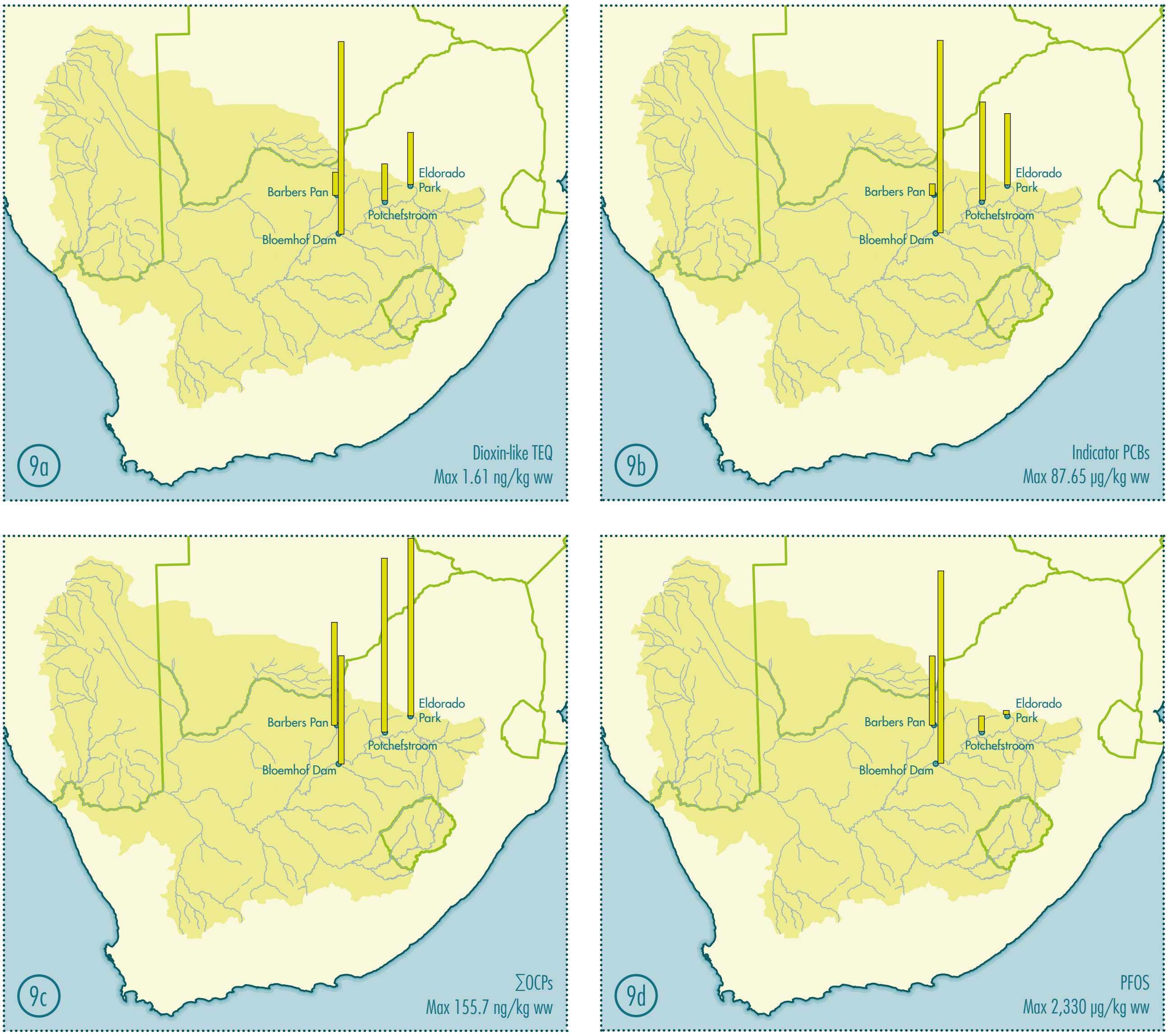

Figure 9: Distribution of pollutants in wild bird eggs from the sampling sites. Bar scale is relative. Max = maximum concentration at any of the sites.

3.2 HEAVY METALS AND TRACE ELEMENTS

Sediment

A summary of the basic statistics for the elements at each of the sites is presented in Table 7 and the mean for each element is indicated in Figure 10. Iron (Fe) and aluminium (Al) had the highest means of all of the 42 elements determined (Table 7).

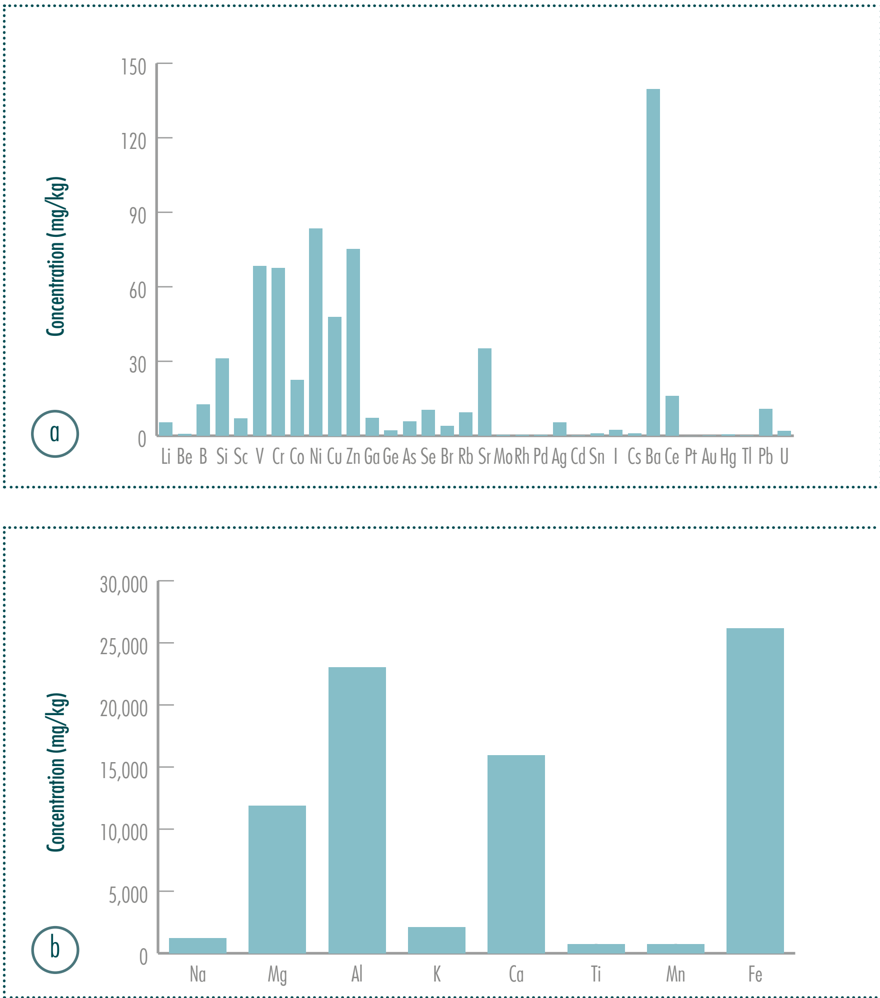

Figure 10: Mean concentrations for (a) the majority of elements in the sediment and (b) for Na, Mg, Al, K, Ca, Ti, Mn and Fe, the concentrations of which were two orders of magnitude higher than the other elements analysed.

The MPI – the geometric mean of all of the elements analysed – was calculated for each of the sediment sites. This revealed that the Molopo Eye (site 56) had the highest MPI (Figure 11).

The geoaccumulation index was also calculated for each of the sites. The formula used to calculate the index is:

$I_{geo} = \log_2(C_{(sample)}/1.5 \times C_{(background)})$,

where: $C_{(sample)}$ = the concentration of the element in the sample

$C_{(background)}$ = the background level of the element

1.5 = a factor that takes account of the variation of the trace metal in the background materials due to lithogenic effects (Ruiz, 2001).

Table 7: The mean concentrations and other summary statistics for the elements detected in the sediment at all sites. Units are mg/kg dw.

	Mean	Standard deviation	Minimum	Maximum	Median
Li	5.7	4.6	1.1	25	3.8
Be	0.9	0.6	0.2	3	0.6
Na	1,203.3	858	250	4,750	925
Mg	12,199.6	10,194.9	1,125	50,000	9,000
Al	22,315.6	15,284.6	3,500	72,500	20,750
K	2,093.3	1,577.3	240	7,000	1,500
Ca	17,357.8	21,941.6	1,650	110,000	11,000
Ga	11.9	37.7	0.8	300	7.3
Ge	2.2	1.3	0.5	6	2.1
Rb	9.4	6.5	1.7	27.5	6.8
Sr	35.1	30	5.5	155	27.5
Cs	0.9	0.7	0.2	3.5	0.6
Ba	277.2	1,073	23.5	8,500	145
Tl	0.3	0.4	0.1	3.3	0.2
Pb	12.1	10.9	3.5	80	10
Sc	6.8	4.6	1.1	21.3	6.3
Ti	713.4	806.1	50	4,250	425
V	69	44.3	15.8	207.5	60
Cr	73.4	60.9	10.5	450	70
Mn	1,725.2	7,603.7	105	60,000	750
Fe	25,975.4	14,959.1	5,000	72,500	25,000
Co	23.7	16.9	3.5	117.5	21.5
Ni	85	52.4	14	250	75
Cu	47.3	28.1	8.8	137.5	42.5
Zn	74.3	55.6	22	300	57.5
Mo	0.5	0.5	0.1	4	0.3
Rh	0.4	0.3	0.1	2.2	0.4
Pd	0.4	0.3	0.1	1.8	0.4
Ag	5.6	4.3	1	23	4.3
Cd	0.1	0.1	0.04	0.9	0.1
Sn	0.9	0.5	0.2	2.8	0.8
Pt	0.04	0.1	0.003	0.2	0.01
Au	0.2	0.3	0	2.3	0.1
Hg	0.5	0.5	0.1	3.5	0.3
B	12.6	9	4.5	67.5	10
Si	31	5.4	14.3	37.5	32.5
As	6.1	3.7	2.5	19.3	5.3
Se	10.3	3.9	0.7	13.8	11.8
Br	3.9	3.2	1.1	16.3	3
I	2.3	4.2	0.1	25	1.1
Ce	18.6	21.1	4.8	170	15
U	1.9	6.3	0.3	50	1.1

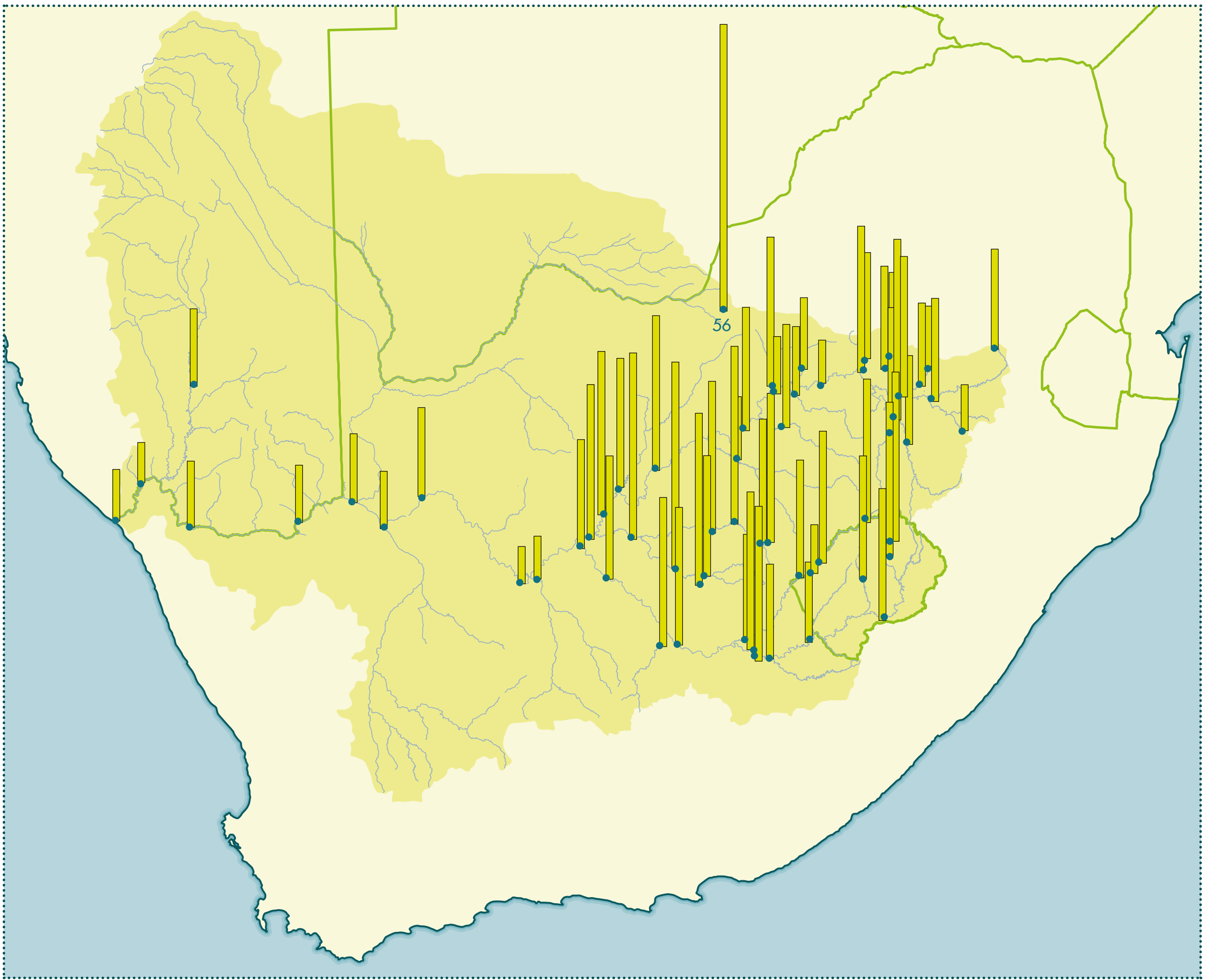

Figure 11: The MPI for the sediment sites. Bar scale is relative.

Only elements for which background levels could be found were used in this calculation, so rhodium (Rh), palladium (Pd), platinum (Pt) and gold (Au) were excluded. The background levels used were general, global values for crustal shale (Wedepohl, 1995). Using the index, pollution status could be interpreted according to the scale below. The results should only be used as an indication of possible pollution, as local geological variation would have a major influence:

$I_{geo} < 1$: unpolluted
$1 < I_{geo} < 2$: very lightly polluted
$2 < I_{geo} < 3$: lightly polluted
$3 < I_{geo} < 4$: moderately polluted
$4 < I_{geo} < 5$: highly polluted
$I_{geo} > 5$: very highly polluted

The I_{geo} classification of the elements at each of the sites is summarised in Tables 8 and 9. As for the MPI, the highest I_{geo} value was calculated for site 56 at the Molopo Eye, the origin of the Molopo River. This finding is difficult to explain because this is a rural area with only agricultural activities in the immediate vicinity. The geology of the site comprises the dolomite rock formations belonging to the Malmani Subgroup of the Transvaal Supergroup. It is possible that underground water from mines in the area found its way to underground caverns close to the site, or simply that the groundwater has naturally high elemental levels.

Table 8: Possible pollution levels of the elements at the sites in the Vaal River catchment as indicated by the geoaccumulation index (I_{geo}).

Table 9: Possible pollution levels of the elements at the sites in the Orange River catchment as indicated by the geoaccumulation index (I_{geo}).

Site		Li	Be	Na	Mg	Al	K	Ca	Ga	Ge	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Mo	Ag	Cd	Sn	Hg	Se	Br	I	Sr	Cs	Ba	Tl	Pb	Ce	U
2	Orange River																																
3	Hartbees River																																
4	Orange River																																
5	Orange River																																
6	Orange River																																
7	Orange River																																
8	Orange River																																
9	Orange River																																
10	Brak River																																
11	Orange River																																
13	Orange River																																
46	Seekoei River																																
47	Orange River																																
48	Caledon River																																
49	Orange River																																
50	Stormberg Spruit																																
51	Orange River																																
52	Orange River																																
53	Leeu River																																
54	Caledon River																																
55	Caledon River																																
56	Molopo Eye																																
57	Malibamatso River																																
58	Matsuko River																																
59	Senquenyane River																																
60	Kelekeque River																																
61	Senqu River																																
62	Fish River																																

- unpolluted
- very lightly polluted
- lightly polluted
- moderately polluted
- highly polluted
- very highly polluted

The I_{geo} results may be misleading, however, given that they were calculated using global background levels. It is possible that the global selenium (Se) and silver (Ag) levels are lower than in southern Africa, because it is unlikely that both Se and Ag would be at such high pollution levels throughout the basin, even in remote areas (Tables 8 and 9). The possible pollution due to mercury (Hg) has a more expected pattern. A better understanding of these results would be possible if the minerals associated with the geology of the sites could be considered.

A third approach was followed to identify sediment sites of concern. For each element, the 25% of sites with the highest concentrations were identified. The sites were ranked according to the percentage elements they had in the upper 25% (Table 10). Elements that form part of the salts usually measured in water quality determinations (I, Br, Li, Ca, K, Na and Mg) were not considered because their influence on the state of the basin would be measured in that way. Silicon (Si) was also removed as it is integral to all minerals and would not be indicative of anthropogenic activities. The geology of the sites was included in the ranking table to facilitate interpretation of its contribution to the measured elemental levels.

Site 43 in the Riet River in the Free State Province had the highest ranking (Table 10).

Other sites having elements with the highest levels were sites 12, 14, 39, 41 and 44, all of which are in the Modder and Riet River systems (Figure 12). This area is known for its kimberlite diamond mining. Sites 39, 43 and 44 have a similar geology, which might explain why these sites in relative close proximity to each other all had high levels of elements. Site 34 has the same geology, but is geographically distant (Figure 12). Sites 12, 14, 39, 41, 43 and 44 are in the vicinity of battlegrounds of the Second Anglo–Boer War (1899–1902), as are sites 49 and 50. In light of the lack of obvious reasons for the high levels of elements at all of these sites, it may be worthwhile to investigate the possible pollution legacy of the conflict. Two sites (57 and 58) in Lesotho (Figure 13) were also in the upper 25% ranking (Table 10), but no mining, agriculture or other obvious activity to which this could be attributed occur there. It is therefore assumed that the elements have naturally high levels, especially since they share the same geology (Table 10).

The only site prominent in all three assessment methods is site 56, which is the Molopo Eye. It is also the site with the most elements with an I_{geo} > 1 (Table 9).

Table 10: The top 25% of sites with the 25% highest concentration of the elements analysed.

Site rank	Site number and name	Geology	Similar geologies = same colour*
1	43 Riet River	Karoo Supergroup, Ecca Group, Volksrust Formation: argillaceous rocks – clay minerals, quartz; thin phosphate and carbonate layers – siderite.	light blue
2	33 Wilge River (up-stream of Frankfort)	Karoo Supergroup, Beaufort Group, Adelaide Subgroup, Normandien Formation: mudstone, lithofeldspathic sandstone – quartz, feldspar, clay minerals.	yellow
3	14 Riet River	Karoo Supergroup, Ecca Group, Pietermaritzburg Formation: mudstone, lenses of sandstone, carbonate cement: quartz, feldspar, clay minerals, carbonate; and Ventersdorp Supergroup: volcano-sedimentary rocks – plagioclase feldspar, ferromagnesian minerals, quartz, clay minerals.	
4	56 Molopo Eye	Transvaal Supergroup, Malmani Subgroup: dolomite – carbonate and chert.	
5	44 Kromellenboog Spruit	Karoo Supergroup, Ecca Group, Volksrust Formation: argillaceous rocks – clay minerals, quartz; thin phosphate and carbonate layers – siderite.	light blue
6	50 Stormberg River	Karoo Supergroup, Beaufort Group, Tarkastad Subgroup: sandstone and mudstone – quartz, clay minerals.	dark grey-green
7	58 Matsuko River	Karoo Igneous Province, Drakensberg Group: basalt – ferromagnesian minerals and plagioclase feldspar.	green
8	57 Malibamatso River	Karoo Igneous Province, Drakensberg Group: basalt – ferromagnesian minerals and plagioclase feldspar.	green
9	39 Modder River	Karoo Supergroup, Ecca Group, Volksrust Formation: argillaceous rocks – clay minerals, quartz; thin phosphate and carbonate layers – siderite.	light blue
10	34 Vaal River (in Villiers)	Karoo Supergroup, Ecca Group, Volksrust Formation: argillaceous rocks – clay minerals, quartz; thin phosphate and carbonate layers – siderite.	light blue
11	55 Caledon River	Karoo Supergroup, Beaufort Group, Tarkastad Subgroup: sandstone and mudstone – quartz, clay minerals.	dark grey-green
12	49 Orange River (up-stream of Gariep Dam)	Karoo Supergroup, Beaufort Group, Tarkastad Subgroup: sandstone and mudstone – quartz, clay minerals.	dark grey-green
13	60 Kelekequ River (close to Maseru)	Karoo Supergroup, Elliot Formation: sandstone and mudstone – quartz, clay minerals.	
14	12 Vaal River (up-stream of Douglas)	Ventersdorp Supergroup: volcano-sedimentary rocks – plagioclase feldspar, ferromagnesian minerals, quartz, clay minerals; and Karoo Supergroup, Dwyka Group: glacial deposits consisting of various facies reflecting the composition of the source; general description could be a carbonaceous mudstone with clasts of various sizes.	
15	41 Koranna Spruit	Karoo Supergroup, Beaufort Group, Adelaide Subgroup, Normandien Formation: mudstone, lithofeldspathic sandstone – quartz, feldspar, clay minerals.	yellow
16	22 Skoon Spruit	Ventersdorp Supergroup, Platberg Group, Rietgat Formation: volcano-sedimentary rocks – plagioclase feldspar, ferromagnesian minerals, quartz, clay minerals.	

*Empty squares do not share any geology; they are all different.

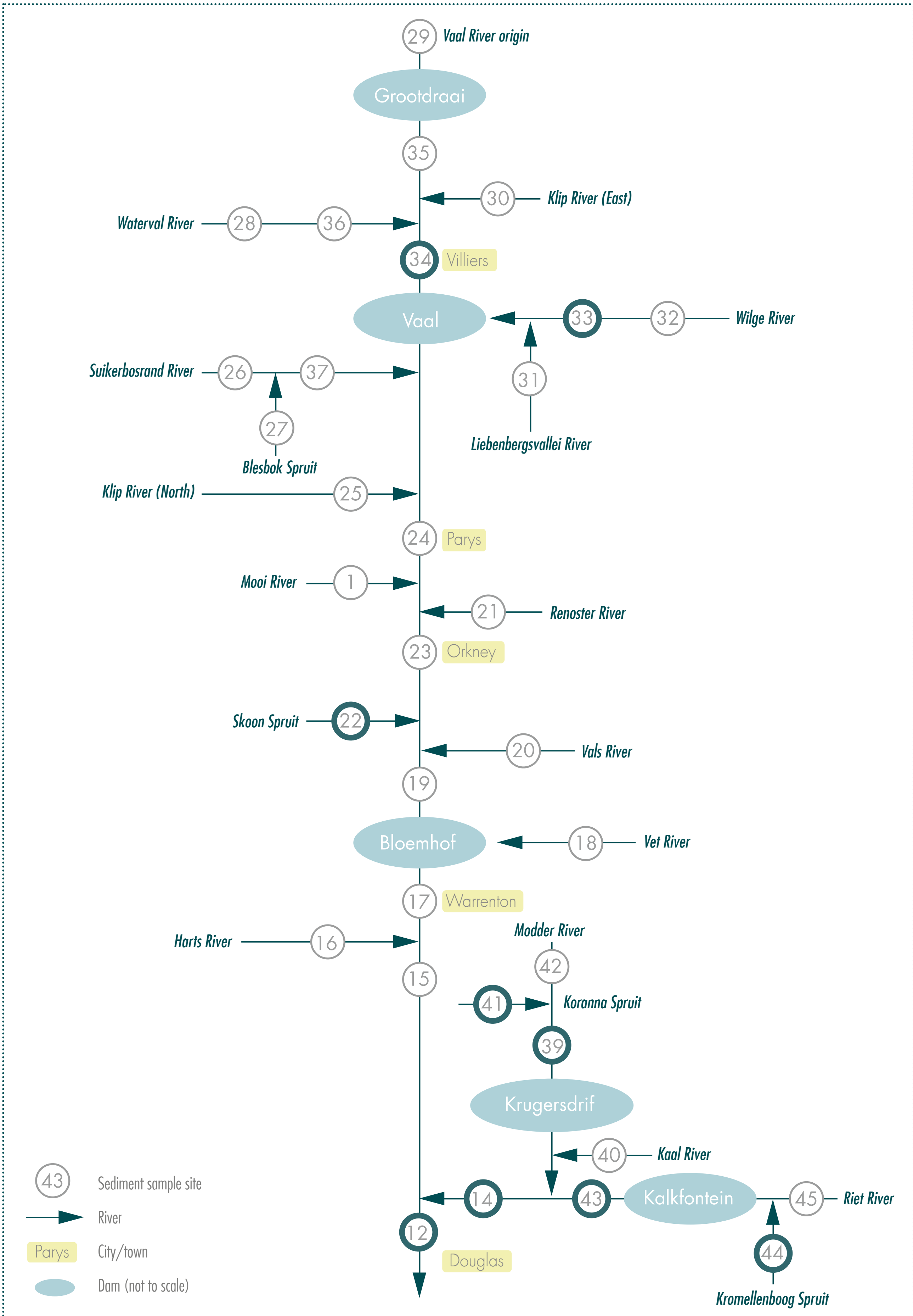

Figure 12: A diagrammatic representation of the sites in the Vaal River catchment. The sites highlighted with dark circles are those containing the 25% highest concentration of measured elements (also see Table 10).

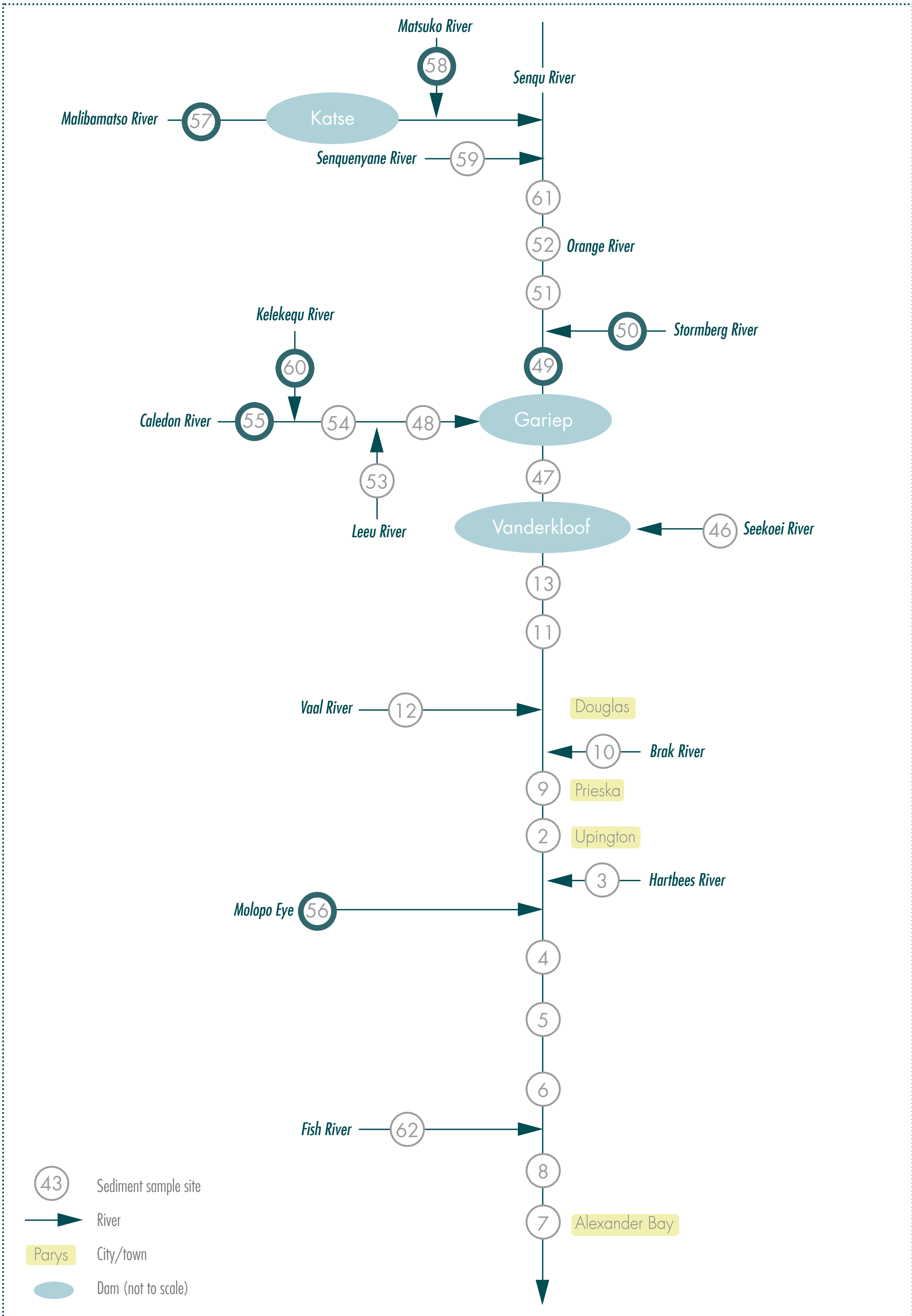

Figure 13: A diagrammatic representation of the sites in the Orange River catchment. The sites highlighted with dark circles are those containing the 25% highest concentration of measured elements (also see Table 10).


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A further analysis of the survey data involved mapping the relative distribution patterns of various elements, including at least one representative of the major groups on the Periodic Table (refer to page 7), or category of elements such as the transitional metals. The elements chosen to represent their group or category were selected on the basis that they correlated well with others in the group or category. A map of the geology of South Africa and Lesotho is also presented (Figure 14).

The Group IA elements, comprised primarily of alkali metals, were represented by caesium (Cs). This element occurred at higher levels in the Free State and Mpumalanga sites, with the highest level of 3.5 mg/kg found at site 43 (Figure 15a) in the Riet River.

The highest level for beryllium (Be), the representative of the Group IIA elements, the alkaline earth metals, was found at site 56, Molopo Eye, at a concentration of 3 mg/kg (Figure 15b). As for Cs, the relatively higher levels of Be were in the Free State and Mpumalanga.

Thallium (Tl) represented the Group IIIA elements and was highest at the Molopo Eye, at 3.25 mg/kg (Figure 15c). The second highest level was at site 1, at the Mooi River.

Of the elements in Group IVA that were analysed, the levels of two – lead (Pb) and tin (Sn) – are depicted, as their concentrations and distribution patterns are very different. The highest Pb level was 80 mg/kg at the Molopo Eye (Figure 15d), while the highest Sn level was only 2.75 mg/kg at site 57, the Malibamatso River in Lesotho (Figure 15e).

The only element in Group VA that was analysed was arsenic (As). The highest level measured, 19.25 mg/kg, was at the Molopo Eye, followed by site 43 in the Riet River and site 41 in Koranna Spruit. The fourth highest level was measured at site 62 in the Fish River in Namibia (Figure 15f).

Selenium (Se) was the only element analysed from the Group VIA elements. The highest level was 13.75 mg/kg at site 14 in the Riet River, but this element was distributed at approximately the same levels throughout the basin, apart from the sites in the lower Orange River (Figure 15g).

Of the Group VIIA elements, the halogens, only bromine (Br) and iodine (I) were analysed. The highest Br level was 16.25 mg/kg at site 39, the Modder River in the Free State, followed by site 15 in the Vaal River (Figure 15h). The same site in the Modder River had the second highest level of I at 21 mg/kg, the highest level being found at site 14, in the Riet River downstream of its confluence with the Modder River (Figure 15i).

Zinc (Zn) was selected as the representative of all of the transitional metals analysed because it correlated significantly with all of them. The highest level at 300 mg/kg was found at site 27 in the Blesbok Spruit (Figure 15j). This river receives effluent from mines on the East Rand and has previously been recognised for its heavy metal pollution (Roychoudhury and Starke, 2006). The second highest Zn level was found at site 25 in the Klip River (West), followed by site 57 in the Malibamatso River in Lesotho and site 37 in the Suikerbosrand River, which receives water from the Blesbok Spruit. Cerium (Ce) was the only lanthanide analysed and the highest level was found at the Molopo Eye, at 170 mg/kg (Figure 15k).

Uranium (U) was the only actinide analysed and was either undetectable or found in low concentrations except for site 15 in the lower catchment of the Vaal River, where the level was 50 mg/kg (Figure 15l). This site is at a small town called Schmidtsdrift where alluvial diamond mining takes place (CMR, 2008), and the river here also receives drainage from lime-mining activities to the north. Furthermore, in 1974 the South African Defence Force (SADF) acquired the Schmidtsdrift farms and established a military training base, which was occupied by the SADF for the next 20 years (Kleinbooi, 2007). The high levels of U at this site might therefore be associated with military activities.

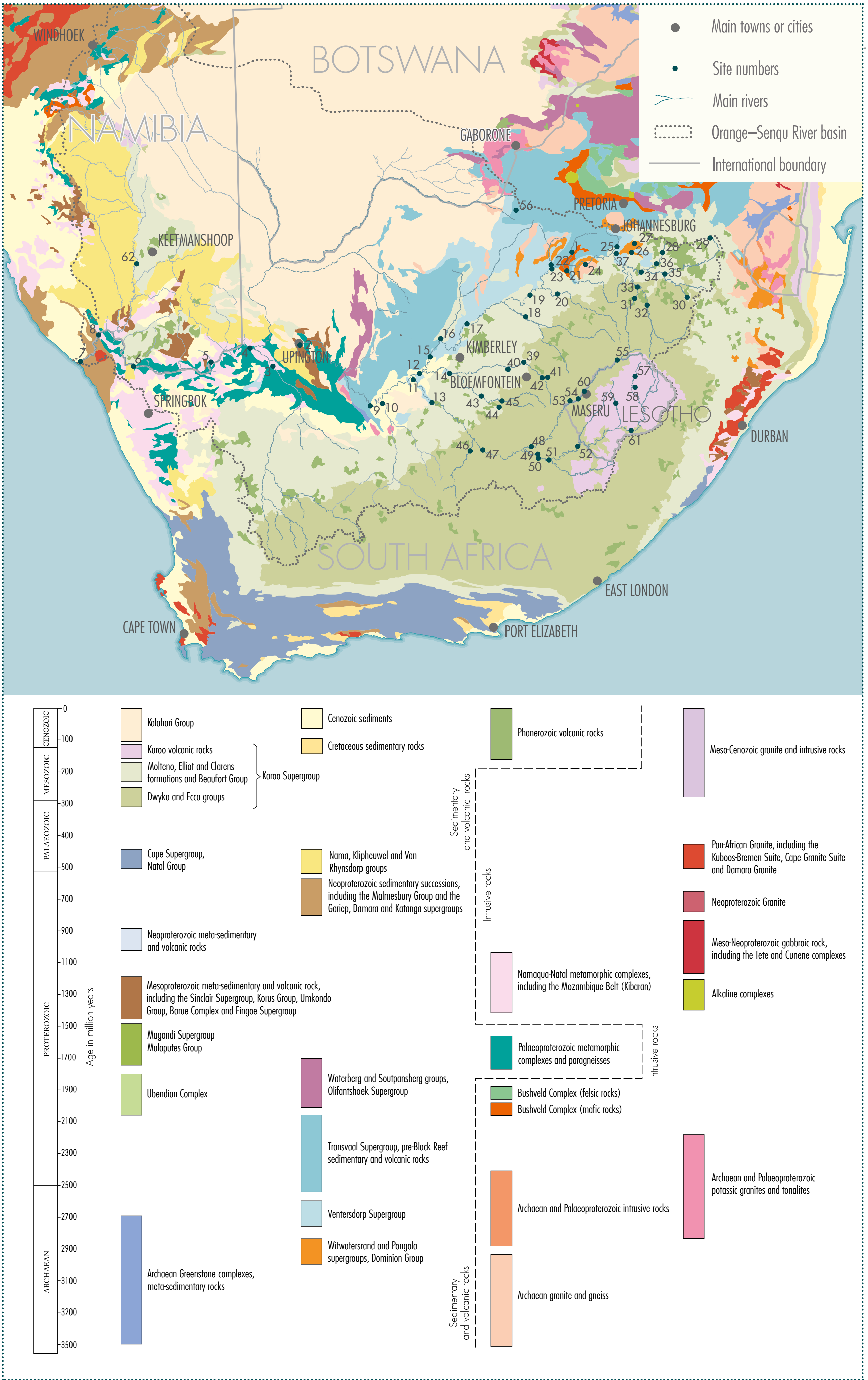

Figure 14: A geological map of southern Africa.

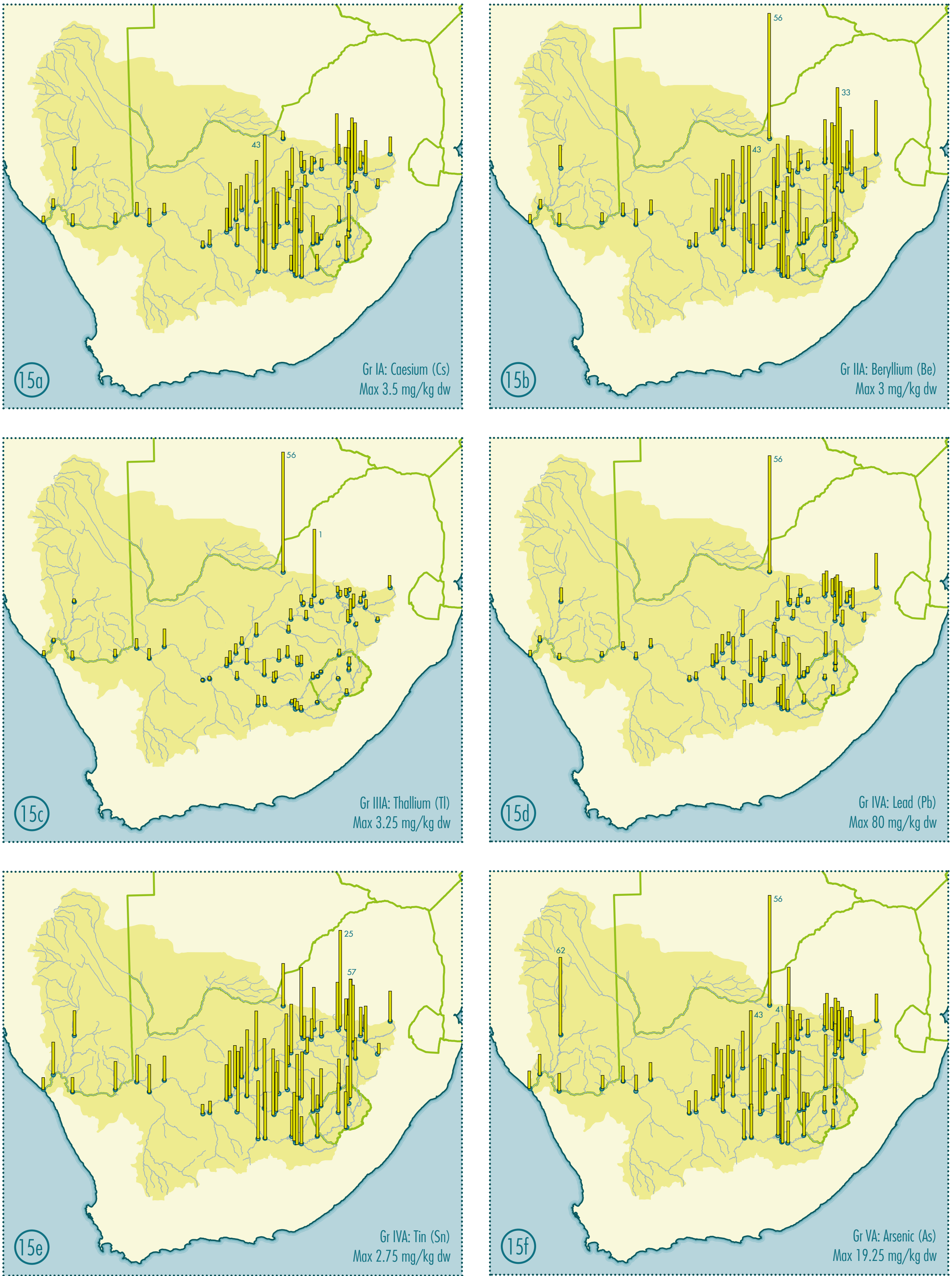

Figure 15: Element levels measured in sediment samples. Elements mapped as representatives of the various groups (Gr) in the Periodic Table (Figure 1, page 7). Bar scale is relative for each element, but not between elements. Numbers on the maps refer to the sites where the highest levels were measured. Max = maximum concentration at any of the sites.