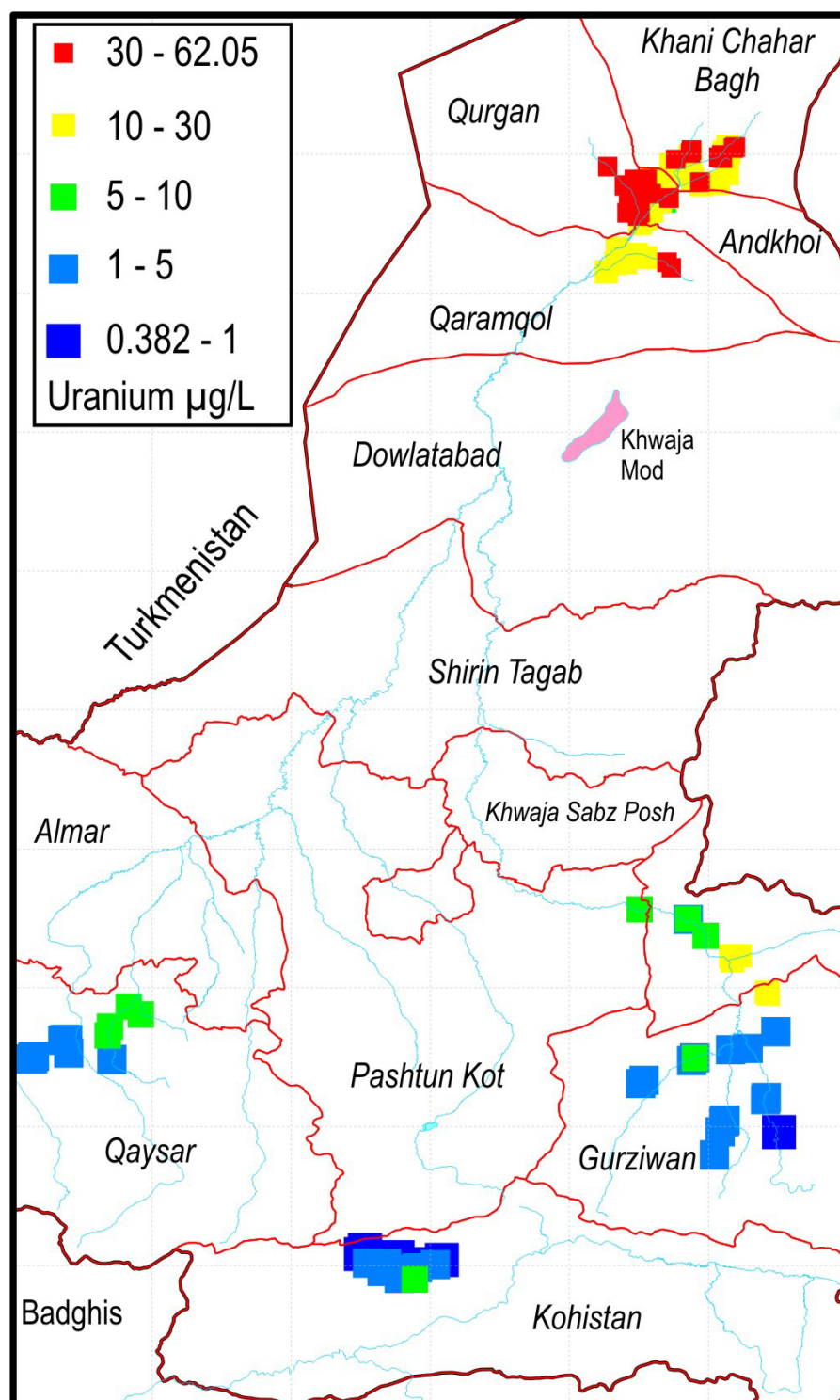
Although the solubility of uranium is limited in reducing environments, it forms stable oxyanions (and other ionic complexes) in oxidising environments, which can be highly soluble.

In Faryab, 26 of 132 samples (20%) exceed the WHO (2011) provisional guideline value of 30 µg/L, exclusively in the northern districts. The highest recorded uranium concentration was 62 µg/L from dug wells in Qurgan and Andkhoi.



**Figure 10.24. Boxplot showing distribution of uranium (U) in N=132 groundwater samples from Faryab.** None of the 132 samples returned a value below the detection limit.

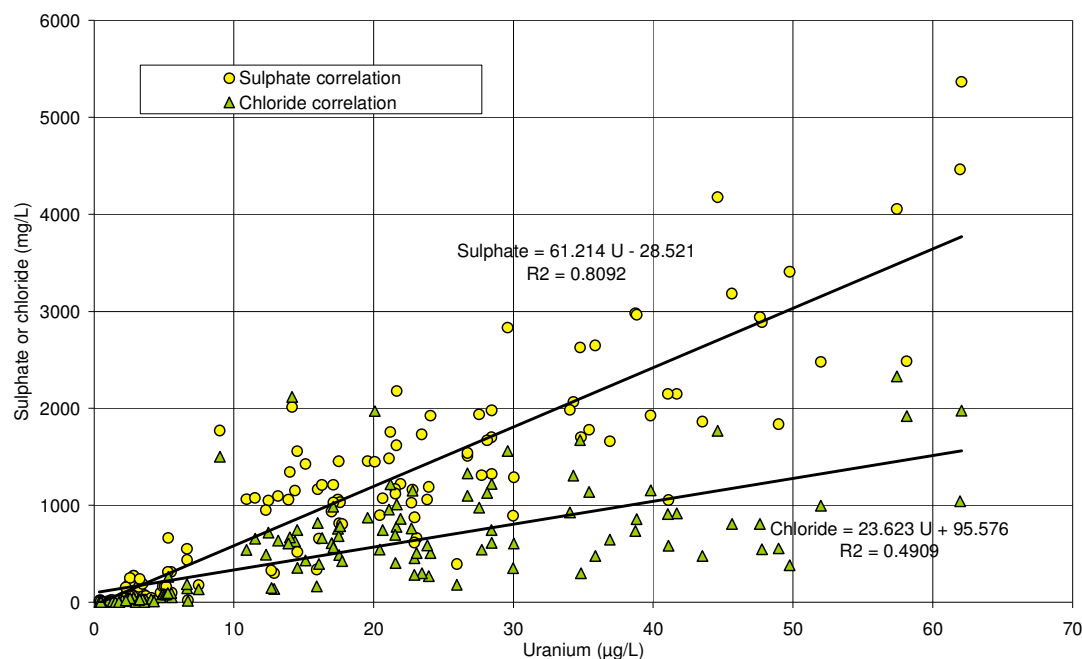
The map in Figure 10.25 is strongly suggestive of groundwater uranium concentrations increasing towards the north, which may also indicate the uranium anionic complexes are susceptible to the same evapoconcentrative processes as many other soluble elements. Alternatively, the high concentrations of uranium in saline groundwaters may be related to mobilization by complexation with salinity-related species, such as sulphate (Frengstad & Banks 2014). Figure 10.26 suggests that uranium complexation with sulphate is a highly plausible mechanism, as there is a much stronger correlation ( $r=0.90$ ) with sulphate than with chloride ( $r = 0.70$ ).



**Figure 10.25. Distribution of uranium (U) concentrations in groundwater in Faryab.** All 132 samples are above the analytical detection limit.

Ultimate sources of uranium can include:

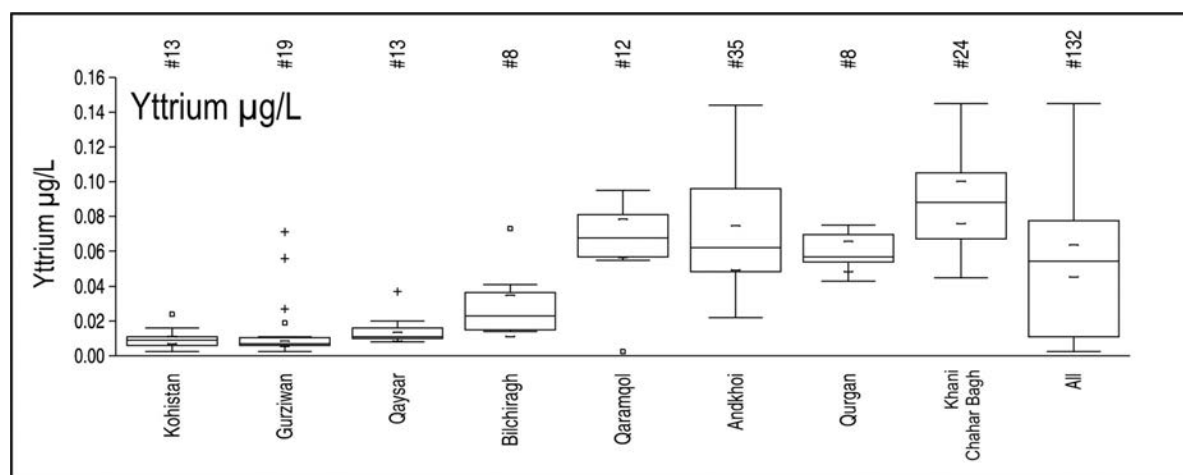
- uranium minerals within igneous or metamorphic rocks (e.g. apatite, zircon)
- uranium within dark organic sedimentary marine mudrocks and shales
- some inorganic fertilisers, especially those derived from apatite.



**Figure 10.26. Scatter-plot showing correlation of uranium with sulphate and chloride. Best fit linear regressions shown.**

## 10.22 Yttrium (Y)

The distribution of yttrium is presented here as a "hydrochemical curiosity" as it is not an element of any especial health significance. Yttrium is one of a group of chemically similar elements called the rare earth elements (REE) and relatively little is known about their occurrence and behaviour in groundwater systems (Banks et al. 1999).



**Figure 10.27. Boxplot showing distribution of yttrium (Y) in N=132 groundwater samples from Faryab.** Six of the 132 samples returned a value below the detection limit (of <0.005 to <0.05 µg/L) and these have been set to a value of 0.0025 mg/L for plotting purposes.

From Figure 10.27 it seems that the occurrence of yttrium is not dissimilar to that of uranium, i.e. steadily increasing concentrations northwards, giving the appearance of broadly the same evapoconcentrative processes, or mobilisation by complexation with salinity-related species. Complexation of REE with chloride, sulphate and other species

is well-known - Lewis et al. 1998). Figure 10.27 does not show the same degree of correlation with chloride and sulphate as uranium does, however.

### Yttrium

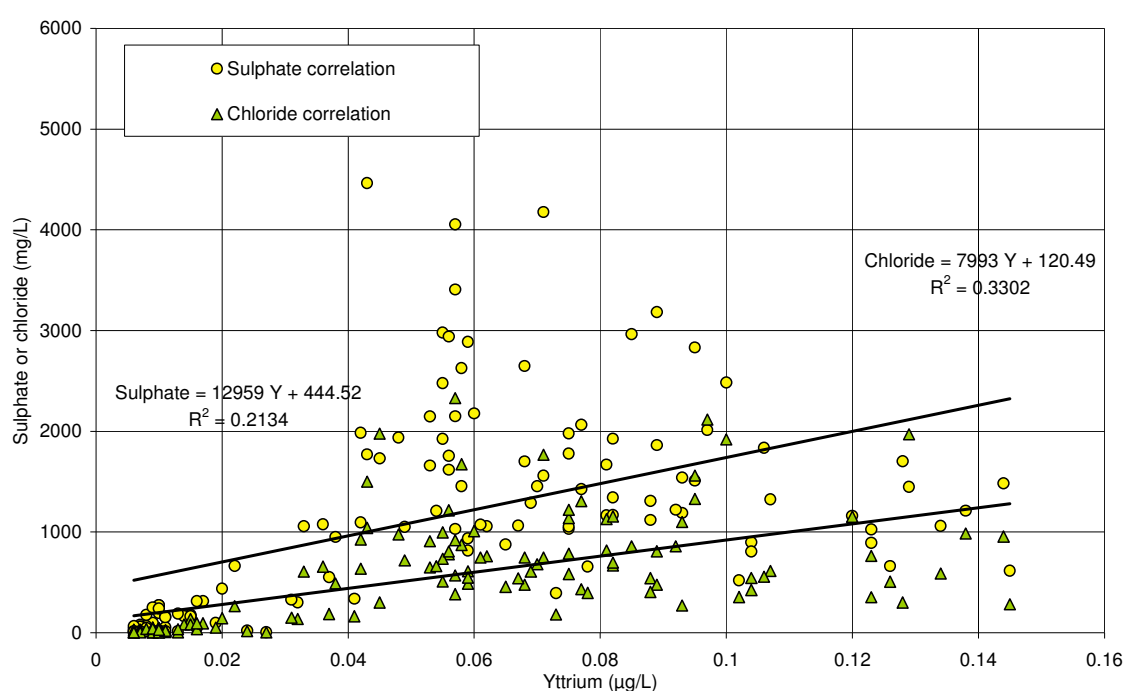
**EC 1998 Directive:** No guideline provided

**WHO (2011):** No guideline provided

25-percentile in Faryab = 0.01 µg/L (N=132)

50-percentile in Faryab = 0.05 µg/L ((N=132

90-percentile in Faryab = 0.10 µg/L (N=132)

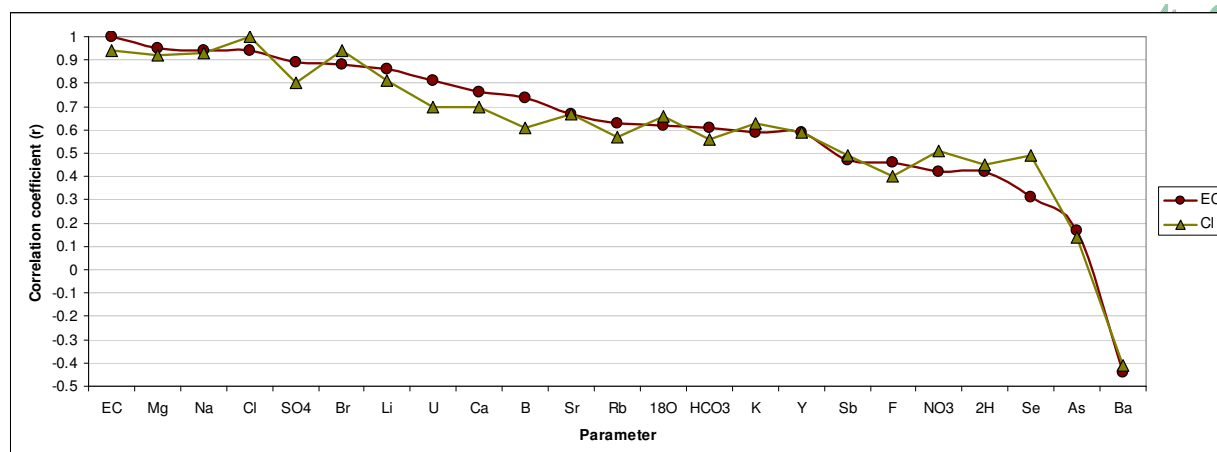


**Figure 10.28. Scatter-plot showing correlation of yttrium with sulphate and chloride.** Best fit linear regressions shown. Six values where yttrium is below detection limit are omitted.

### 10.23 Correlation with salinity

A number of the parameters discussed in this chapter show a clear correlation with salinity and an accumulation in groundwater towards the north.

The correlation coefficient ( $r$ ) of these parameters in the 132 sampled groundwaters has been evaluated in the program DAS, by the Technical University of Vienna, after arbitrarily setting values less than the analytical detection limit to a value half of the lowest analytical detection limit. The result is Figure 10.29, which shows correlation coefficients with field electrical conductivity and with chloride. A correlation coefficient of +1 implies a perfect correlation, -1 implies a perfect negative correlation, while 0 implies no correlation.



**Figure 10.29. Correlation coefficients of selected parameters with electrical conductivity and chloride concentration, as surrogates of groundwater salinity. N = 132 groundwater samples from Faryab. 18O refers to the stable isotope  $\delta^{18}\text{O}$  (see Chapter 11) and 2H to the stable isotope  $\delta^2\text{H}$ .**

It will be seen that the most “salinity-related” parameters are magnesium, sodium, chloride, sulphate and bromide, followed by lithium and uranium.

The stable isotope  $\delta^{18}\text{O}$  is susceptible to fractionation by evapoconcentration, and shows some correlation ( $r > 0.6$ ) with salinity, suggesting that at least some component of salinisation is related to evapoconcentrative processes.

Arsenic shows a rather poor correlation with salinity and barium shows a relatively good negative correlation.