

9. Faryab: Groundwater Hydrochemical Types

9.1 Ion Balance Error

In 2013, 132 wells, boreholes and springs were sampled in Kohistan, Qaysar, Gurziwan, Bilchiragh and the four northern districts around Andkhoy. The samples were analysed by inductively coupled plasma mass spectroscopy (ICP-MS), ion chromatography and other techniques at the laboratory of the British Geological Survey (BGS) at Keyworth, Nottinghamshire, UK. The analytical data from this sampling round will be discussed further in Chapter 10.

The major ion concentrations in the samples were converted to milliequivalents per litre (meq/L) - i.e. millimoles per litre of charge - and ion balance errors were calculated. The vast majority of samples (88%) had an ion balance within $\pm 5\%$, while 93% were within 10%. The larger ion balance errors were typically in favour of anions and were from the earliest batches of samples from Gurziwan and Bilchiragh, where filtration techniques had not yet been perfected and where any particulates in the water may have led to overestimates of bicarbonate alkalinity.

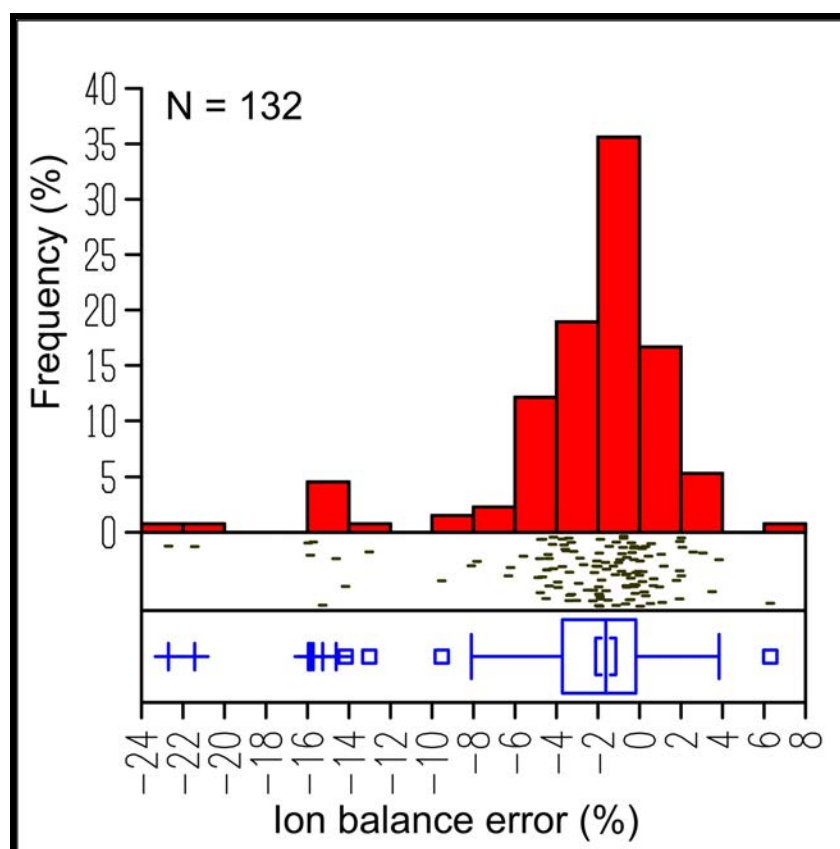


Figure 9.1. Distribution of ion balance errors in 132 samples from Faryab, shown as a histogram, scatterplot and boxplot.

9.2 Durov diagram

Having converted the 132 analyses to meq/L, they could now be plotted on a so-called Durov diagram (Figure 9.2), kindly prepared for us by the Geological Survey of Norway.

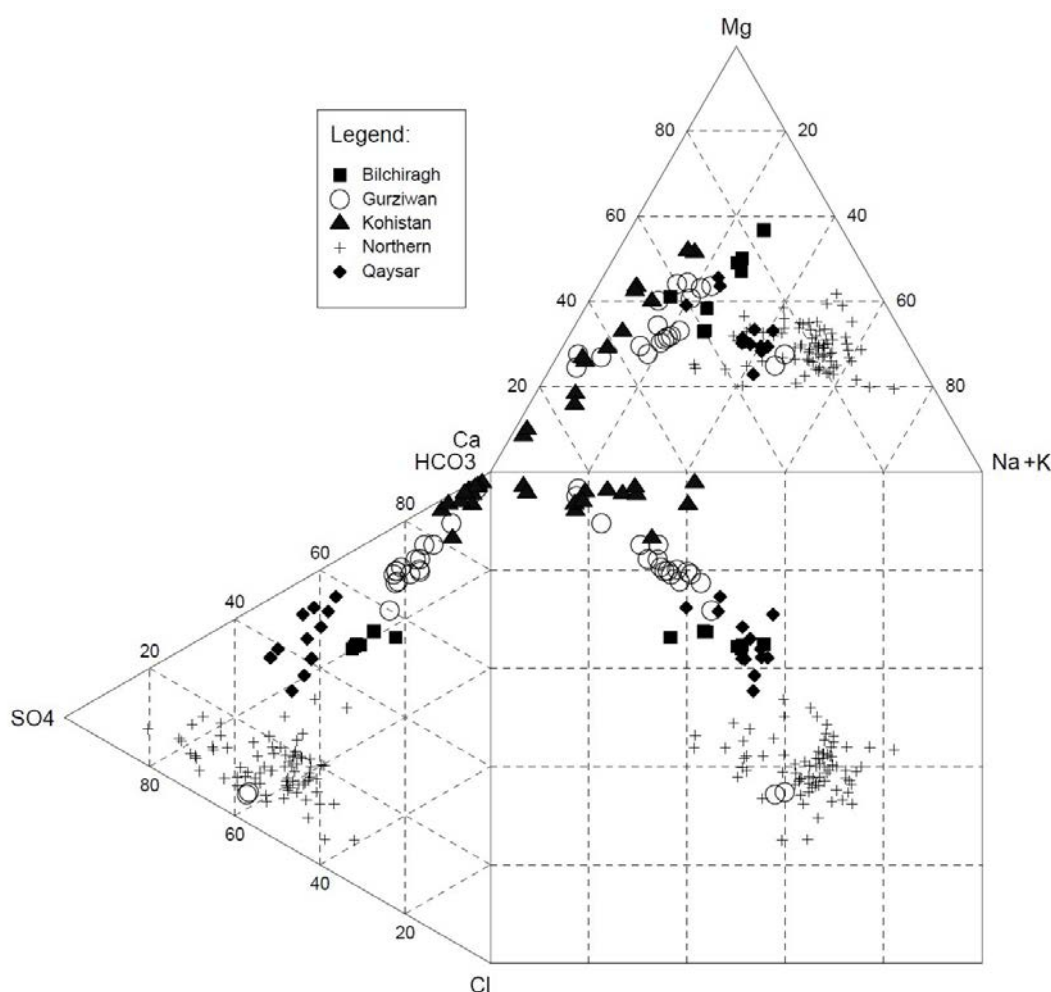


Figure 9.2. Durov diagram showing the major ion composition of 132 groundwaters in Faryab (sampled 2013) in terms of Na-Ca-Mg / $\text{SO}_4\text{-HCO}_3\text{-Cl}$ ion composition. Plotted according to meq/L concentration (K is added to Na in the plot). Many thanks to Dr. Bjørn Frengstad, of the Geological Survey of Norway, for plotting this diagram.

It will be seen that the southern samples from Kohistan and Gurziwan (also the least saline) are dominated by calcium (sometimes magnesium) as the main cation and bicarbonate as the main anion. We say therefore that these are Ca-HCO_3 or Mg-HCO_3 waters.

Further north, in Bilchiragh, groundwaters are more likely to be Mg-HCO_3 . In Qaysar samples are without a characteristic dominant ion. The dominant anion could be sulphate or bicarbonate, whereas the cations are relatively evenly balanced, the dominant one being either sodium or magnesium.

In the four northern districts, sodium becomes the dominant cation, with sulphate (or sometimes chloride) becoming the dominant anion. The groundwaters with the sodium chloride composition are typically beneath the very centre of Andkhoi city (Figure 9.3). In the north of the Andkhoi delta, in Khani Chahar Bagh, there are even a few groundwaters of dominant calcium sulphate composition.

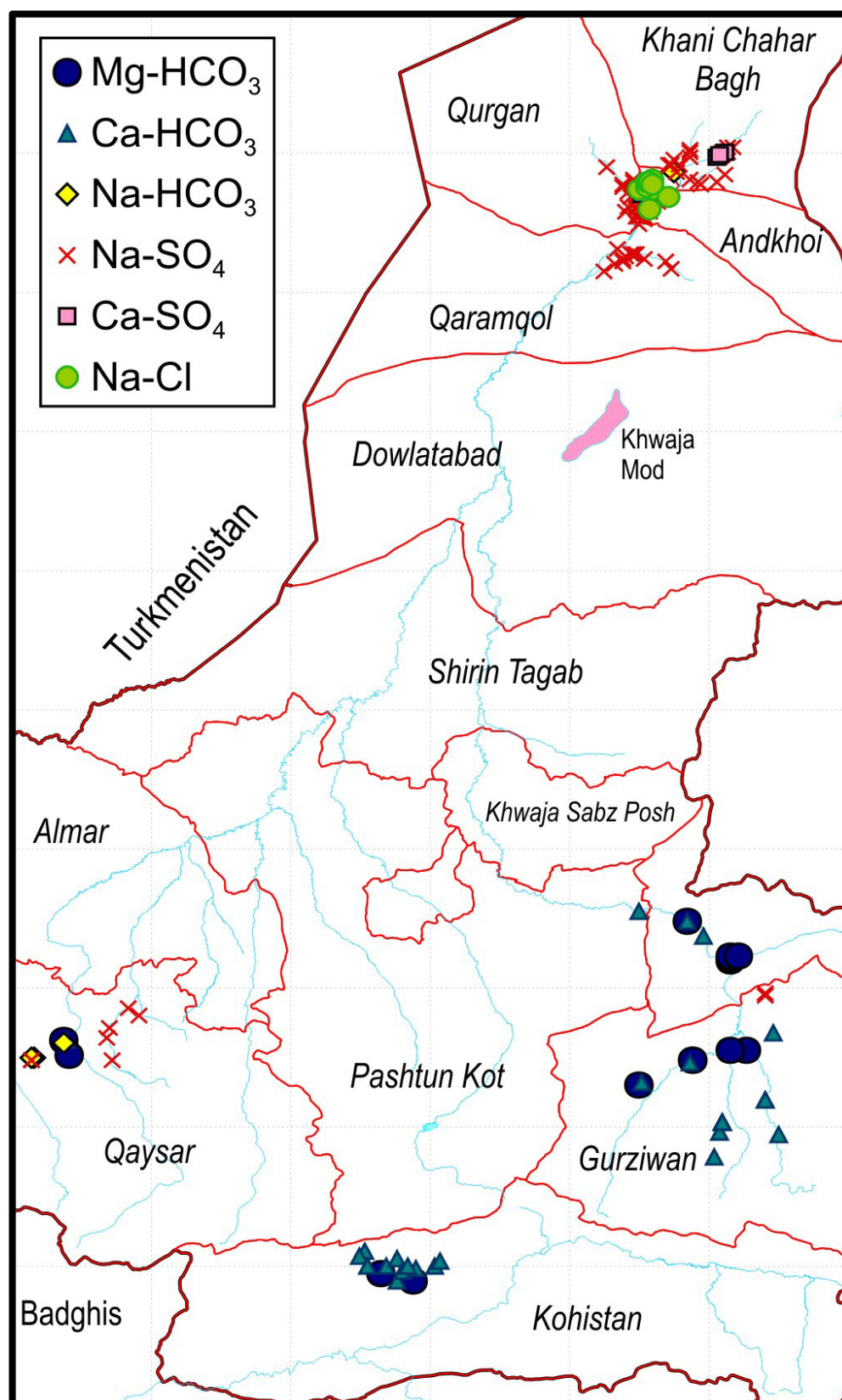


Figure 9.3. The 132 groundwaters sampled in 2013, classified according to dominant cation and anion, according to meq/L concentration.

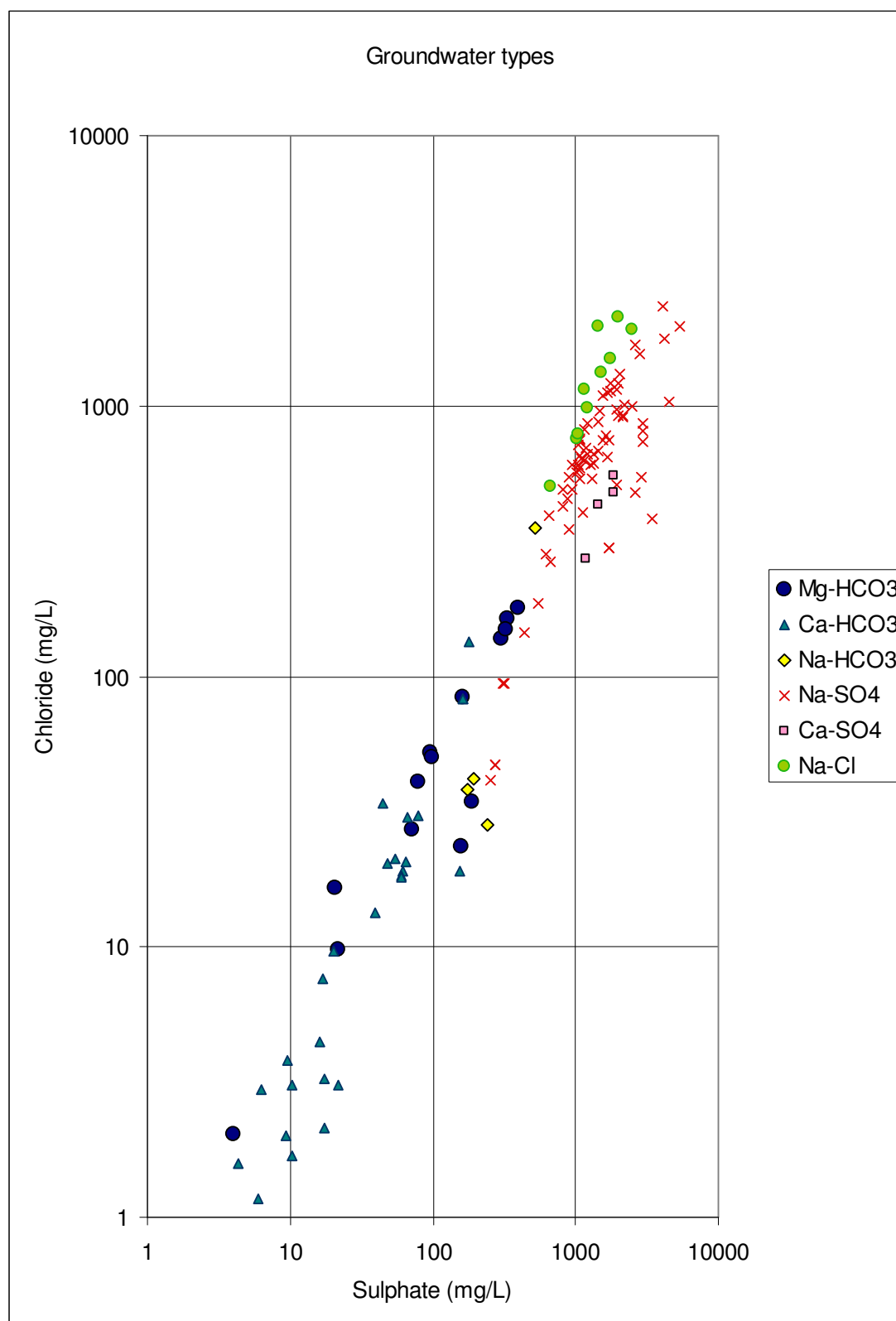


Figure 9.4. Chloride concentrations in the 132 groundwaters sampled in 2013, plotted against sulphate concentrations, and subdivided according to water type. Note the logarithmic scales in both axes.

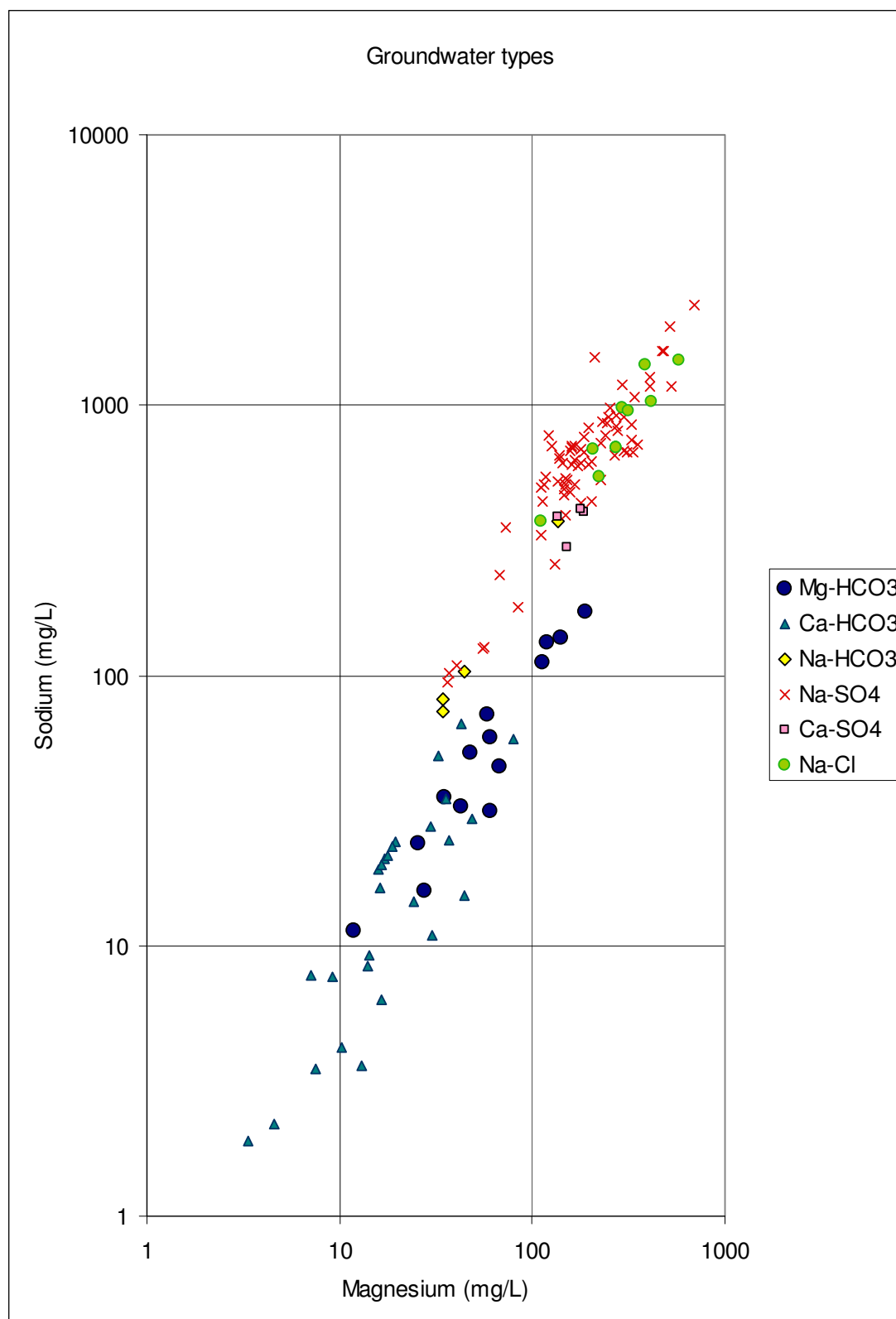


Figure 9.5. Sodium concentrations in the 132 groundwaters sampled in 2013, plotted against magnesium concentrations, and subdivided according to water type. Note the logarithmic scales in both axes.

We can create a large number of plots to clarify the evolution of major ion concentrations in the groundwaters. A small selection of these is shown in Figures 9.4 - 9.7.

Figure 8.4 shows chloride concentrations, plotted against sulphate concentrations, and subdivided according to water type. The following features should be noted:

- That the plotted waters appear to largely fall on a *continuum*;
- The chloride and sulphate concentrations increase roughly in proportion with each other (the gradient of the line is almost, but not exactly, 1:1).

These two observations are strongly indicative of evaporative processes driving up-concentration of the waters from south to north.

- The dominant cation in the water changes with increasing $\text{SO}_4^{2-}/\text{Cl}^-$ concentration - from Ca in the lowest salinity waters, to Mg in the medium salinity waters and finally to Na in the most saline waters.
- The dominant anion in the water changes with increasing salinity - from HCO_3^- in the lowest salinity waters, to SO_4^{2-} or Cl^- in the most saline waters.

Figure 9.5 shows a similar plot for sodium concentrations against magnesium concentrations. This plot shows similar characteristics to Figure 9.4, except that the slope is greater than 1:1 - in other words, sodium accumulates in the water to a greater extent than magnesium (which should be unsurprising, as sodium “overtakes” magnesium as the dominant cation in the most saline waters).

9.3 Major ion ratios

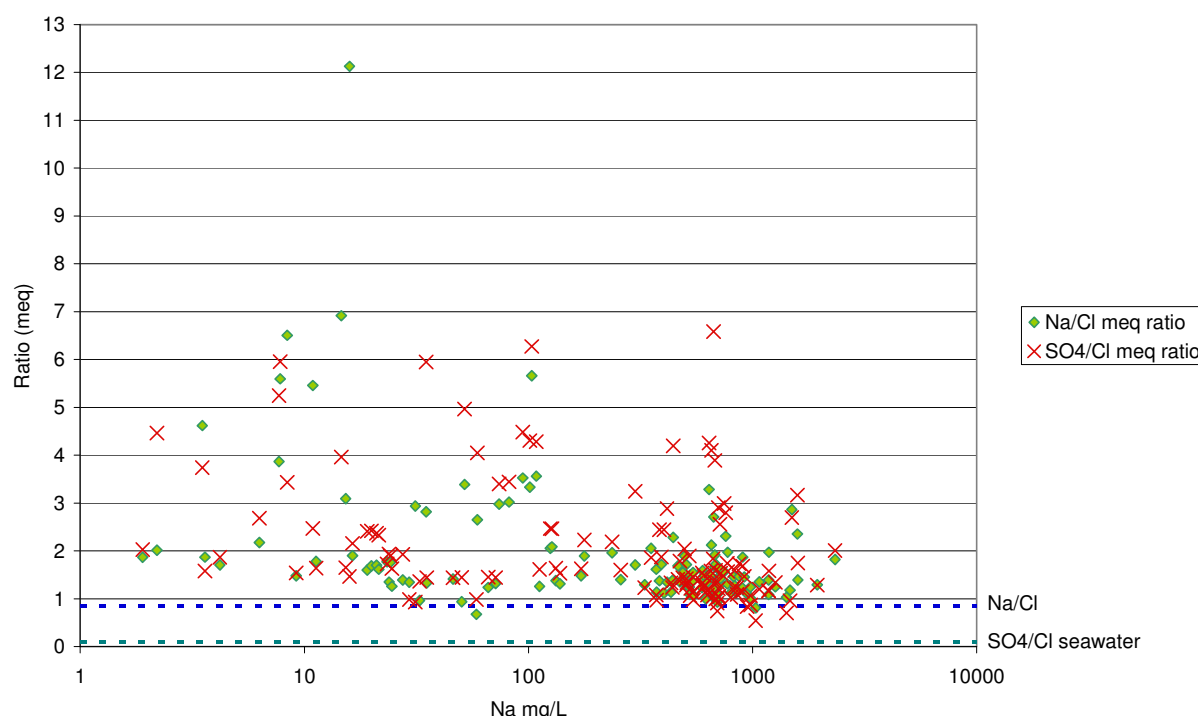


Figure 9.6. Milliequivalent ratios of Na/Cl^- and $\text{SO}_4^{2-}/\text{Cl}^-$ in the 132 Faryab groundwater samples of 2013. Seawater ratios are shown by the dotted lines and are derived from data in Dickson & Goyet (1994).

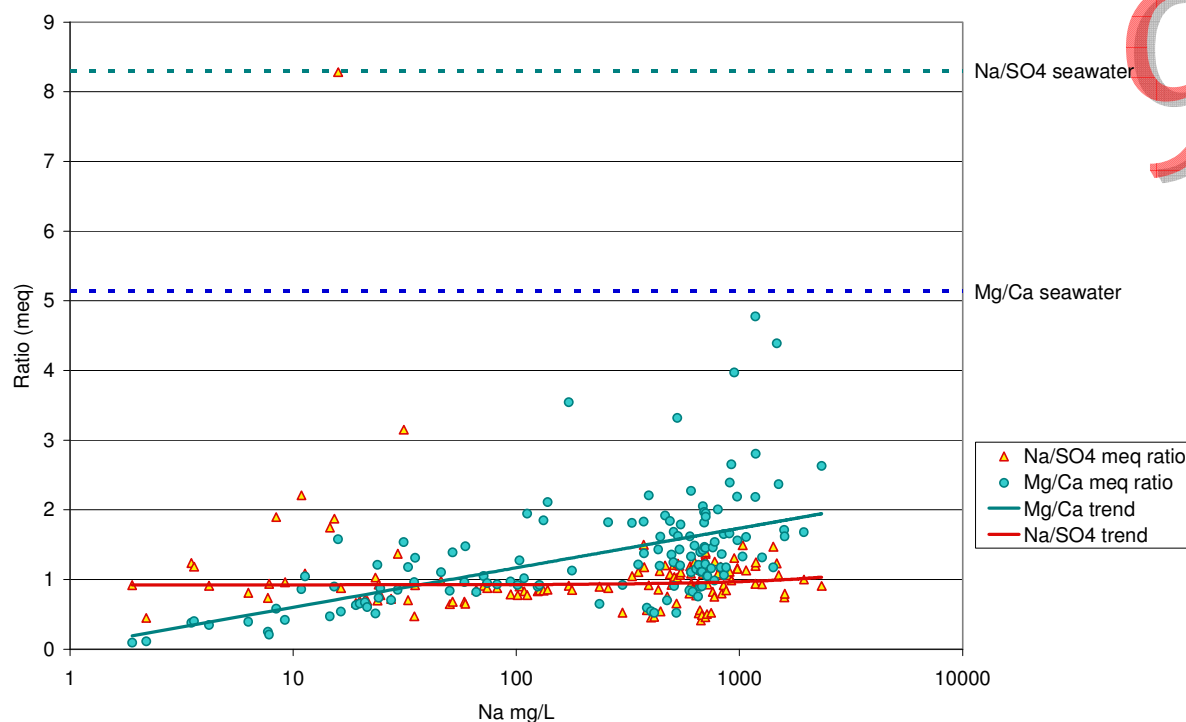


Figure 9.7. Milliequivalent ratios of Mg/Ca and Na/SO₄⁼ in the 132 Faryab groundwater samples of 2013. Seawater ratios are shown by the dotted lines and derived from data in Dickson & Goyet (1994).

Figure 9.6 shows the ratios of sodium to chloride and sodium to sulphate as meq, with increasing sodium concentration. There is a very wide scatter in the data. However, at low salinities, the ratios tend to vary from 1 to 7. As salinity increases to high values, the ratios tend to converge towards values between 1 and 2, as the waters become dominated by Na⁺, Cl⁻ and SO₄⁼ in their major ion composition.

Figure 9.7 shows the ratios of sodium to sulphate and magnesium to calcium as meq, with increasing sodium concentration. The Mg/Ca ratio shows a steady increase with increasing salinity, from around 0.1 at low salinity to over 2 at high salinity. The ratio of 0.1 is characteristic of geologically recent intermediate-high magnesium calcite dissolution (Carpenter & Lohmann 1992, Railsback 2006 - see also Figure 9.11). In the most saline groundwaters of Faryab, the Mg/Ca ratio begins to approach the seawater ratio of c. 5. The sodium : sulphate meq ratio is relatively independent of salinity. It is typically around unity, although the variability decreases with increasing salinity.

9.4 Groundwater evolution

In Figure 9.9, the 132 waters have been sorted according to increasing sodium concentration and the relative proportions of their major cations and anions are shown as %-bar diagrams. In the top diagram, we can see that the proportion of sodium increases consistently throughout the series - in other words, **sodium is accumulated as a solute - there are few controls on its solubility**. In contrast, the proportion of calcium diminishes - **there appears to be a control on calcium accumulation**. Potassium is a minor, but consistent component of all samples. As regards anions, the proportion of bicarbonate diminishes - there appears to be a control on its accumulation. Sulphate and chloride concentrations appear to accumulate at the expense of bicarbonate, with few apparent controls on their solubility. It should be noted, however, that, in the lowest salinity samples, sulphate represents a considerably

greater proportion of the anion content than chloride, while the relative content of chloride is greater in the higher salinity samples.

Figure 9.10 shows how the absolute concentrations of the major ions increase as chloride concentration (a surrogate for salinity) increases. It will be seen that the trends for sodium and sulphate are generally identical, both typically exhibiting higher concentrations than chloride (though admittedly with significant variation: we know there are a number of waters where chloride is the dominant anion). Sodium, chloride and sulphate all exhibit approximately linear best-fit trends - they accumulate in proportion to each other with no apparent limits on solubility.

Calcium, on the other hand, does not accumulate in the same way. Its solubility appears to be limited at somewhere around 25 meq/L in the most saline samples and the trend line flattens out. The same applies to bicarbonate alkalinity: concentrations do not accumulate beyond c. 10 meq/L.

It is tempting to suggest that calcium and bicarbonate concentrations are limited by a calcite (CaCO_3) solubility ceiling. In the low salinity samples, calcium and bicarbonate dominate, as they can be dissolved relatively rapidly from calcite in the limestone and sedimentary rocks in the south of the province.

As regards magnesium (Figure 9.10) this accumulates more efficiently than calcium or bicarbonate, but its solubility also appears to be inhibited in the more saline samples. Magnesium could be being removed by re-precipitation as high-Mg calcite, dolomite ($\text{CaMg}(\text{CO}_3)_2$) or sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$), for example.

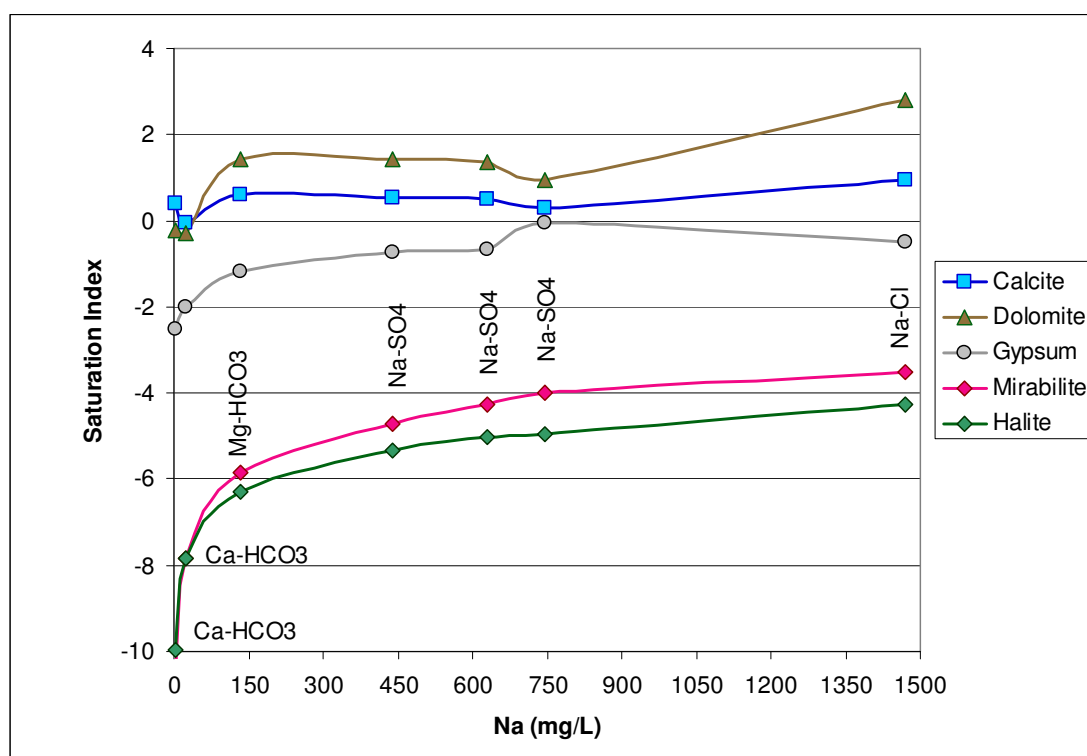


Figure 9.8. Results of PHREEQCI modelling of seven of the 132 Faryab groundwaters sampled in 2013. A saturation index of zero or above indicates that the water is saturated (or oversaturated) with the mineral in question. A negative index indicates that it is undersaturated. Water type is indicated for each sample.

The programme PHREEQC Interactive (PHREEQCI), described by Parkhurst (1995), was used to hydrochemically model seven of the 132 groundwaters, sampled in 2013, spanning the range of salinity variation. The waters selected for modelling had low ion

balance errors and did not have excessive nitrate concentrations (which might be indicative of contamination). The PHREEQC and MINTEQ v. 4 thermodynamic databases were utilised for the lower salinity groundwaters, while the PITZER database (see Plummer et al. 1988) was applied to the higher salinity waters (although the differences between the PITZER/MINTEQ/PHREEQC results were very modest). Figure 9.8 shows the results of the modelling for selected mineral phases.

All samples are saturated with respect to **calcite** (CaCO_3). Calcite is ubiquitous in rocks and sediments and dissolution is rapid. A modest oversaturation appears to develop in the most saline samples. Calcite saturation means that, unless either calcium or carbonate alkalinity are removed from the water, these ions cannot efficiently accumulate further (as is demonstrated in Figure 8.10).

While **dolomite** ($\text{CaMg}(\text{CO}_3)_2$) is very slightly undersaturated in the two lowest salinity samples, it is saturated in all the other samples. At face value this would suggest that further accumulation of magnesium would be problematic. However, we empirically observe that magnesium continues to accumulate in the water (Figure 9.10) and that significant oversaturation with dolomite begins to develop (Figure 9.8). These observations suggest that dolomite is not effective at limiting Mg concentrations, possibly because of kinetic constraints on its precipitation from groundwaters. Some suppression of Mg accumulation is observed in the most saline samples (Figure 9.10), which could also be due to saturation with respect to the more soluble “disordered dolomite” structure or **magnesite** (MgCO_3).

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) only approaches saturation in the most saline samples. This suggests that, if the salinity were to increase beyond the most saline samples, further sulphate accumulation in the system may be hindered by gypsum saturation. There is little sign of this in the samples collected in 2013 in the NORPLAN study, but it may help to explain why the most saline waters mapped by Mishkin (1968 - Figure 8.1) are predominantly sodium chloride, rather than sodium sulphate waters. Gypsum saturation would not completely prevent the further accumulation of gypsum, however, if sulphate exceeds calcium in the groundwater, and if the water is saturated with calcite, continued evaporative concentration, or exposure to sulphate minerals in sediments, might allow further sulphate accumulation at the expense of calcite precipitation to remove calcium.

None of the minerals **halite** (NaCl), **mirabilite** ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), **thenardite** (Na_2SO_4) or **epsomite** ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) reach saturation in the modelled samples. There are thus no solubility controls on sodium and chloride, which can continue to accumulate in the waters unhindered.

In summary, the evolution of the water systems in Faryab is very similar to that observed by Parnachev et al. (1999) and Banks et al. (2004) in the semi-arid steppe environment of southern Siberia. The fundamental features in the Siberian model were:

- Rainfall and recharge solutes in a continental environment are not characterised by marine or industrial salts (as is the case in Britain and Norway) but by dissolution of wind blown salts, potentially including halite, gypsum/anhydrite and mirabilite from saline soils or solonchaks.
- These salts are up-concentrated by evaporation during recharge, and are supplemented by Ca, Mg and HCO_3 from dissolution of calcite from limestone and sedimentary rocks, and by Na, Ca, HCO_3 and other base cations from hydrolysis of feldspars and other silicates.
- In the total hydrological system (recharge - surface water - [agricultural irrigation in the case of Faryab] - groundwater) solutes are steadily concentrated by evaporative processes and dissolution of evaporite minerals such as gypsum and halite from soils. This leads to parallel accumulation of Cl^- , Na^+ , SO_4^{2-}

- Saturation with respect to calcite hinders further accumulation of calcium and alkalinity in waters.
- Dolomite precipitation is not wholly effective at constraining Mg accumulation, due to kinetic factors.

All of these factors are also readily recognisable in Faryab. It should be emphasised that, when we talk of *evapoconcentrative processes* dominating groundwater evolution, this term could encompass:

- Direct evapoconcentration of dissolved salts in recharge water during evapotranspiration of rainfall on vegetation or in shallow soils.
- Dissolution of wind-blown evaporite salts by recharging rainfall or snowfall.
- Direct evaporation of river water and subsequent infiltration to the aquifer system.
- Evapotranspiration of river water or groundwater used for irrigation of fields, followed by re-infiltration to the ground.
- Dissolution of evaporite salts in the unsaturated or saturated zone of the groundwater system. These evaporite salts could be recent and represent salts deposited in shallow soil by evaporating surface water or rainwater (see Table 9.1). They could also represent geologically older palaeo-evaporite salts, such as the gypsum and halite reportedly found in Neogene strata.

This latter may seem not to be an evapoconcentrative process - but the presence of evaporites in, say Neogene sediments, essentially represents geologically stored “evapoconcentration”.

9.5 Soluble salts in soils

Let us therefore look briefly at the contents of soluble salts in soils of Faryab. Soils were sampled in January-March 2013. At each of eight sites, two samples of c. 1.5 kg were taken from 40 cm depth and two of 1.5 kg from 70 cm depth. Samples were returned to the laboratory of DACAAR and air-dried. Samples were then sieved through a 2 mm nylon mesh. Then:

- 20 g of the <2 mm dry soil fraction were added to 400 mL distilled water in a clean 500 mL flask and shaken for 1 hr.
- The flask was stood for 20 hours and the sediment allowed to settle.
- The supernatant liquid was then extracted with a clean polypropylene syringe and injected, via a new 0.45 µm filter, into a new clean 60 mL flask.
- The 60 mL flasks were shipped to the laboratory of the British Geological Survey at Keyworth UK, for analysis by ion chromatography and ICP-MS methods. Samples of the distilled water were also shipped for control analysis.

With the exception of modest concentrations of a very few elements, the distilled water was found to be of good quality. The samples were corrected for any minor element concentrations in the distilled water “blank”. The concentration (Table 9.1) of the soluble element or ion (C_{sol}) in mg/kg of the air-dried, sieved sediment was back-calculated from the corrected concentration in the liquid extract (C_{liq}) by:

$$C_{sol} \text{ (mg/kg)} = C_{liq} \text{ (mg/L)} \times (400 \text{ mL} / 1 \text{ L}) \times (1 \text{ kg} / 20 \text{ g}) = C_{liq} \times 20$$

Sample locations are shown in the map of Figure 9.11. Most of the soils sampled could be described as silty clays, while the underlying geology is indicated in Table 9.1.

There is no clear indication that the content of soluble salts increases in a northerly direction, nor that shallow soils on Neogene sedimentary rocks or loess always have high salt contents. We should remember that these soil samples are shallow and may not represent the soluble salt content of the underlying geological materials, which may have been dissolved / weathered away from the shallow soil profile. Figure 9.11, which plots the meq/L ratio of some soluble ion contents in the soils does show some interesting features, however.

In five of the eight samples, the calcium : sulphate ratio is much greater than unity, suggesting the calcite, or sorbed calcium on ion exchange sites, may be the main readily soluble calcium source in these soils. Figure 9.11 shows that the Mg/Ca molar ratio in the southernmost samples is around 0.1, probably representing the ratio in calcite (CaCO_3) and also reflecting the ratio in groundwaters of the southern area. The Mg/Ca ratio of soils (and groundwaters) increases to the north.

The sodium to chloride ratio is around 1 in the southernmost soil samples but tends to increase to the north. This may reflect the accumulation of other sodium minerals in the soil zone (in addition to halite - NaCl), such as mirabilite (sodium sulphate).

In each case, where the ratio is close to unity, this may be an indication that the mineral phase represented by that ratio may be a dominant salt component in the soil. For example:

- At Qezel Qul, both sodium : chloride and sodium : sulphate are close to unity suggesting that mirabilite and halite may be a dominant component in the soil or in windblown dust / precipitated salts impacting the soil.
- At Qara Sheikhy, Faizabad and Chakozi, the sodium : sulphate ratio is close to unity, suggesting the mirabilite may be a soil component. In these samples, both the calcium : sulphate ratio and the sodium : chloride ratio are greater than unity, suggesting that gypsum and halite are less important.
- At Yam Boleg, Tortqol Baloj and in the Qaramqol semi-desert, the calcium : sulphate ratio is close to unity, suggesting the gypsum may be an important soil component.
- In the Qaramqol sample, while the calcium : sulphate ratio is close to unity, the sodium : chloride ratio is greater than unity and the sodium : sulphate is less than unity. This is consistent with both modest amounts of halite and mirabilite being present, in addition to gypsum as the dominant component (if 1 mmol mirabilite and 1 mmol halite were present in addition to 5 mmol gypsum, the sodium sulphate ratio would be 1/2, the sodium : chloride ratio 3 and the calcium ratio 5/6)

Table 9.1. Soluble element / ion concentrations in soil samples	Depth	Ca	Mg	Na	K	Cl ⁻	SO ₄ ²⁻	Total S	NO ₃ ⁻	F ⁻	Total P	Sr	B	As	U
Sample location	cm	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	µg/kg	µg/kg	µg/kg
Qezel Qul, Pashtun Kot district Neogene sediments	40	436	25	12	27	24	27	<20	<0.4	2.5	<0.2	2.6	170	24	4
	40	418	23	12	32	19	25	<20	<0.4	3.2	<0.2	2.5	190	25	6
	70	468	27	16	23	21	34	<20	<0.4	3.1	<0.2	2.8	210	27	5
	70	402	26	14	17	15	32	<20	<0.4	3.6	<0.2	2.5	150	27	5
Median		427	26	13	25	20	30	<20	<0.4	3.1	<0.2	2.6	180	26	5
Yam Boleg, Maimana district Recent Quaternary alluvium	40	508	27	10	12	3	756	260	27	28	<0.2	34	250	31	31
	40	4812	74	12	17	2	12042	4240	17	28	<0.2	110	190	6.6	52
	70	518	31	14	87	121	670	240	15	14	<0.2	19	270	32	11
	70	4564	90	14	23	0.9	10936	3460	10	25	<0.2	83	230	11	61
Median		2541	52	13	20	3	5846	1860	16	26	<0.2	59	240	21	42
Sarbulaq, Maimana district Pleistocene loess	40	420	63	38	4.6	9	30	<40	21	4.2	<0.2	7.0	350	16	34
	40	390	56	44	4.2	11	40	<40	25	5.4	<0.2	6.6	370	21	43
	70	488	97	142	5.2	130	48	<40	46	8.0	<0.2	10	450	19	83
	70	418	92	90	5.2	45	207	100	45	8.4	<0.2	11	470	22	78
Median		419	77	67	4.9	28	44	100	35	6.7	<0.2	8.8	410	20	61
Qara Sheikhy, Shirin Tagab district DACAAR, who collected sample, believe site to be on Neogene (geol. map suggests site may just be on Quaternary alluvium)	40	508	44	16	100	14	77	<40	11	1.7	<0.2	4.2	210	26	7
	40	476	49	18	109	19	28	<40	8.6	1.7	<0.2	3.5	290	25	6
	70	432	46	12	128	13	41	<40	8.0	1.7	<0.2	3.8	210	15	7
	70	382	42	14	135	13	39	<40	5.6	2.1	<0.2	3.5	190	21	7
Median		454	45	15	118	14	40	<40	8.3	1.7	<0.2	3.7	210	23	7
Tortkol Baloj, Shirin Tagab district DACAAR, who collected sample, believe site to be on Neogene (geol. map suggests site may just be on Quaternary alluvium)	40	1858	96	20	30	8	3999	1460	11	19	<0.2	59	250	8.6	24
	40	1660	108	22	29	4	3747	1340	3.0	16	<0.2	42	230	7.8	18
	70	1342	150	18	25	50	3109	1100	48	3.6	<0.2	31	490	7.0	13
	70	1370	166	34	29	19	3259	1160	36	4.2	<0.2	38	550	9.4	15
Median		1515	129	21	29	13	3503	1250	23	10	<0.2	40	370	8.2	17
Faizabad, Shirin Tagab District Pleistocene loess	40	508	45	10	37	9	17	<20	<0.4	3.1	<0.2	4.5	190	24	12
	40	422	37	16	19	5	20	<20	<0.4	3.1	<0.2	3.4	270	24	10
	70	406	56	20	11	7	47	<20	3.4	3.7	<0.2	5.5	230	27	15
	70	418	82	16	14	5	14	<20	1.2	4.8	<0.2	7.7	170	18	23
Median		420	50	16	16	6	18	<20	<1.2	3.4	<0.2	5.0	210	24	14
Chakozi, Dawlatabad district Recent Quaternary alluvium	40	330	35	10	53	1	20	<20	28	2.1	<0.2	3.8	170	24	17
	40	366	35	14	53	4	32	<20	10	1.9	<0.2	4.2	130	34	14
	70	384	44	16	30	3	40	<20	43	2.6	<0.2	5.4	270	20	26
	70	558	54	14	41	2	24	<20	21	3.0	<0.2	7.0	110	14	36
Median		375	40	14	47	3	28	<20	24	2.3	<0.2	4.8	150	22	22
Semi-desert, Qaramqol district Recent Quaternary alluvium	40	540	110	376	45	278	1422	480	5.8	5.4	<0.2	25	1050	16	5
	40	408	78	212	47	63	878	300	5.8	3.5	<0.2	21	930	19	7
	70	426	76	176	51	37	794	280	5.6	4.6	<0.2	20	870	24	7
	70	402	73	140	52	18	683	240	8.1	4.9	<0.2	20	810	23	8
Median		417	77	194	49	50	836	290	5.8	4.7	<0.2	20	900	21	7

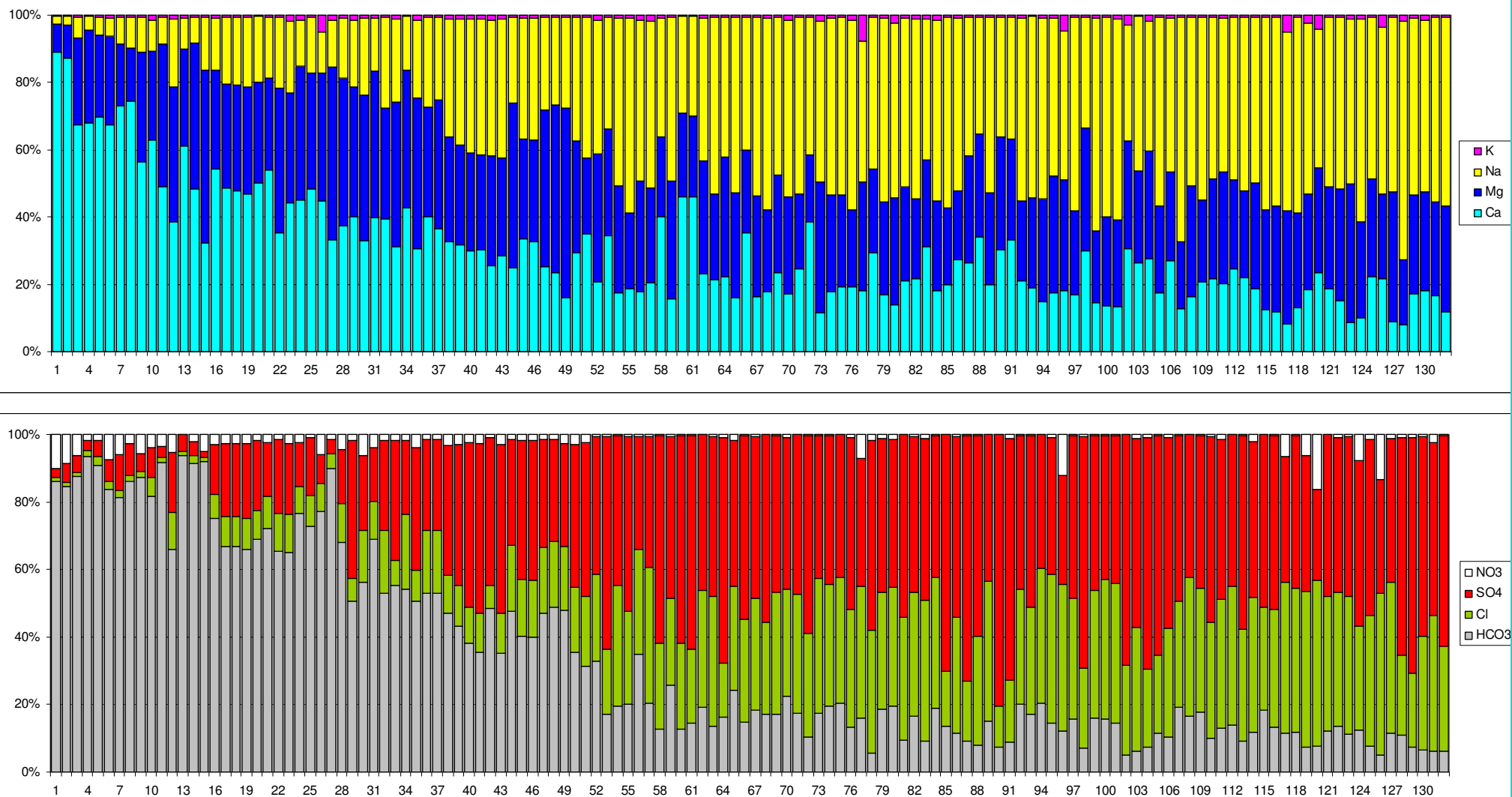


Figure 9.9. Percentage composition (as meq/L) of cation and anion content of the 132 groundwaters from Faryab, sampled in 2013, sorted according to increasing sodium concentration. The number on the x-axis represents the “rank” of the sample according to increasing Na concentration.

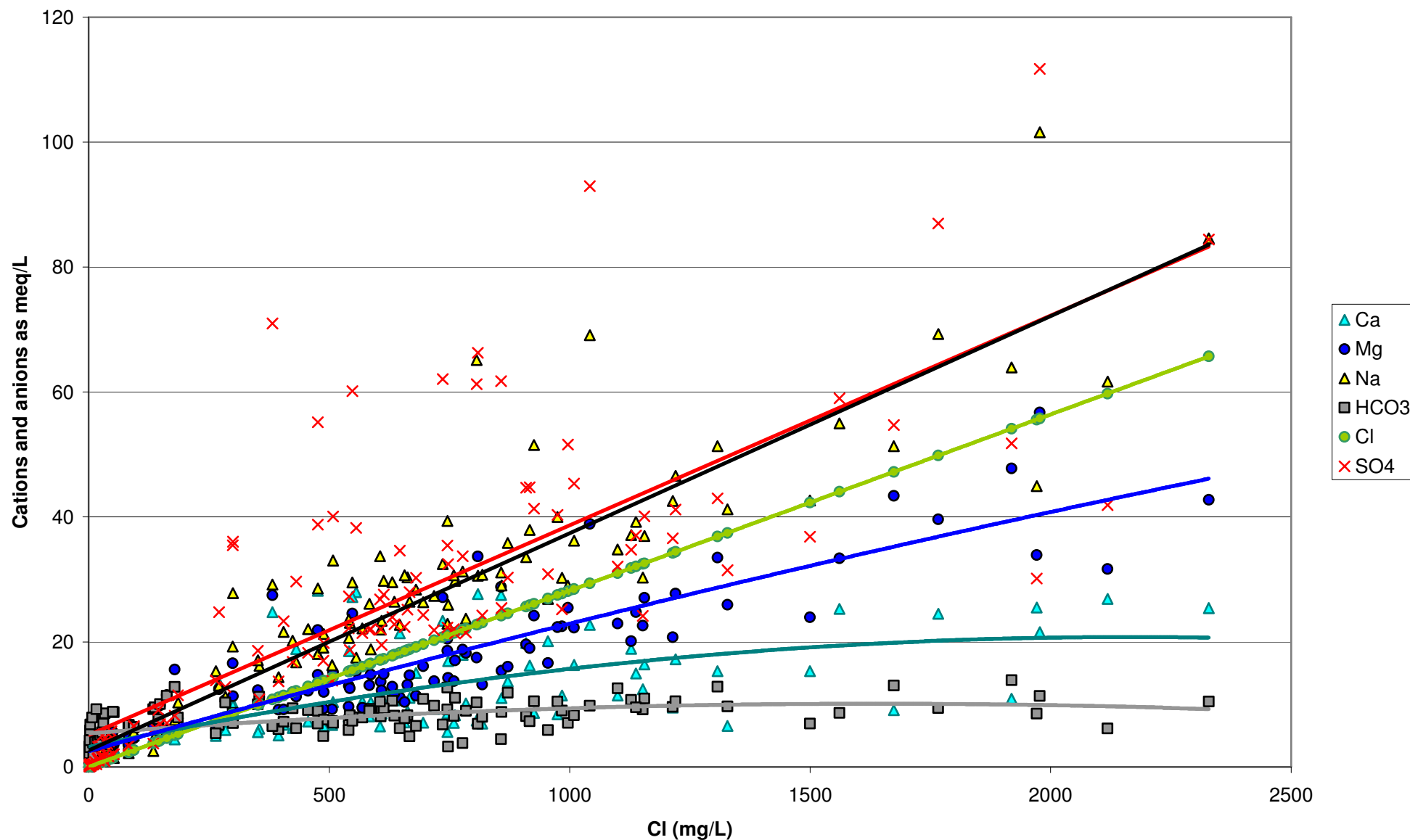


Figure 9.10. Major cation and anion concentrations (as meq/L) in the 132 groundwaters from Faryab sampled in 2013, plotted against chloride concentration (mg/L). Trend lines are either linear or parabolic best fits to widely spread data. Chloride, of course plots as a 1:1 line.

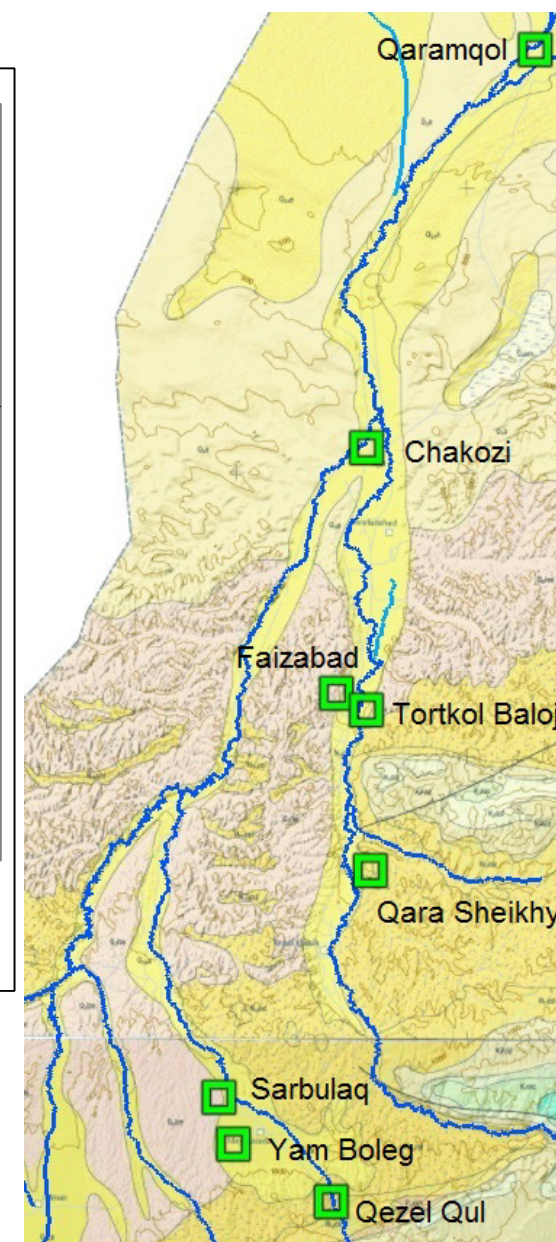
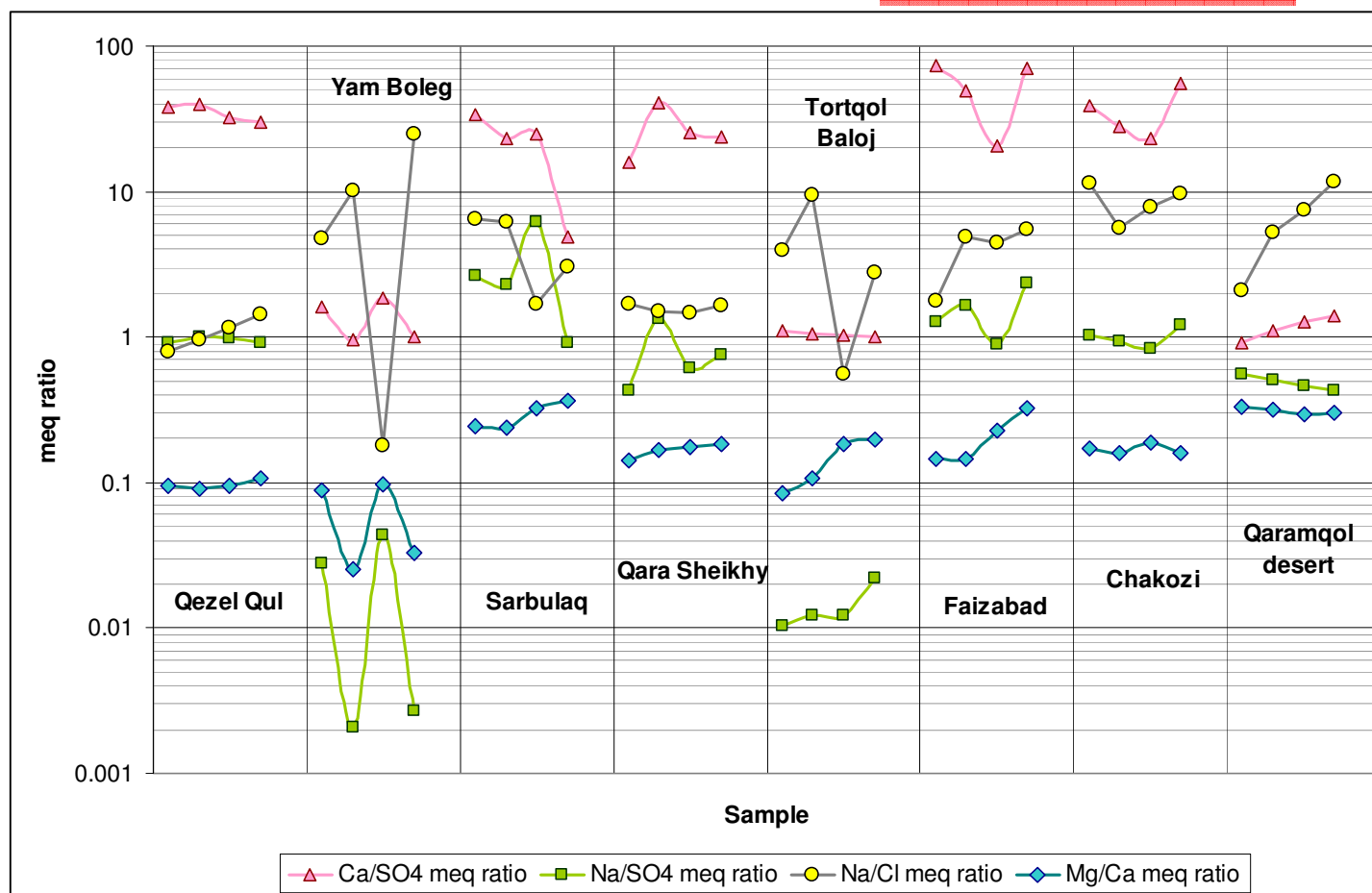


Figure 9.11. meq/L ratios of readily soluble components of soils in Faryab.

Contents represent meq concentrations in distilled water extracts from soil samples - see Table 9.1.

Samples are arranged from south-north from left to right.