INTERIM REPORT ON POPS AND ELEMENTAL LEVELS IN SEDIMENT, FISH AND WILD BIRD EGGS

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8 July 2011

1 Introduction

The four southern African countries, Lesotho, South Africa, Botswana and Namibia which each has a contribution to the catchment of the Orange-Senqu River System, have all consented to the Stockholm Convention on Persistent Organic Pollutants (SC). The SC originally focused on 12 chemicals or chemical classes, the so called dirty dozen. Initially included in this list were polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzo furans (PCDFs), aldrin, dieldrin, 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane (DDT) and its major metabolites 1,1-dichloro-2,2-bis (p-chlorophenyl)ethane (DDD) and 1,1-dichloro-2,2 (p-chlorophenyl) ethylene (DDE), endrin, chlordane, hexachlorobenzene (HCB), mirex, toxaphene and heptachlor. Nine new POPs were added to the SC in May 2009. They are chlordecone, hexabromobiphenyl, hexabromodiphenyl ether (hexaBDE), tetrabromodiphenyl ether (tetraBDE), pentabromodiphenyl ether (pentaBDE) heptabromodiphenyl ether (heptaBDE), HCH (including α-HCH, β-HCH and γ-HCH), pentachlorobenzene, perfluorooctane sulfonic acid (PFOA) and perfluorooctane sulfanyl fluoride (Stockholm Convention on POPs, 2010).

From a previous brief overview of scientific publications (refer to survey design report of this study) POPs researched on in SA were mainly on the OCs with special emphasis on DDT and its metabolites because it is still used in the country. Although the malaria areas in SA do not lie in the Orange-Senqu River catchment, bird eggs from the Vaal River do have levels of DDT and its metabolites (Bouwman et al. 2008). Industrial pollutants investigated include PCBs mostly in marine organisms (in the previous millennium) and more recently in environmental matrices such as sediment, soil and air. PCBs, PBDEs and some OCs were also on the list of compounds detected in bird eggs, from the Vaal River. Industrial and urban areas were targeted as suspected hot-spots and sources of industrial POPs and this is the main reason for focussing on the stretch of the Vaal River going through the Vaal Triangle. Other urban areas such as Durban, Cape Town, Bloemfontein, Richard's Bay and Soweto are included in a current Water Research Commission project the authors are involved in and preliminary unpublished data show that some sites in Soweto, Durban, Cape Town and Bloemfontein have high levels of POPs, but still at the lower end when compared to highly industrial countries.

One of the main ores mined in SA, is gold and the very deep gold mines within the Witwatersrand basin are contaminating ground water that drains into the Vaal River (Duane et al., 1997). Water collected from four of the mines had Pb, Cu, Zn, Cr, Fe, Cd, U, As, Mn and other trace elements. It is not only the water from the active mines that pollute groundwater but the mine tailings dumps also.

A study on the Natal Spruit (Naicker et al., 2003) (which is in the catchment of the Vaal River) showed that shallow ground water is contaminated as a result of mining activities. Mining activities impacts on the quality of the water from the Witwatersrand watershed. The type of pollution is not only affecting the pH of the water but contributes heavy metals to surface water. Evaporation of ground water off the capillary zone above the water table creates a surface soil layer along the banks of the Natal Spruit which is extremely enriched in heavy metals. During the dry winter months a gypsum crust develops on this surface. This also adds to the metal load in the stream when surfaces soil and the crust dissolves.

Apart from heavy metal measurements in sediment, heavy metals and the bio-accumulation thereof in biota had also been investigated. Studies carried out on the Vaal River have shown that fishes in the Vaal River system accumulate heavy metals discharged into the system by industries (Crafford, 2000; Groenewald, 2000; Kotze, 2003; Retief, 2006). It has been proven that some of the internal parasites (tapeworm) of yellow fish from the Vaal Dam bio-concentrate many of the heavy metals (Retief, 2006).

2 Materials and methods

2.1 Site selection

2.1.1 Sediment site selection

The entire Orange-Senqu River catchment was targeted for sediment collection and a total of 61 sites were sampled in September 2010. Of the 61 sites, 33 belonged to the Vaal River catchment. The remaining 28 sites were from that region of the Orange River catchment that does not drain into the Vaal River (Table 1). Only one site from Namibia was collected and five from Lesotho.

Table 1: Sediment sites in the Orange/Senqu Catchment. It is also indicated whether the tributary drains into the Vaal River first or directly into the Orange River (last column). If a site is inside the borders of a town, the town's name is indicated in parenthesis.

Site number	River	Coordinates		Country	Vaal or Orange/Senqu River
		longitude	latitude		
1	Mooi River (Potchefstroom)	27.10	-26.68	SA	Vaal
2	Orange River (Upington)	21.24	-28.47	SA	Orange/Senqu
3	Hartbees River	20.64	-28.86	SA	Orange/Senqu
4	Orange River	20.15	-28.50	SA	Orange/Senqu
5	Orange River (Onseepkans)	19.30	-28.74	SA	Orange/Senqu
6	Orange River (Vioolsdrif)	17.61	-28.75	SA	Orange/Senqu
7	Orange River (mouth)	16.47	-28.60	SA	Orange/Senqu
8	Orange River (Sendelingsdrif)	16.89	-28.12	SA	Orange/Senqu
9	Orange River (Prieska)	22.75	-29.66	SA	Orange/Senqu
10	Brak River	23.02	-29.62	SA	Orange/Senqu
11	Orange River (Douglas)	23.70	-29.16	SA	Orange/Senqu
12	Vaal River (Douglas)	23.84	-29.04	SA	Vaal
13	Orange River (Hopetown)	24.11	-29.60	Sa	Orange/Senqu
14	Riet River	24.50	-29.04	SA	Vaal
15	Vaal River	24.07	-28.72	SA	Vaal
16	Harts River	24.30	-28.38	SA	Vaal
17	Vaal River (Warrenton)	24.87	-28.09	SA	Vaal
18	Vet River	26.13	-27.94	SA	Vaal
19	Vaal River	26.22	-27.52	SA	Vaal
20	Vals River	26.81	-27.49	SA	Vaal
21	Renoster River	27.00	-27.04	SA	Vaal
22	Skoon Spruit (Klerksdorp)	26.66	-26.93	SA	Vaal
23	Vaal River (Orkney)	26.68	-27.01	SA	Vaal
24	Vaal River (Parys)	27.40	-26.91	SA	Vaal
25	Klip River (West)	28.06	-26.55	SA	Vaal
26	Suikerbosrand River	28.38	-26.65	SA	Vaal
27	Blesbok Spruit	28.43	-26.48	SA	Vaal
28	Waterval River	29.03	-26.63	SA	Vaal
29	Vaal origins	30.03	-26.31	SA	Vaal
30	Klip River (East)	29.60	-27.47	SA	Vaal

31	Liebenbergsvallei River	28.48	-27.53	SA	Vaal
32	Wilge River	28.75	-27.65	SA	Vaal
33	Wilge River	28.53	-27.31	SA	Vaal
34	Vaal River (Villiers)	28.60	-27.02	SA	Vaal
35	Vaal River	29.10	-27.04	SA	Vaal
36	Waterval River	28.91	-26.85	SA	Vaal
37	Suikerbosrand River	28.05	-26.68	SA	Vaal
39	Modder River	26.11	-28.81	SA	Vaal
40	Kaal River	25.77	-28.95	SA	Vaal
41	Koranna Spruit	26.64	-29.09	SA	Vaal
42	Modder River	26.52	-29.10	SA	Vaal
43	Riet River	25.20	-29.47	SA	Vaal
44	Kromellenboog Spr uit	25.59	-29.68	SA	Vaal
45	Riet River	25.65	-29.56	SA	Vaal
46	Seekoei River	24.96	-30.53	SA	Orange/Senqu
47	Orange River	25.24	-30.51	SA	Orange/Senqu
48	Caledon River	26.31	-30.43	SA	Orange/Senqu
49	Orange River	26.46	-30.57	SA	Orange/Senqu
50	Stormberg Spruit	26.47	-30.65	SA	Orange/Senqu
51	Orange River	26.71	-30.68	SA	Orange/Senqu
52	Orange River	27.34	-30.40	SA	Orange/Senqu
53	Leeu River	27.14	-29.53	SA	Orange/Senqu
54	Caledon River	27.32	-29.49	SA	Orange/Senqu
55	Caledon River	28.15	-28.72	SA	Orange/Senqu
56	Molopo River (eye)	25.89	-25.89	SA	Orange/Senqu
57	Malebamatso River	28.55	-29.02	Lesotho	Orange/Senqu
58	Matsuko River	28.56	-29.23	Lesotho	Orange/Senqu
59	Senquenyane River	28.15	-29.55	Lesotho	Orange/Senqu
60	Kelekeque River	27.45	-29.34	Lesotho	Orange/Senqu
61	Senque River	28.51	-30.06	Lesotho	Orange/Senqu
62	Fish River	17.79	-26.80	Namibia	Orange/Senqu

The relationship between tributaries are indicated in the schematic representation (Figures 1 and 2, not according to scale). Note the complex association between the Riet Spruit and Modder Rivers sites in the Free State before draining into the Orange River upstream of its confluence with the Vaal River (Figure 2).

The sites are indicated on a map of the four countries in which the Orange/Senqu Basin is positioned (Figure 3).

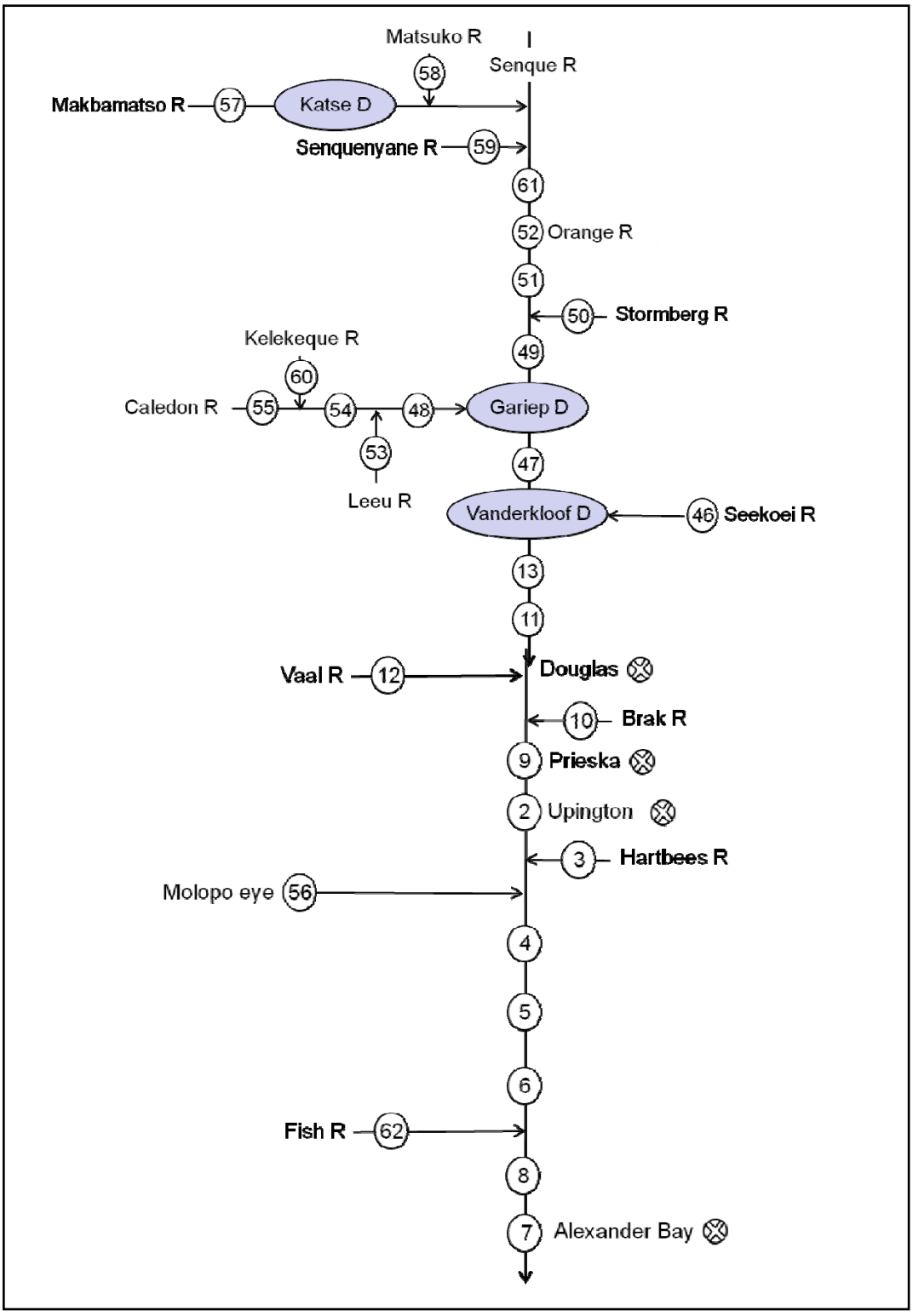

Figure 1: A diagrammatic representation of the Orange/Senqu Rivers Catchment without the Vaal River system (cf Fig 2) = city/town, R = River, D = Dam

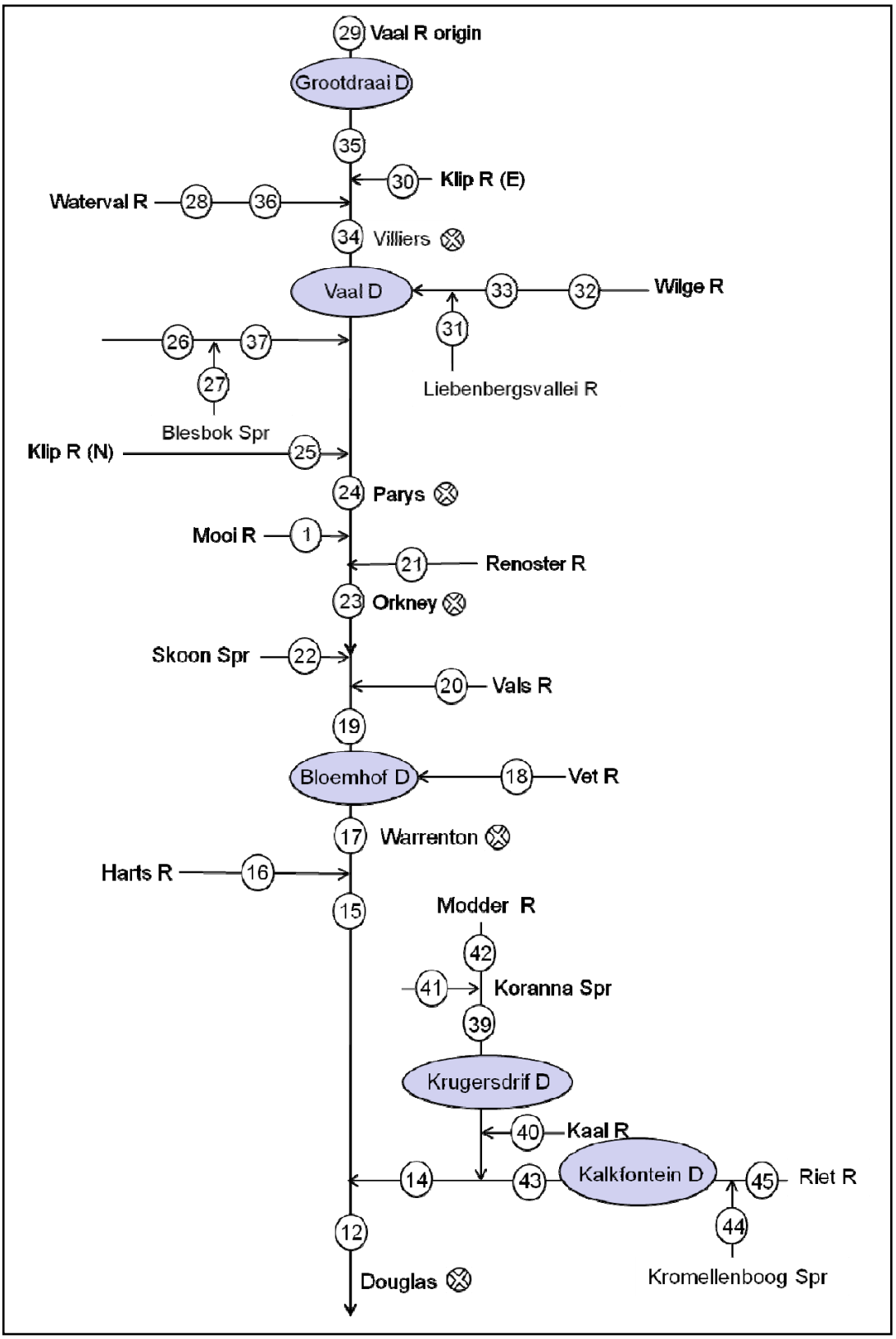

Figure 2: A diagrammatic representation of the Vaal River system only. = city/town R = River, D = Dam, Spr = Spruit

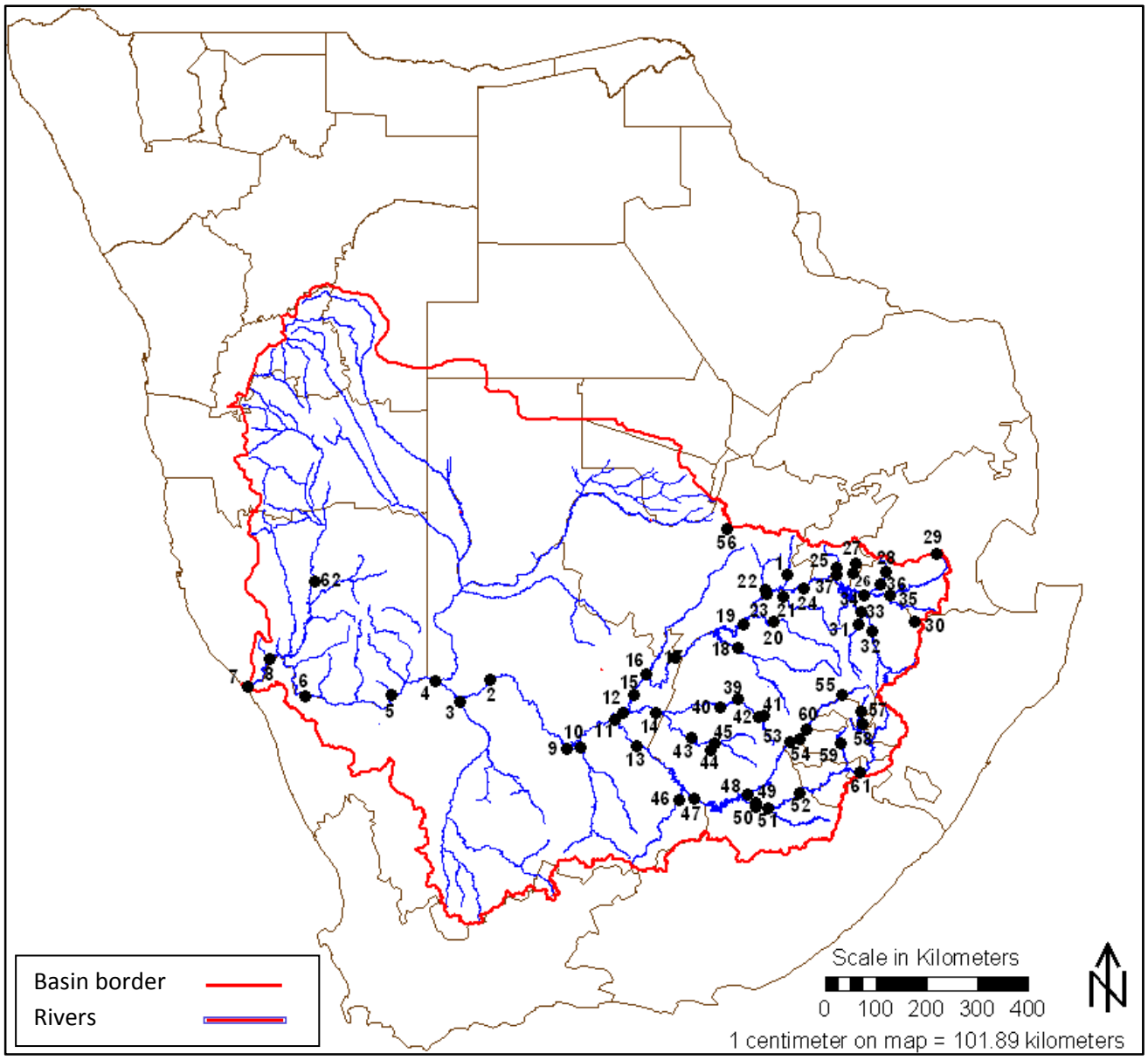

Figure 3: A map of the four countries in which the Orange/Senqu River Basin is situated indicating the sediment sampling points.

2.1.2 Fish and bird eggs sites

Fish and wild bird eggs were also sampled to indicate the levels of the compounds and elements in the biota of the Orange/Senqu River Basin (Table 2; Figure 4).

Although 5 fish sampling sites were targeted, we were successful at only four of the sites. As the main tributary, and also the most polluted river, the Vaal River was targeted for fish sampling (V1 and V2; Figure 3). V1 is at Standerton in Mpumulanga and thus up-stream of Gauteng, the industrial hub in the Basin and potentially contributing to most of the pollution. V2 is downstream of Gauteng, at the Free State town of Parys, and should a comparison between V1 and V2 reveal the influence of the Gauteng Province on pollutant levels in fish. Two sites were selected in the Orange River, one close to the Lesotho border at Aliwal North (O2), and another downstream of the Orange River's confluence with the Vaal River. Unfortunately, not enough fish could be collected at O2 and a comparison between a up-stream and downstream site in the Orange River could not be done.

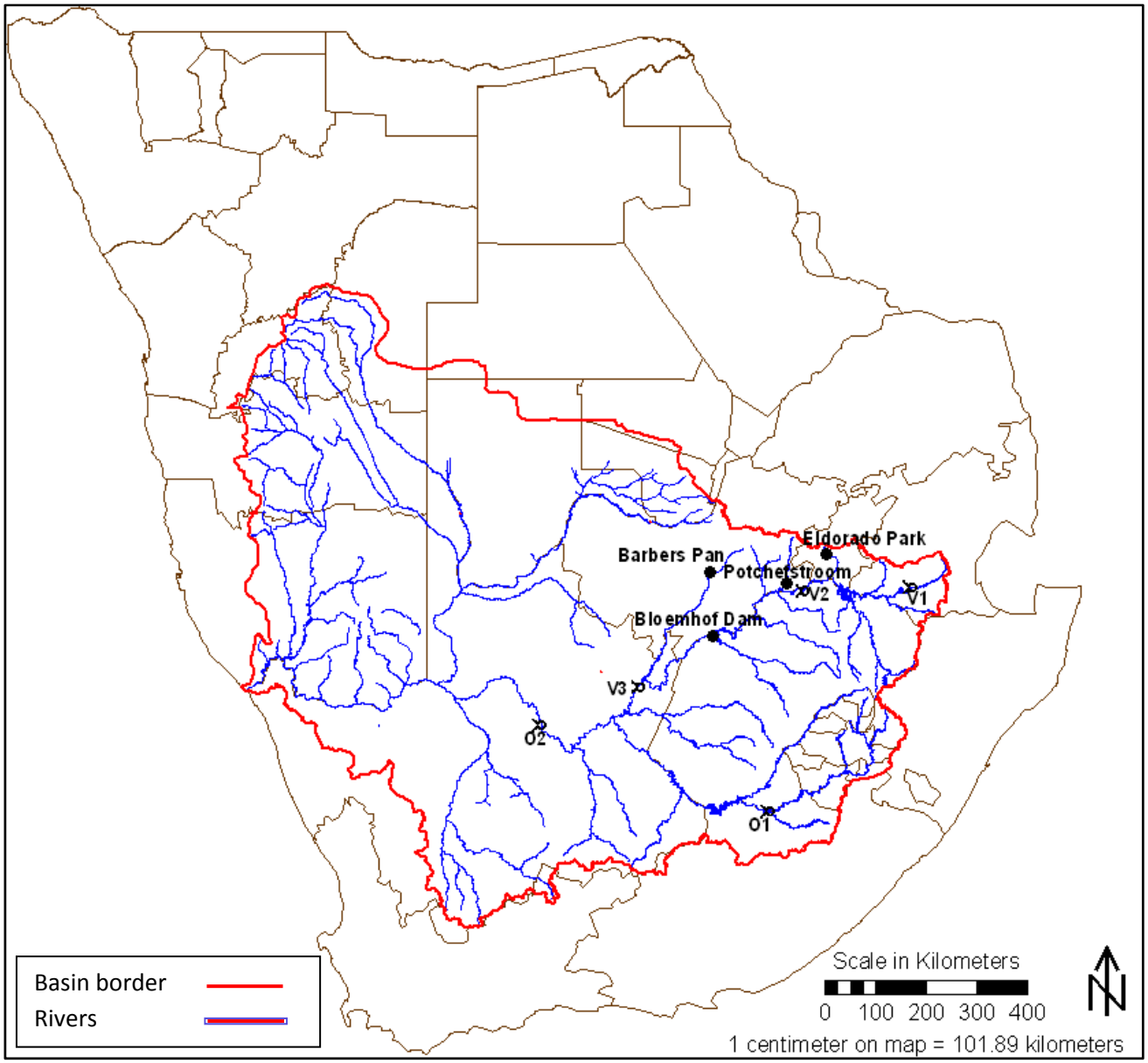

Figure 4: The fish sampling sites (V1-3 & O1-2) as well as the sites where wild bird eggs (●) were collected.

Table 2: Fish and wild bird eggs sampling sites

Sample type	Site name/label	Coordinates		Location name	River
		longitude	latitude		
Wild bird eggs	Potchefstroom	27.09	-26.78		Mooi River
	Barbers Pan	25.57	-26.60		Harts River
	Bloemhof Dam	25.64	-27.70		Vaal River
	Eldorado Park	27.88	-26.30		Klip River (West)
Fish	V1	29.51	-26.86	Standerton	Vaal River
	V2	27.40	-26.92	Parys	Vaal River
	V3	24.16	-28.56	Rooipoort	Vaal River
	O1	26.71	-30.68	Aliwal North	Orange River
	O2	22.21	-29.21	Boegoeberg	Orange River

Wild bird eggs of aquatic birds that were roosting during the summer of 2010-2011 were collected at the sites listed in table 2. Roots were located through a low flying aerial survey of the Orange River and visiting sites previously known to have roosts of aquatic birds.

Bird eggs are regarded as good indicators of organohalogen compounds in the environment because of the high lipid content of the yolk (Van den Steen et al., 2006). When eggs are formed in the female's body, these pollutants are transferred to the eggs, thus reflecting the body burden of the female bird (Braune, 2007). Eggs are ideal monitoring tools since eggs (Medvedev & Markove, 1995; Lebedev et al., 1998):

- have a fairly consistent composition and decompose slowly;
- are produced by a specific portion of the population;
- are easy to handle and sampling is relatively fast and cost effective;
- represent pollutant uptake by the female bird in a period before the egg is laid;
- are susceptible to random sampling

2.2 Sampling and sample preparation

2.2.1 Sediment sampling

Pooled samples were prepared at each site by collecting the top 5 cm within a 10 m radius and stirring the mixture thoroughly. Sub-samples were stored in high density polyethylene bottles at -20 °C and protected from UV degradation. While sampling, the pH level of the sediment was determined. Unfortunately, the pH meter broke down half way through the sampling period and was the pH o the remaining samples determined upon thawing of the sediment in the laboratory at the NWU. The sediment was allowed to air dry, grinded and sieved (mesh size 0.5 µm) and shipped to an accredited laboratory in Germany (Oekometric GmbH in Beyreuth) for POPs analysis. The analysis was done for all 12 the traditional POPs classes as well as the 9 "new" POPs.

All sampling equipment is made of stainless steel or glass and contamination of samples was prevented by rinsing every utensil before a sampling event with acetone and hexane to first remove polar compounds and secondly the non-polar contaminants.

Duplicate sediment samples were analysed for 42 elements (Figure 5) , using the inductively coupled plasma mass spectrometry (ICP-MS) at the NWU. The samples were digested with concentrated HNO_3 at 50-60 °C and allowed to evaporate to 5 ml. The samples were further treated with H_2O_2 and allowed to cool before 3 M HCl was added and gently heated for another hour. These samples were diluted and injected into the ICP-MS.

2.2.2 Fish sampling

After obtaining the necessary permits from the appropriate provinces, Sharptooth Catfish (*Clarias gariepinus*) was collected at each of the sites. Fillet was collected for chemical analysis because this is the tissue likely to be consumed by humans. The Sharptooth Catfish is completely omnivorous. It preys and scavenges on any available organic food source including fish, birds, frogs, small mammals, reptiles, molluscs, crustaceans, seeds, fruit and even plankton. They sometimes hunt in packs, herding and trapping small fish in shallower water (Skelton, 2001). Because they often feed close to the bottom, and the fact that they are omnivorous, make them an ideal fish to sample for determining the levels of pollutants in biota: the higher an animal is in the food chain, the more likely it is to bio-accumulate pollutants. The Catfish is hardy, and survive conditions unhospitable to many other fish species. Thus, they survive long enough so that, if bio-accumulation occur, they will show it. They also have a large

distribution and occur through the entire Basin which allows a comparison between sites, using the same species. It's also a species that is often consumed by subsistence fisherman.

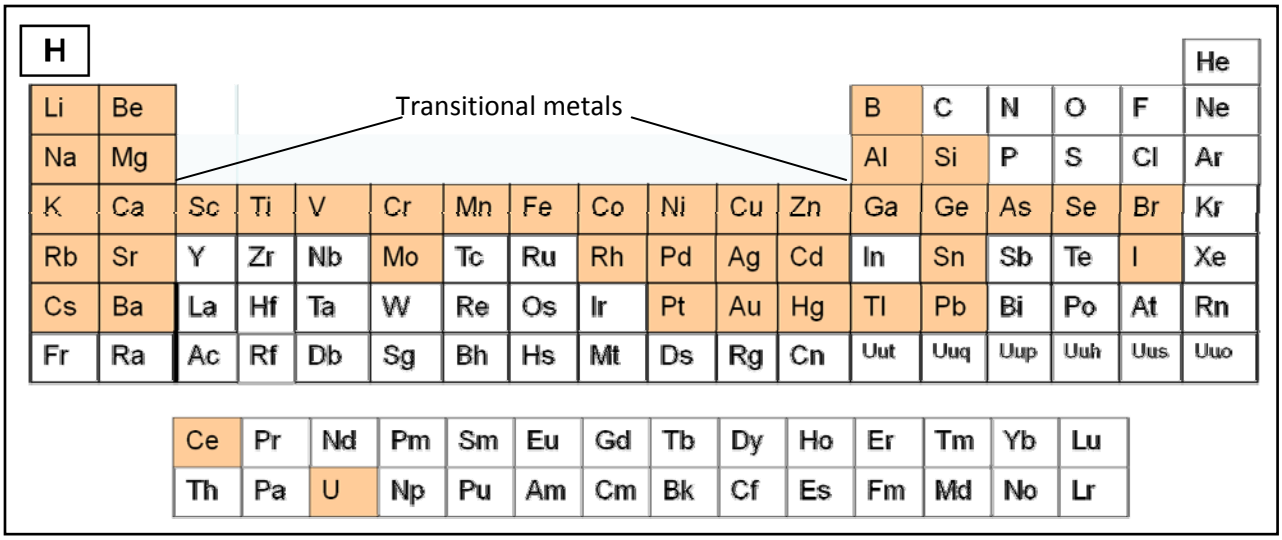

Figure 5: The elements for which concentrations were determined are highlighted.

Fish were collected using fyke nets, and electro fishing and temporarily held in a keep net until at least 10 per site were caught. The fish were measured (Table 3) and sacrificed so that fillet could be collected. Fillet for POPs analysis were wrapped in pre-cleaned aluminium foil. (Pre-cleaned = rinsed with acetone and hexane). Protocols to prevent cross contamination during the dissection process were followed. The fillets were transported and stored frozen until analysis could be done. Fillet destined for elemental analysis were stored in plastic bags, and transported and stored frozen until analysis.

The fish were pooled in the laboratory at the NWU. Males and females were pooled separately so that two pools per site were created (Table 3). Approximately the same mass of fillet were cut from each fillet. Samples for POPs analysis were shipped frozen to the German laboratory. Samples for elemental analysis were freeze dried before undergoing the same acid and heat digestive treatments that were described for the sediment samples (cf Section 2.2.1).

Table 3: Dimensions and gender of the *Clarias gariepinus* individuals that constituted the pools

Pool no	Site label	Body mass (g)	Gender	Total length (mm)	Standard length (mm)	Girth (mm)
Pool 1	O2	1 920	Male	670	610	290
		1 540		610	550	260
		3 020		790	720	330
		3 280		795	710	335
		2 880		560	500	260
Pool 2		2 240	Female	700	640	300
		1 300		570	530	255
		2 340		730	680	300
		2 740		710	640	320
		2 240		740	670	295
Pool 3	V1	3 160	Male	780	690	340

		2 950		760	730	300
		5 900		1 030	930	490
		4 900		1 040	930	375
		4 260		810	740	360
Pool 4		3 280	Female	760	690	360
		6 400		990	890	300
		3 800		860	790	345
		2 700		760	680	310
Pool 5	V2	4 200	Male	800	730	345
		4 340		790	700	350
		4 140		850	770	350
		4 700		790	760	340
Pool 6		3 520	Female	720	660	320
		3 960		760	690	340
		4 140		770	700	340
		4 150		770	750	330
		3 560		750	660	320
		4 560		830	760	340
Pool 7	V3	3 660	Male	820	740	370
		9 060		1 070	980	505
		12 380		1 200	1 060	555
		11 000		1 200	1 070	560
		2 960		745	660	335
Pool 8		7 560	Female	980	890	500
		2 940		750	670	335
		3 860		840	760	370

*Length from the tip of the head to end of peduncle, i.e. where the tail starts.

2.2.3 Egg sampling

Bird eggs were collected at four breeding colonies. Attempts were made to locate more colonies but this failed. The breeding colonies at Upington were washed away by the floods. Eggs were sampled by either climbing trees with nests using rock climbing gear, or using ladders on smaller trees. Eggs were carefully stored and transported to the lab, where they were photographed and stored in a freezer. On the day of sample preparation, egg dimensions were measured, and the eggs then thawed. Eggs from the same species from different localities were pooled to obtain a large enough sample volume. This is indicated in Table 4. Egg contents were transferred into Nalgene containers, and homogenised using ultrasonic homogenization. A subsample was taken for elemental analysis. Samples of the 16 pools were shipped to the various laboratories with all necessary permits. Elemental and POPs analysis was as for fish and sediment.

Table 4: A summary of the wild bird species from which eggs were collected as well as the sites.

Location	Pools	Commonn name	Species name
Barbers Pan	1	Grey Heron	*Ardea cinerea*

	5	African Darter	*Anhinga rufa*
	14	Blackheaded Heron	*Ardea melanocephala*
Bloemhof Dam	2	Great White Egret	*Ardea alba*
	3	Grey Heron	*Ardea cinerea*
	6	African Darter	*Anhinga rufa*
	8	Reed Cormorant	*Microcarbo africanus*
	10	Sacred Ibis	*Threskiornis aethiopicus*
	11	Little Egret	*Egretta garzetta*
	16	Cattle Egret	*Bubulcus ibis*
Eldorado Park	4	Sacred Ibis	*Threskiornis aethiopicus*
Potchefstroom	7	Reed Cormorant	*Microcarbo africanus*
	9	Glossy Ibis	*Plegadis falcinellus*
	12	Blackheaded Heron	*Ardea melanocephala*
	13	Blackheaded Heron	*Ardea melanocephala*
	15	Cattle Egret	*Bubulcus ibis*

3 Results & Discussion

3.1 Persistent Organic Pollutants

Analysis has been completed for sediment, fish and bird eggs for all POPs initially requested. These will be briefly presented and discussed below.

3.1.1 Sediment

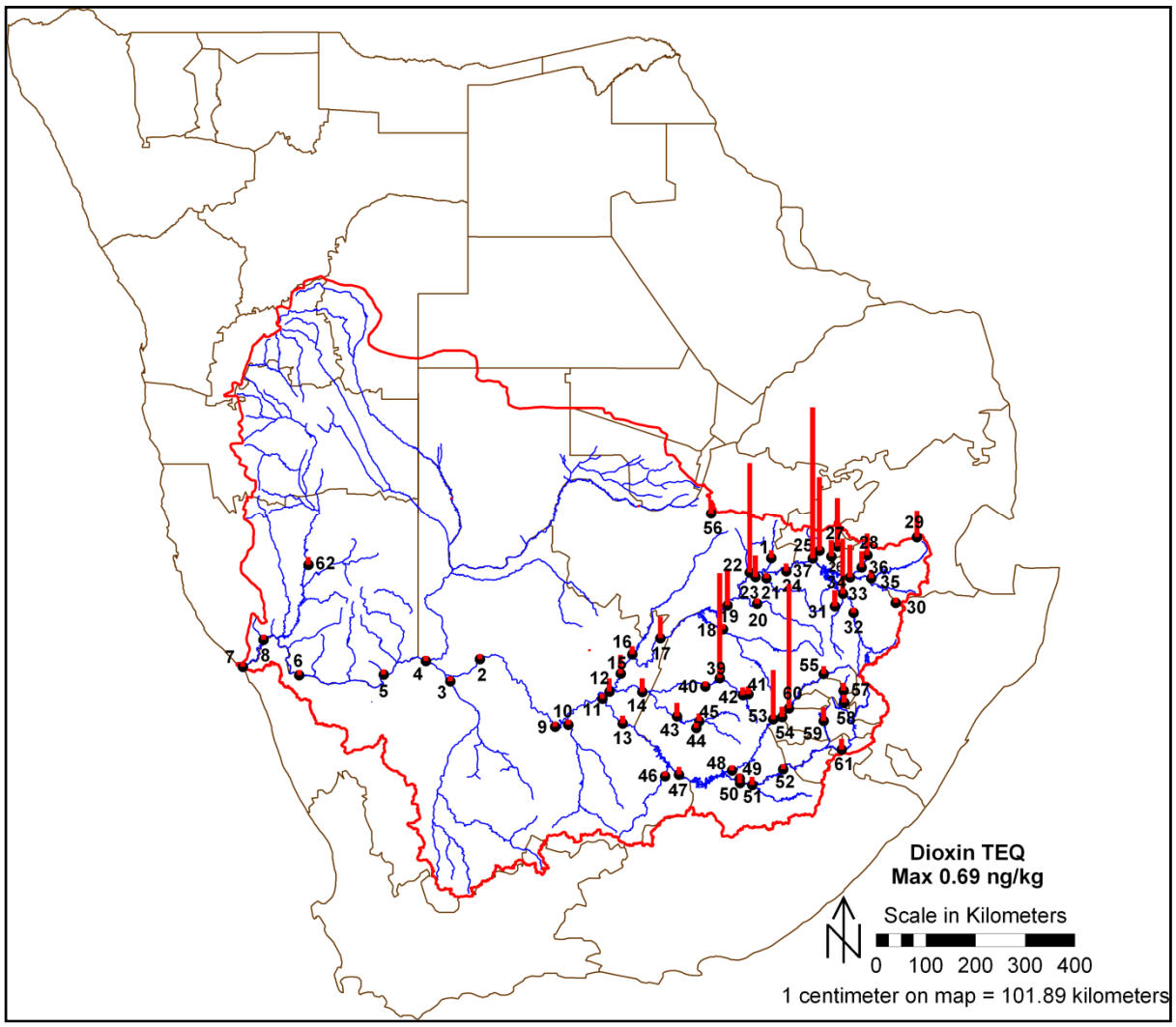

Figure 3.1.1: Distribution of dioxin TEQ in sediment from the sampling sites. Sites indicated with small red dots have TEQ levels at or below detection limit. Bar scale is relative.

In general, the levels detected were quite low. Figure 3.1.1 shows levels of TEQ above detection limits in Gauteng, Klerksdorp, Orkney, Modder River, and Kelekeque River. The first three sites can be associated with industry, urban activities, and mining, while the sources for the last two are unknown. The last two may be associated with smaller industry and urban activities. The general massage from this map is that dioxin-like TEQ seems to remain isolated in certain hotspots and either is not transferred downstream, or is diluted or broken down very quickly. However, note needs to be taken of the hotspots as this survey was intended to obtain a “big-picture” and not to characterise and describe smaller areas. We are particularly concerned about the areas around Soweto and Klerksdorp.

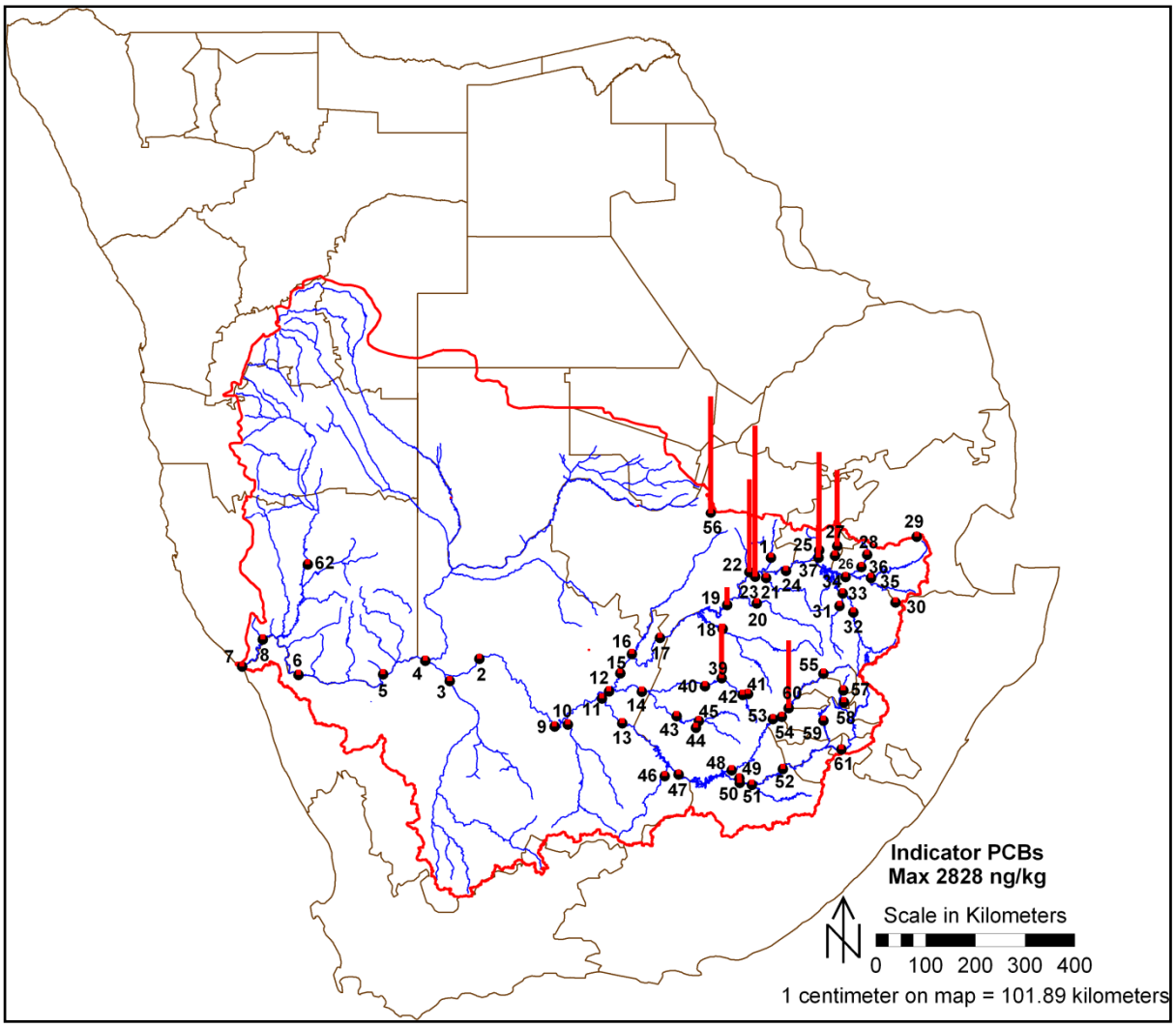

Figure 3.1.2: Distribution of indicator PCBs in sediment from the sampling sites. Sites indicated with small red dots have PCB levels at or below detection limit. Bar scale is relative.

The PCB distribution (Figure 3.1.2) reflects the TEQ distribution (Figure 3.1.1). We believe that the same sources are involved, and therefore the same concerns.

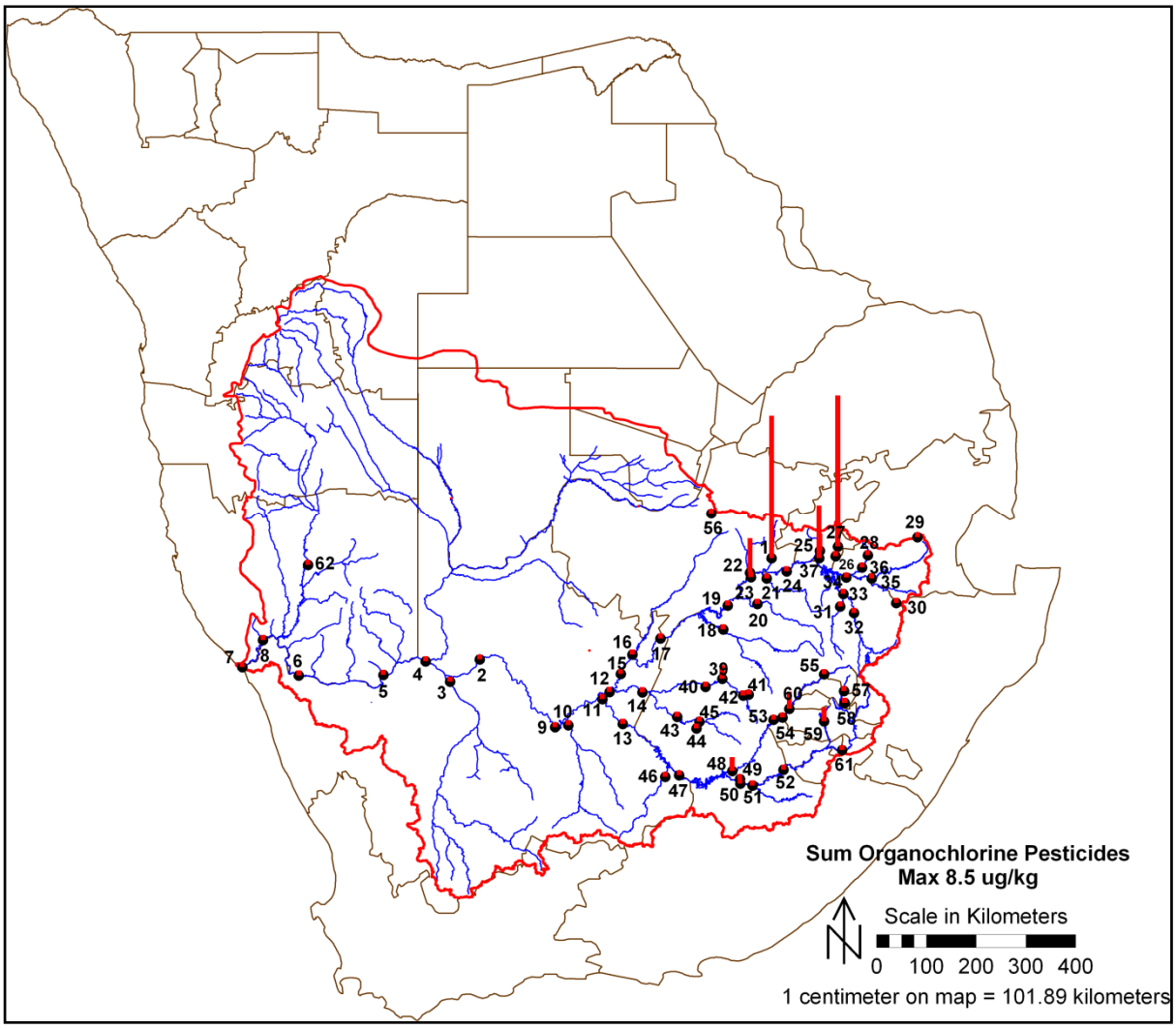

Figure 3.1.3: Distribution of summed organochlorine compounds (OCs) in sediment from the sampling sites. Sites indicated with small red dots have OC levels at or below detection limit. Bar scale is relative.

Blesbokspruit, Suikerbosrand, Potchefstroom, and Klerksdorp had the highest levels of organochlorine compounds (OCs), mainly in the form of legacy DDT. Again, it seems that pollution remains isolated and does not travel downstream, or is diluted or broken down quickly.

No PFOS was detected in sediment, so no map is displayed, but the reader will note that PFOS was detected in fish and sediment in a pattern different from the above (Figures 3.1.7 and 3.1.11).

3.1.2 Fish

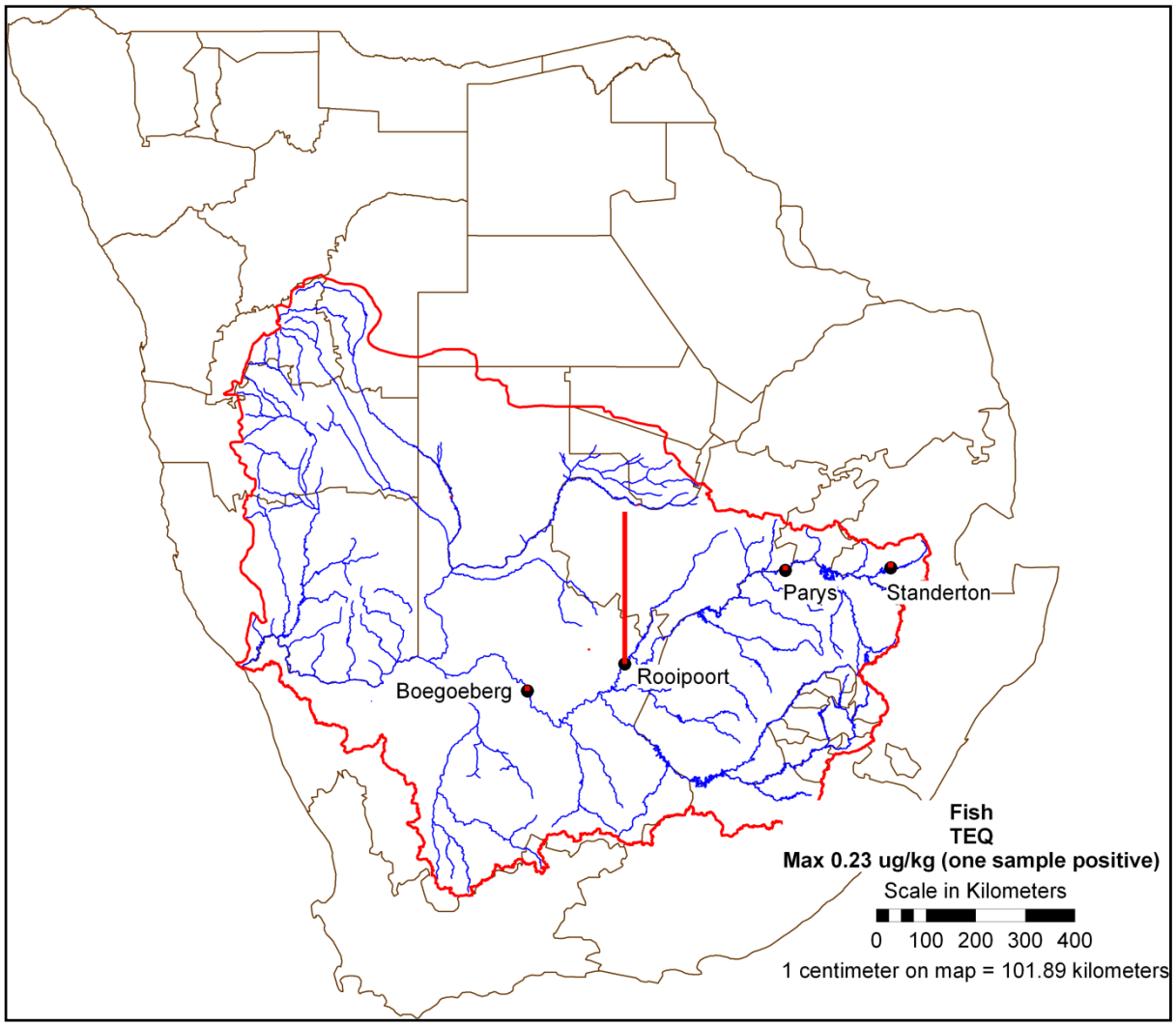

Figure 3.1.4: Distribution of dioxin-like TEQ in fish from the sampling sites. Sites indicated with small red dots have TEQ levels at or below detection limit. Bar scale is relative.

TEQ was detected in *Clarias gariepienus* (sharptooth catfish) from only one of the four sites where fish were collected, namely Rooipoort (Figure 3.1.4). Why this site would have the higher levels is not known. Potential upstream sources associated with this site include mining, urban, industrial, and sewage associated with Kimberly and the smaller urban and rural areas. This indicates that a local source of TEQ might be present. It also shows that we may need to analyze fish closer to Soweto and Lenasia, and downstream of Orkney since the sediment TEQ distribution (Figure 3.1.1) showed hotspots there as well.

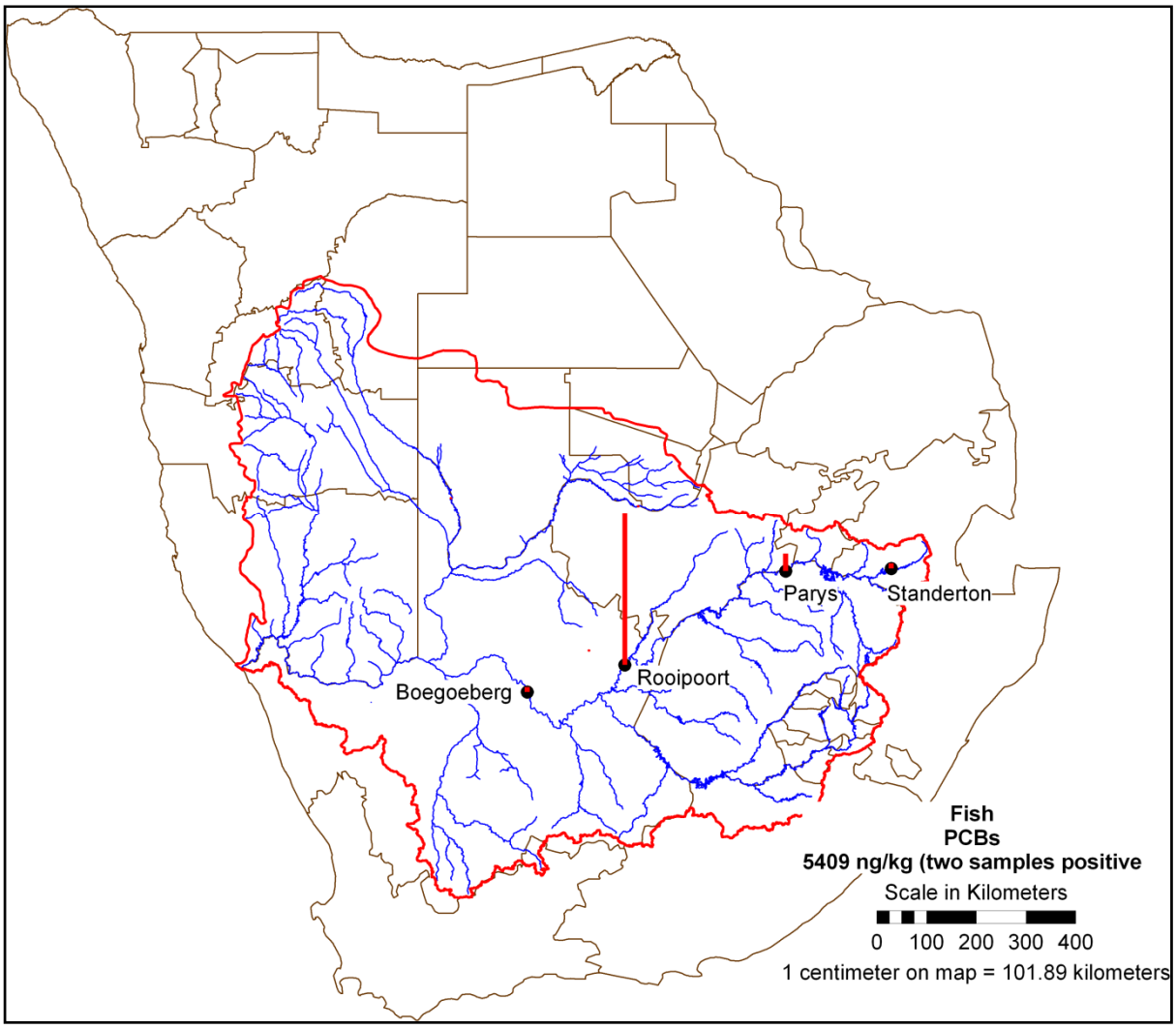

Figure 3.1.5: Distribution of indicator PCBs in fish from the sampling sites. Sites indicated with small red dots have PCB levels at or below detection limit. Bar scale is relative.

As for sediment TEQ (Figure 3.1.1) and PCB (Figure 3.1.2) distributions, the fish PCB distribution (Figure 3.1.5) reflects the TEQ distribution (Figure 3.1.4). The same sources and concerns are therefore applicable. It does show however, that sediment levels do not always reflect levels in biota in this system.

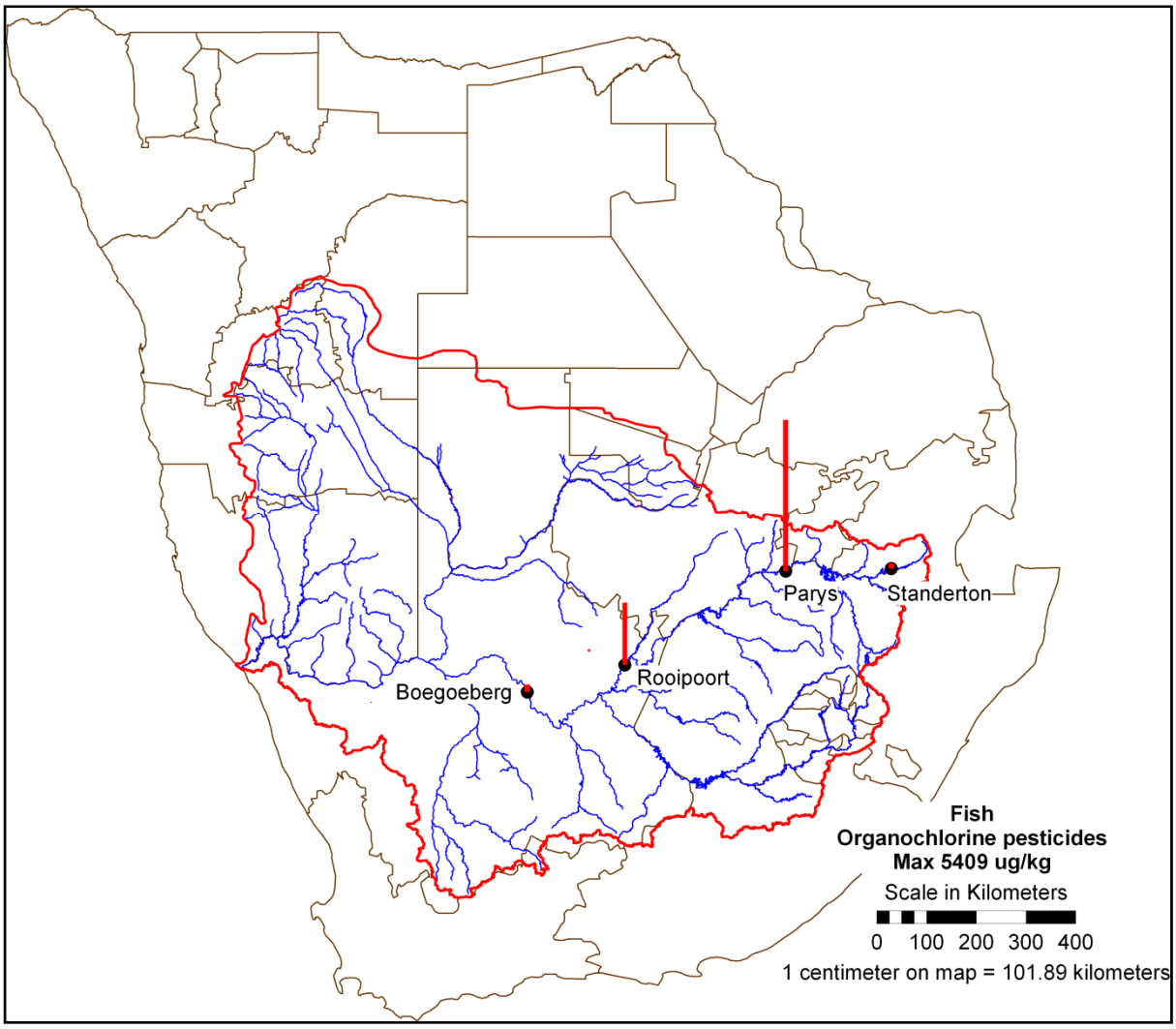

Figure 3.1.6: Distribution of OCs in fish from the sampling sites. Sites indicated with small red dots have OC levels at or below detection limit. Bar scale is relative.

Parys and Rooipoort had the highest levels of OCs, again mainly DDT and metabolites (Figure 3.1.6). How and where these metabolites come from is not known, and needs further investigation. Since there is intensive recreational and subsistence fishing along these rivers, the health risks may need to be investigated.

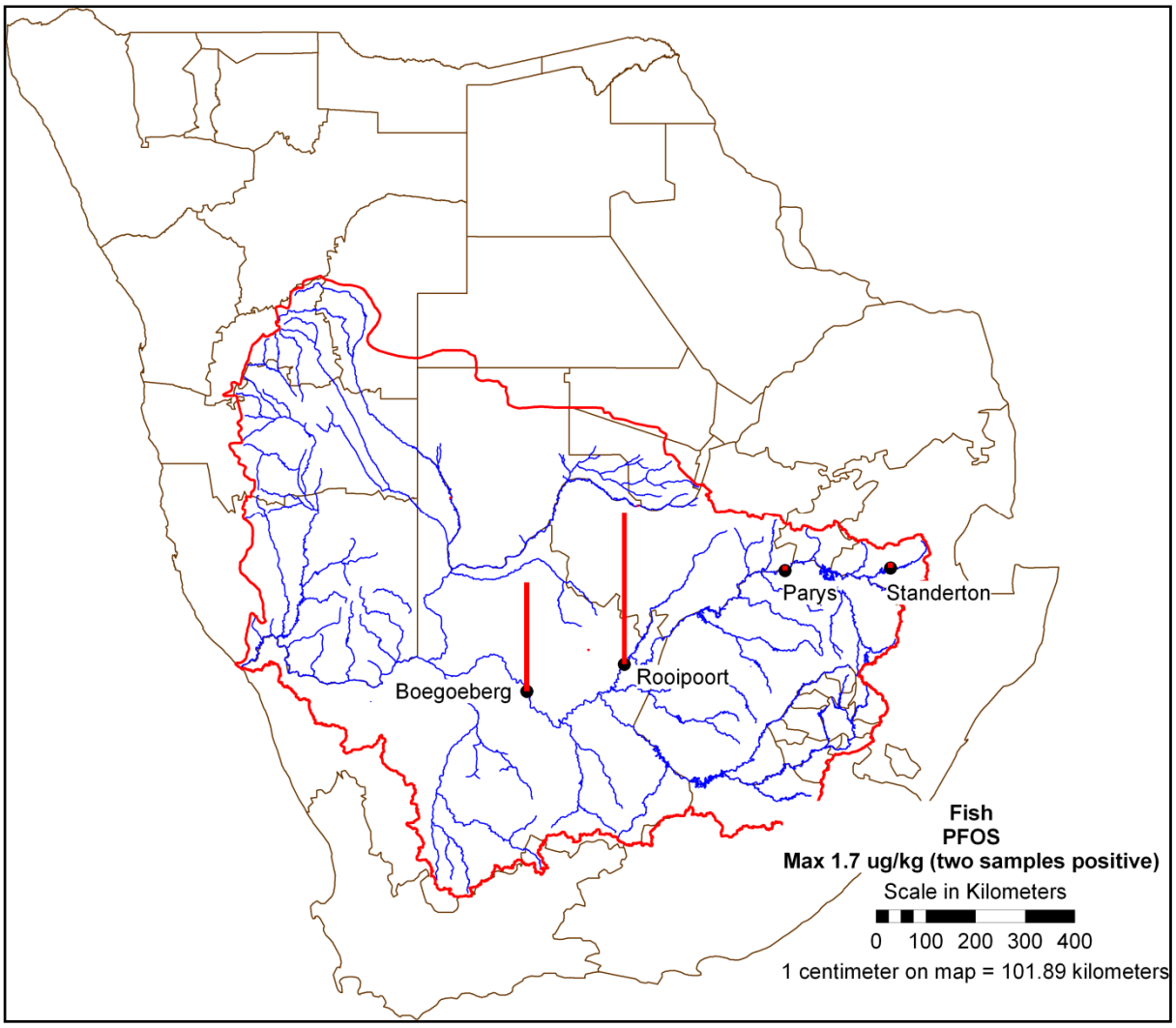

Figure 3.1.7: Distribution of PFOS in fish from the sampling sites. Sites indicated with small red dots have PFOS levels at or below detection limit. Bar scale is relative.

This surprising distribution (Figure 3.1.7) cannot be explained. PFOS is an industrial and consumer chemical and it would have been expected at higher concentrations near industrial centres and cities. PFOS is also very persistent. The pattern we see might be due to past use whereby residues have now found their way downstream or it reflects local use of unknown source. Very little of this chemical is known in Africa, and this is most likely the first environmental data from Africa. The reasons for this distribution pattern need further investigation.

3.1.3 Wild bird eggs

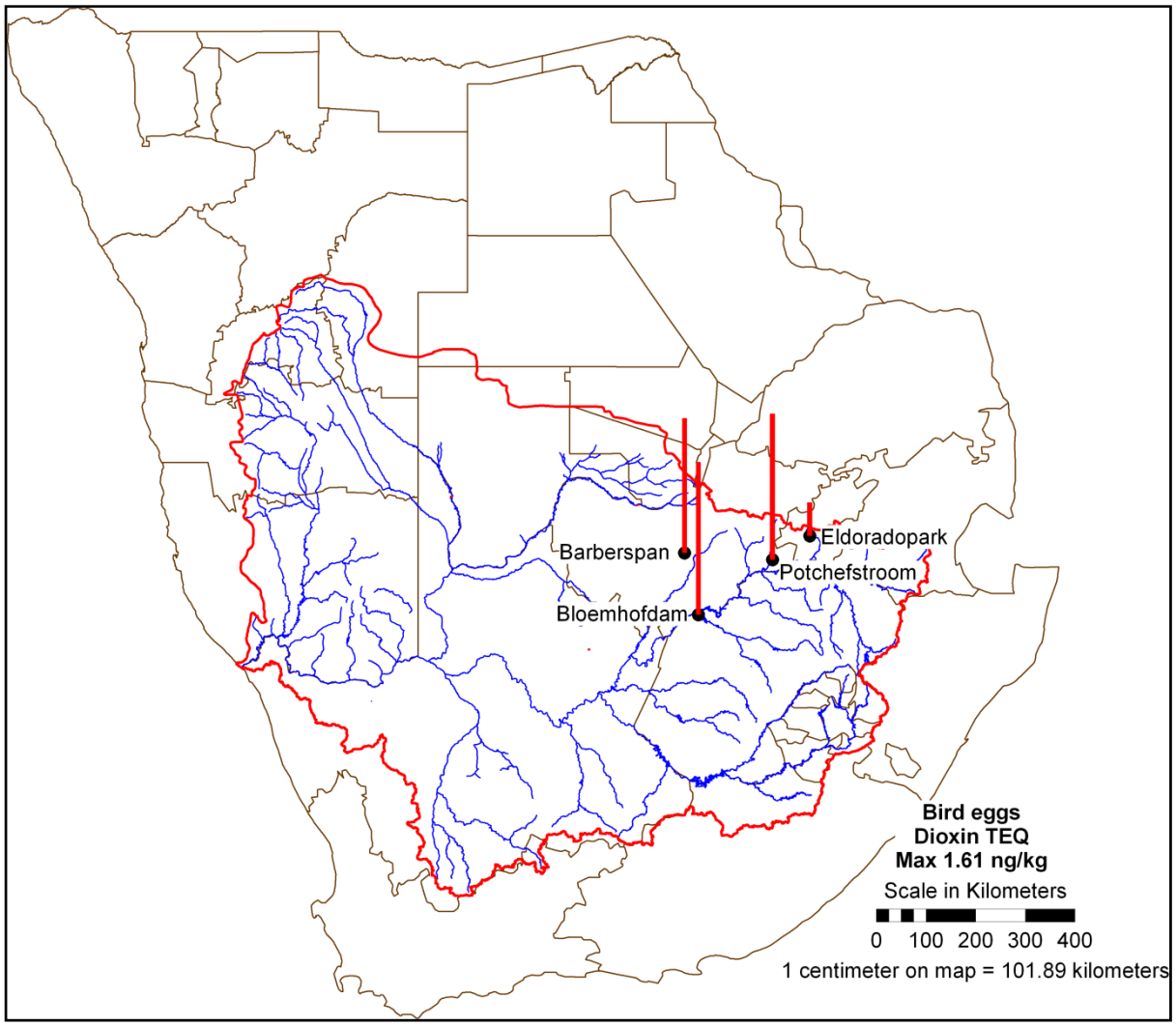

Figure 3.1.8: Distribution of Dioxin TEQ in bird eggs from the sampling sites. Bar scale is relative.

This surprising map indicates widespread distribution of TEQ (Figure 3.1.8). The levels were and order of magnitude higher than the single positive fish value (Figure 3.1.1). We expected higher levels in eggs from birds from Eldoradopark. Birds also move around quite a bit; the distribution may reflect this. However, data needs further interpretation as the bars represent maxima from each site, but not all species were represented at each site.

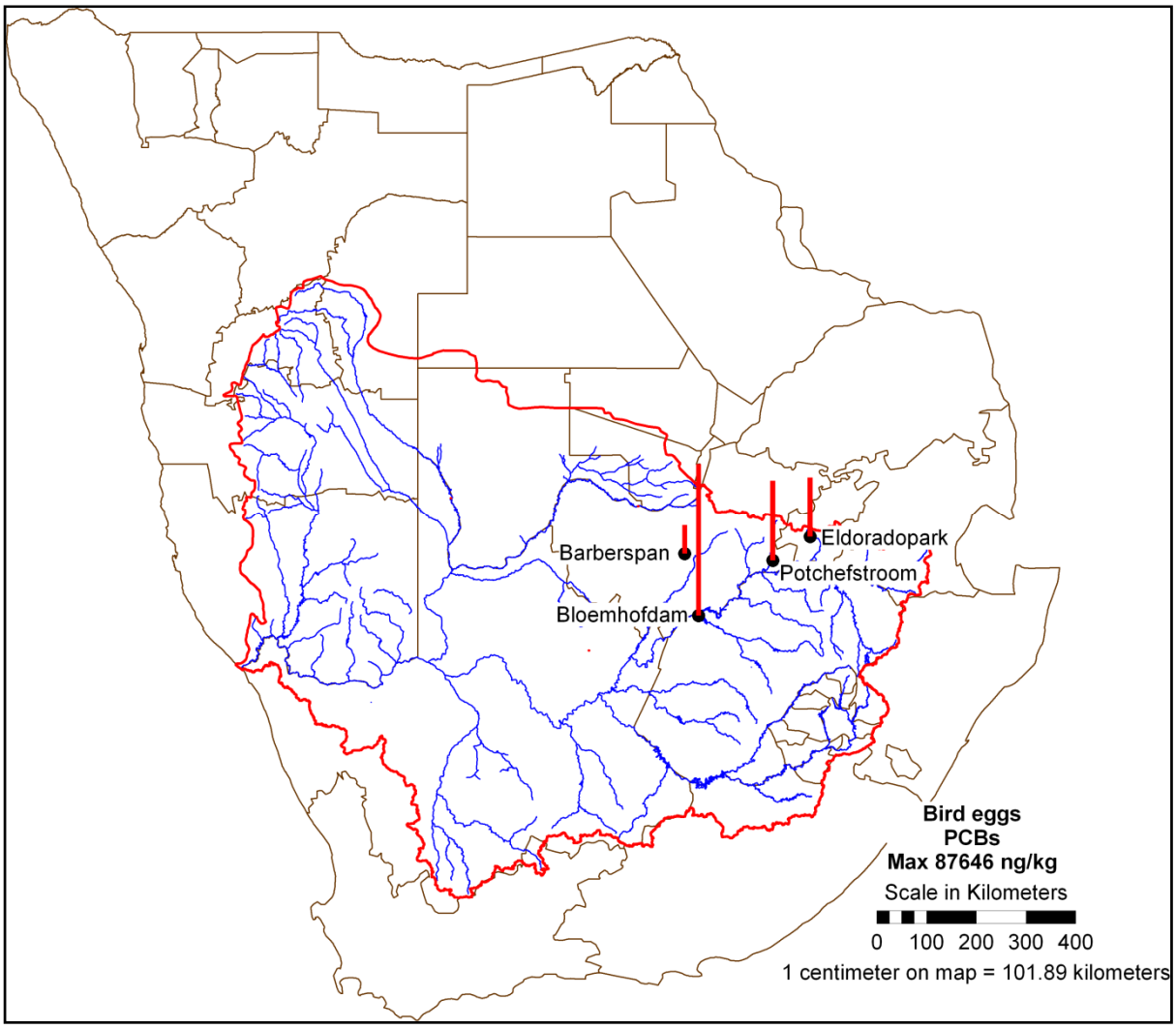

Figure 3.1.9: Distribution of PCBs in bird eggs from the sampling sites. Bar scale is relative.

There seems to be an increase in levels from Eldoradopark towards Bloemhofdam along the Vaal River (Figure 3.1.9). Bloemhofdam may represent a retaining effect of PCBs in biota, but not in sediment (Figure 3.1.2). Confirmation is needed, as well as a more elaborate species assessment.

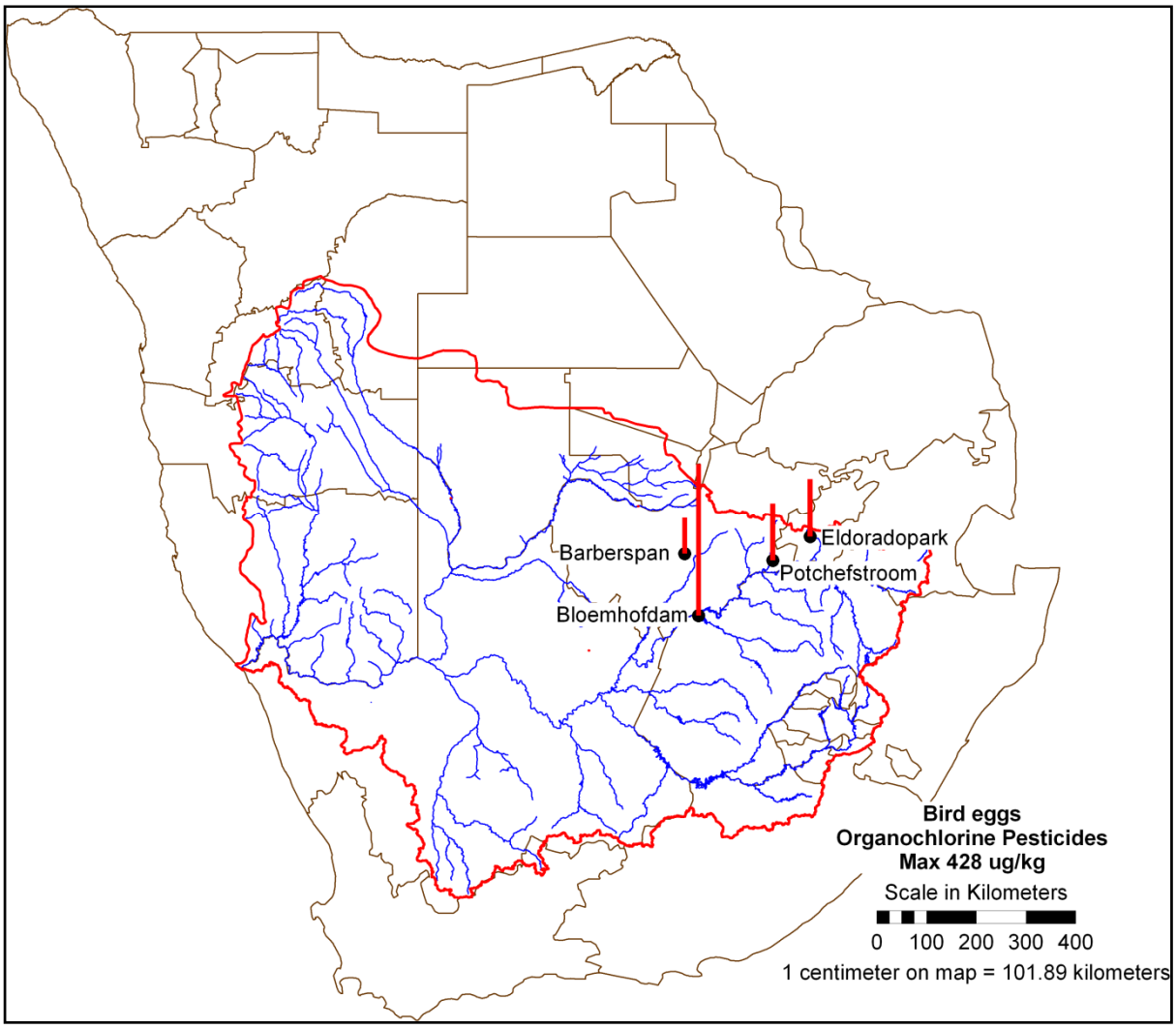

Figure 3.1.10: Distribution of OCs in bird eggs from the sampling sites. Bar scale is relative.

The relatively high levels of OCs in the bird eggs were expected, but that the highest was from Bloemhofdam was not (Figure 3.1.10). Just as with PCBs (Figure 3.1.9) it seems that Bloemhofdam might retain OCs as it does with PCBs. However, a careful species assessment needs to be done.

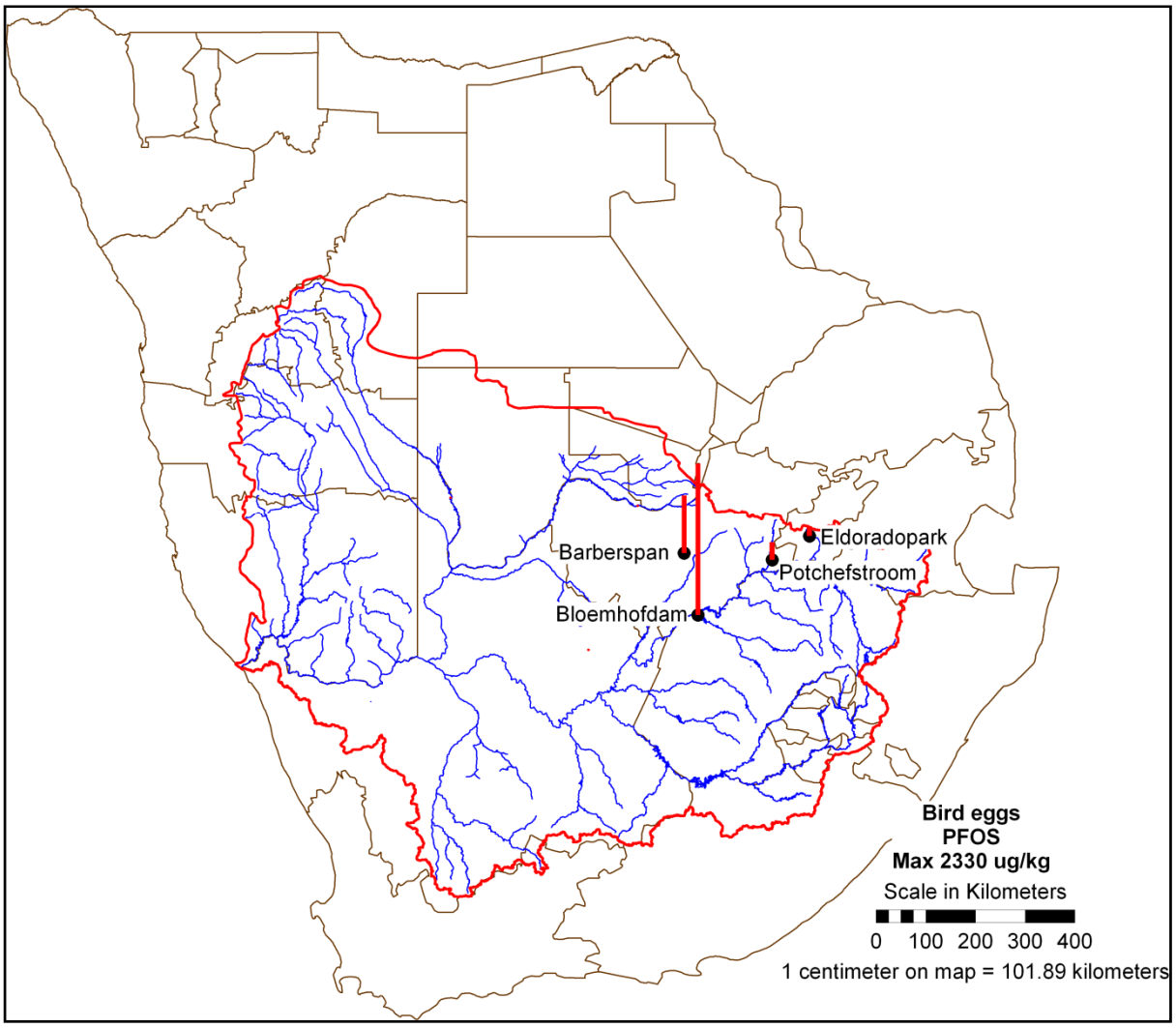

Figure 3.1.11: Distribution of PFOS in bird eggs from the sampling sites. Bar scale is relative.

This map represents perhaps the most surprising finding of the project thus far concerning POPs. These are relatively high levels, higher than the OCs represented in Figure 3.1.10 and not much less than the PCB levels represented in Figure 3.1.9. We expected higher levels at Eldoradopark and less at Bloemhofdam. Again, it might be that Bloemhofdam acts as a retainer of pollutants, but species assessments and a more careful analysis of the data is required. It is a pity that we were not able to collect eggs at Upington. This would have given an indication of how these compounds might travel via water and biota, ending up in higher trophic levels such as birds.

3.2 Heavy metals and trace elements

3.2.1 Sediment

A summary of the basic statistics for the elements at each of the sites is found in Table 3.2.1 and the mean for each element is indicated in Figures 3.2.1 and 3.3.2. Iron (Fe) and aluminium (Al) had the highest means of all of the 42 elements analysed for (Table 3.2.1).

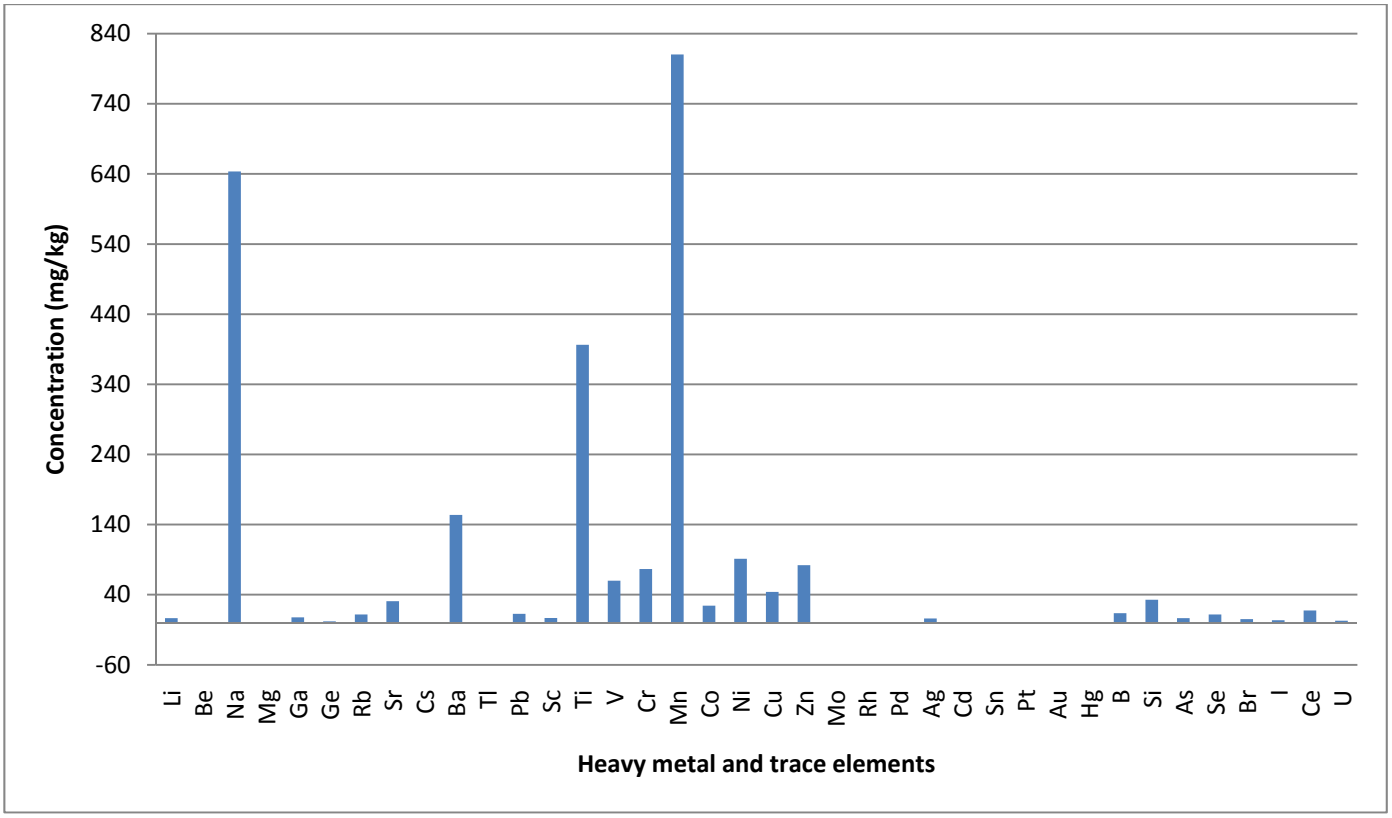

Figure 3.2.1: Mean concentrations for the majority of the heavy metals and trace elements in the sediment.

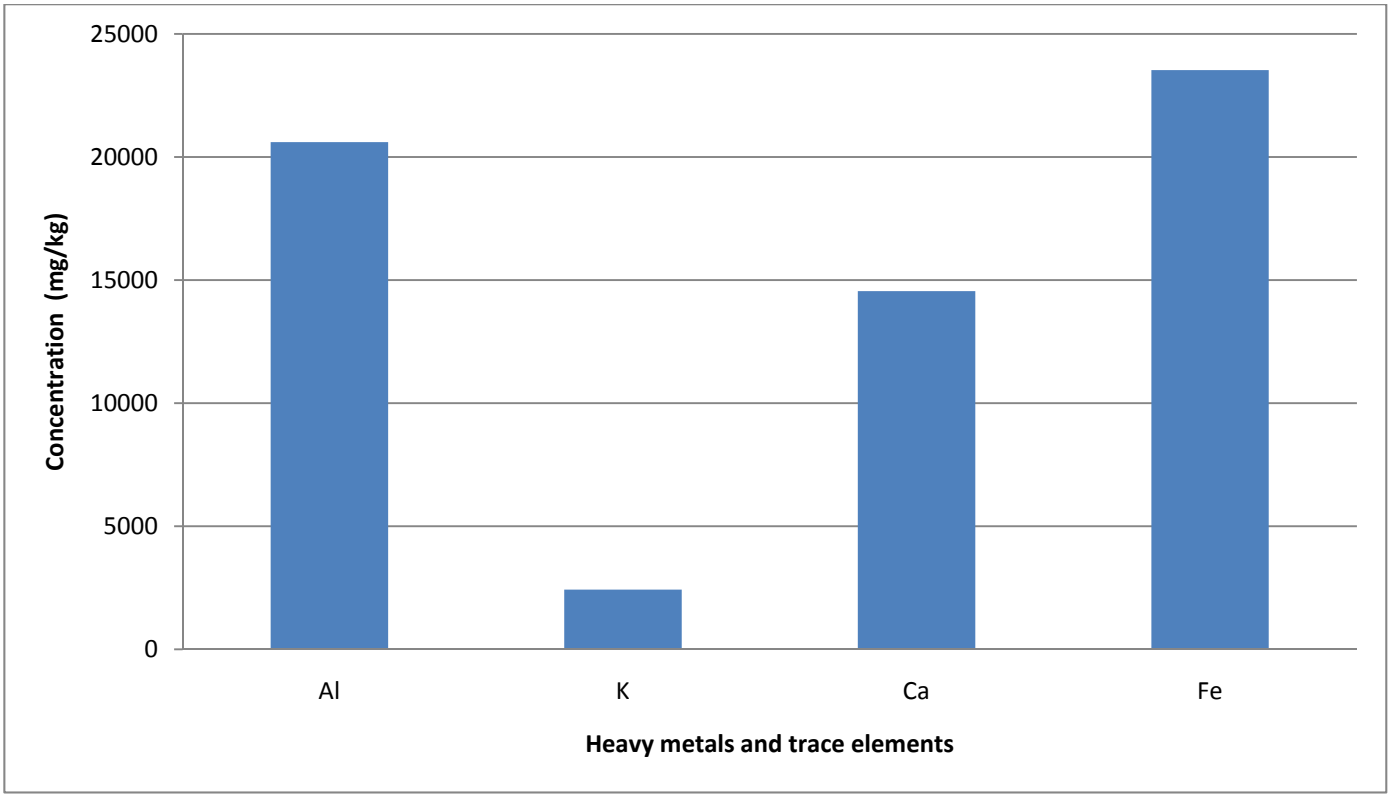

Figure 3.2.2: Mean concentrations for Al, K, Ca and Fe in the sediment. Their concentrations were two orders higher than those elements in Fig 3.2.2.

Table 3.2.1: A summary of the means, and other simple statistics to describe the range and magnitude of the elements found in the sediment.

	mean (mg/kg)	standard deviation	minimum (mg/kg)	maximum (mg/kg)	median (mg/kg)
Li	6.5	5.0	1.1	25.0	5.5
Be	1.0	0.5	0.2	2.3	1.0
Na	643.5	187.7	250	975	625
Mg	12 016.5	10 195	850	50 000	8 875
Al	2 0602	10 352	3 500	45 000	21 375
K	2 426.2	1822.5	240	7000	2 000
Ca	14 549	18229	1650	9 0000	1 0000
Ga	7.7	4.3	0.8	19.0	7.3
Ge	2.0	0.9	0.5	4.5	2.1
Rb	12	7	2	28	11
Sr	30.7	30.0	5.5	155.0	23.3
Cs	1.0	0.7	0.2	3.5	1.0
Ba	154	75	24	350	153
Tl	0.3	0.3	0.1	1.8	0.2
Pb	13	6	4	28	13
Sc	7	4	1	14	7
Ti	396	322	50	1400	275
V	60	28	18	153	58
Cr	77	26	25	153	83
Mn	810	398	120	1975	775
Fe	23 530	10 820	5 000	52 500	24 000
Co	24	10	7	55	23
Ni	91	47	17	200	88
Cu	44	18	12	93	43
Zn	82	65	22	300	60
Mo	0.4	0.3	0.1	1.7	0.3
Rh	0.4	0.2	0.1	1.2	0.4
Pd	0.5	0.3	0.1	1.8	0.4
Ag	6.2	4.3	2.0	21.8	4.8
Cd	0.1	0.2	0.0	0.9	0.1
Sn	1.0	0.5	0.3	2.3	1.0
Pt	0.0	0.0	0.0	0.2	0.0
Au	0.2	0.4	0.0	2.3	0.1
Hg	0.5	0.6	0.2	3.5	0.4
B	14	11	7	68	11
Si	33	3	19	38	33
As	7	3	3	17	6
Se	12	2	4	14	12
Br	5	4	3	16	4
I	3.6	5.4	0.3	25.0	1.7

Ce	17	8	5	38	17
U	2.8	8.5	0.4	50.0	1.2

The Metal Pollution Index (MPI) was also calculated for each of the sediment sites. The MPI is the geometric mean of all of the elements (Figure 3.2.3). The highest value was calculated for site no 56, where sediment was collected from the origins of the Molopo River. This is difficult to explain because this is a rural area with only agricultural activities. However, the geology of the site belongs to the Transvaal Supergroup, the Malmani Subgroup, with dolomite rock formations. It is possible that underground water from the mines to the northern and eastern parts of the site find its way to underground caverns from which the Molopo eye originates.

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

Only the elements for which background levels could be found, were used in this calculation. It is for this reason that Rh, Pd, Pt, and Au were not included. The background levels used are general, global values for crustal shale (Wedepohl, 1995). The results of the I_{geo} is an indication of pollution:

$I_{geo} < 1$: 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 pollution classification of the elements at each of the sites are summarised in tables 3.2.2. and 3.2.3

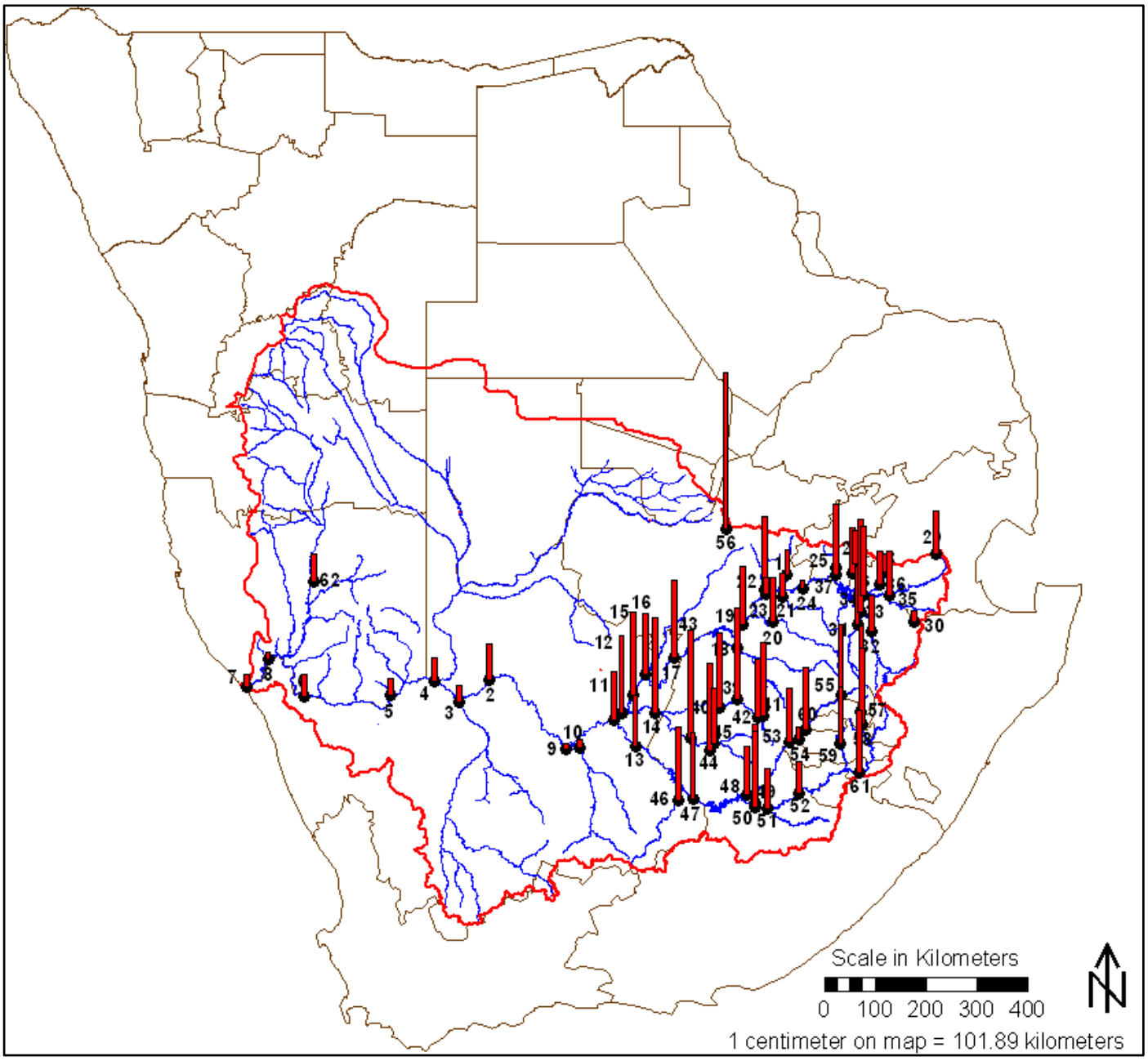

Figure 3.2.3: The Metal Pollution Index (MPI) at each of the sediment sites.

Table 3.2.2: Possible pollution levels of the elements at the sites in the Vaal River catchment as indicated by the geoaccumulation index (I_{geo})

		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
1	Mooi R																																
12	Vaal R																																
14	Riet R																																
15	Vaal R																																
16	Harts R																																
17	Vaal R																																
18	Vet R																																
19	Vaal R																																
20	Vals R																																
21	Renoster R																																
22	Skoon Spr																																
23	Vaal R																																
24	Vaal R																																
25	Klip R West																																
26	Suikerbosrand R																																
27	Blesbok Spr																																
28	Waterval R																																
29	Vaal eye																																
30	Klip R East																																
31	Liebenbergsvallei R																																
32	Wilge R																																
33	Wilge R																																
34	Vaal R																																
35	Vaal R																																
36	Waterval R																																
37	Suikerbosrand R																																
39	Modder R																																
40	Kaal R																																
41	Koranna Spr																																
42	Modder R																																
43	Riet R																																
44	Kromellenboog Spr																																
45	Riet R																																

unpolluted; very lightly polluted; lightly polluted; moderately polluted highly polluted; very highly polluted

Table 3.2.2: Possible pollution levels of the elements at the sites in the Orange River catchment as indicated by the geoaccumulation index (I_{geo})

		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 R																																
3	Hartbees R																																
4	Orange R																																
5	Orange R																																
6	Orange R																																
7	Orange R																																
8	Orange R																																
9	Orange R																																
10	Brak R																																
11	Orange R																																
13	Orange R																																
46	Seekoei R																																
47	Orange R																																
48	Caledon R																																
49	Orange R																																
50	Stormberg Spr																																
51	Orange R																																
52	Orange R																																
53	Leeu R																																
54	Caledon R																																
55	Caledon R																																
56	Molopo (eye)																																
57	Malebamatso R																																
58	Matsuko R																																
59	Senquenyane R																																
60	Kelekeque R																																
61	Senque R																																
62	Fish R																																

unpolluted; very lightly polluted; lightly polluted; moderately polluted highly polluted; very highly polluted

When interpreting the I_{geo} results it is important to remember that they were calculated using global background levels. It is therefore possible that the global, Se and Ag levels are lower than what it should be for South Africa, because it is difficult to believe that both Se and Ag could be at such high pollution levels through-out the entire Basin and even in the remote areas (Tables 3.2.1. and 3.2.2). The possible pollution due to Hg has a more expected pattern. Much better understanding of these results will be possible once the minerals from the geology of the sites are considered.

In the following section graphs are presented representing the relative distribution patterns of various elements between sites. These graphs occur at the end of this section. At least one representative of the major groups, eg. GrIA, on the Periodic Table or category of elements such as the transitional metals are presented. The elements that were chosen to represent their group or category were selected because it correlated well with the others in the group or category.

The highest level of Cs was found at site 43, which is a site in the Riet River (Fig 2 & 3). It seems as if the higher levels were generally found in the Free State and Mpumulanga Highveld (Fig 3.2.4).

The highest level for the representative of the Group IIA elements , Be was found at the Molopo eye,site 56 (Fig 3.2.5). Again, the higher levels of Be were distributed through the Free State, and eastern Mpumulanga.

Of the Group IIIA elements, Th was the representative and the highest level again was at the Molopo eye (site 56). The second highest level was at site 1, which is the Mooi River. Compared to the other sites, they had very low levels of Th (Fig 3.2.6).

The only two elements in Group IV that were analysed for, are Pb and Sn and they are both represented on the graph (Fig 3.2.7). Their concentrations are not presentative relative to each other, because of the large difference in levels. In stead, the concentrations of the two elements are relative between the sites, as if they were depicted independently of each other. In this manner, it is clear to see that the highest Pb level was at the Molopo eye (site 56). The highest Sn level was found at site 57, the Malebamatso River in Lesotho.

The only element that was analysed for in Group VA, was arsenic (Fig 3.2.8). The highest level was 19.25 mg/kg and it was measured at the Molopo eye. The second highest level was measured at the site in Namibia, site no 62 in the Fish River.

Selenium was the only element of the Group VIA elements that was analysed for. The highest level was 13.75 mg/kg at site 14, a site in the Riet River. However, this element was distributed at approximately the same levels through-

out all of the sites in the Basin (Fig 3.2.9). Most of the sites in the Lower Orange River (sites no 2 to 10) had low Se levels, but when their I_{geo} values are considered (Table 3.2.2), they too are regarded as highly polluted by Se.

Of the halogens (Group VIIA elements), only Br and I were analysed for (Fig 3.2.10). Their levels are represented relative to each other as their levels were in the same order of magnitude. The highest Br level was at site 39, the Modder River in the Free State, followed by site 15 at 15.25 mg/kg, a site in the Vaal River. The same site in the Modder River also had the second highest level of I (20.75 mg/kg). The highest level of I was found at site 14, which is a site in the Riet River, downstream of its confluence with the Modder River (Fig 2).

Zn was selected as the representative of all of the transitional metals analysed for because it correlated significantly with all of the transitional metals that were analysed for in this study. The highest level was found at site 27 (Fig 3.2.11), which is a site in the Blesbok Spruit. This river receives effluent from mines on the East Rand and is

renowned for its heavy metal pollution (Roychoudhury & Starke, 2006). The second highest Zn level was found at site 57 (207.5 mg/kg) which is in the Malebamatso River in Lesotho . The third highest level is 185 mg/kg at site 37, which is a site in the Suikerbosrand River. The Suikerbosrand River receives water from the Blesbok Spruit (Fig 2).

Ce was the only lanthanide analysed for and yet again, the highest level was found at the Molopo eye, 170 mg/kg (Fig 3.2.12.).

U was the only actinide analysed for and the highest level (50 mg/kg) was found to be at site 15, in the lower catchment of the Vaal River (Fig 3.2.12). At this point the river also receives drainage from a lime mining activities to the North.

3.2.2 Fish

In this section of the interim report, a very cursory view is presented on the levels of the elements. The main focus is in those elements with known toxic effects and for which guideline levels in fish fillet could be found. The guidelines levels are those levels acceptable in fish fillet and regarded as safe for human consumption. These elements include mainly the heavy metals: chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd) and metalloids, arsenic (As),and selenium (Se).

The range of international standards for Cu in fish fillet is 10 to 100 mg/kg and for Cr it is 1 mg/kg (Wagner & Boman, 2003). This means that the levels measured for pooled fish fillets in this study is well within the allowable levels (Fig 3.2.13). The levels for the two elements are not depicted relative to each other.

The levels of Zn found in the fillet of this study is almost half of what is allowed by international standards for fish fillet. The standards varies between 40 to 100 mg/kg (Wagner & Boman, 2003). The concentration also seems to be very similar between the four sites (Fig 3.2.14)

The highest As levels were found in the fillet of the fish caught in the only Orange River site (O2). The highest Se levels were in the fish at site V3 (Fig 3.2.15). The levels for the two elements are not depicted relative to each other. According to the international levels, As may vary between 0.1 to 5 mg/kg depending on the fish species (Wagner & Boman, 2003). The levels for As in this study falls within this range. However, the Se levels measured in the South African fish is higher than that considered to be safe by international standards (0.3 to 2 mg/kg).

The international levels for Cd are 0.05 to 2 mg/kg (Wagner & Boman, 2003), for Pb they are 0.5 to 10 mg/kg (Wagner & Boman, 2003) and for Hg they are 0.5 to 1 mg/kg (EC, 2006). The levels of Cd, Pb and Hg in the fish analysed in this study (Fig 3.2.16) were well below that regarded as acceptable by international standards. The highest Hg level was found in fish from the Orange River site (O2) and although the level was twice as high as fish from the other sites, it is still below accepted international levels.

3.2.3 Eggs

The data for the bird eggs was only recently received and no meaningful interpretation could be done yet.

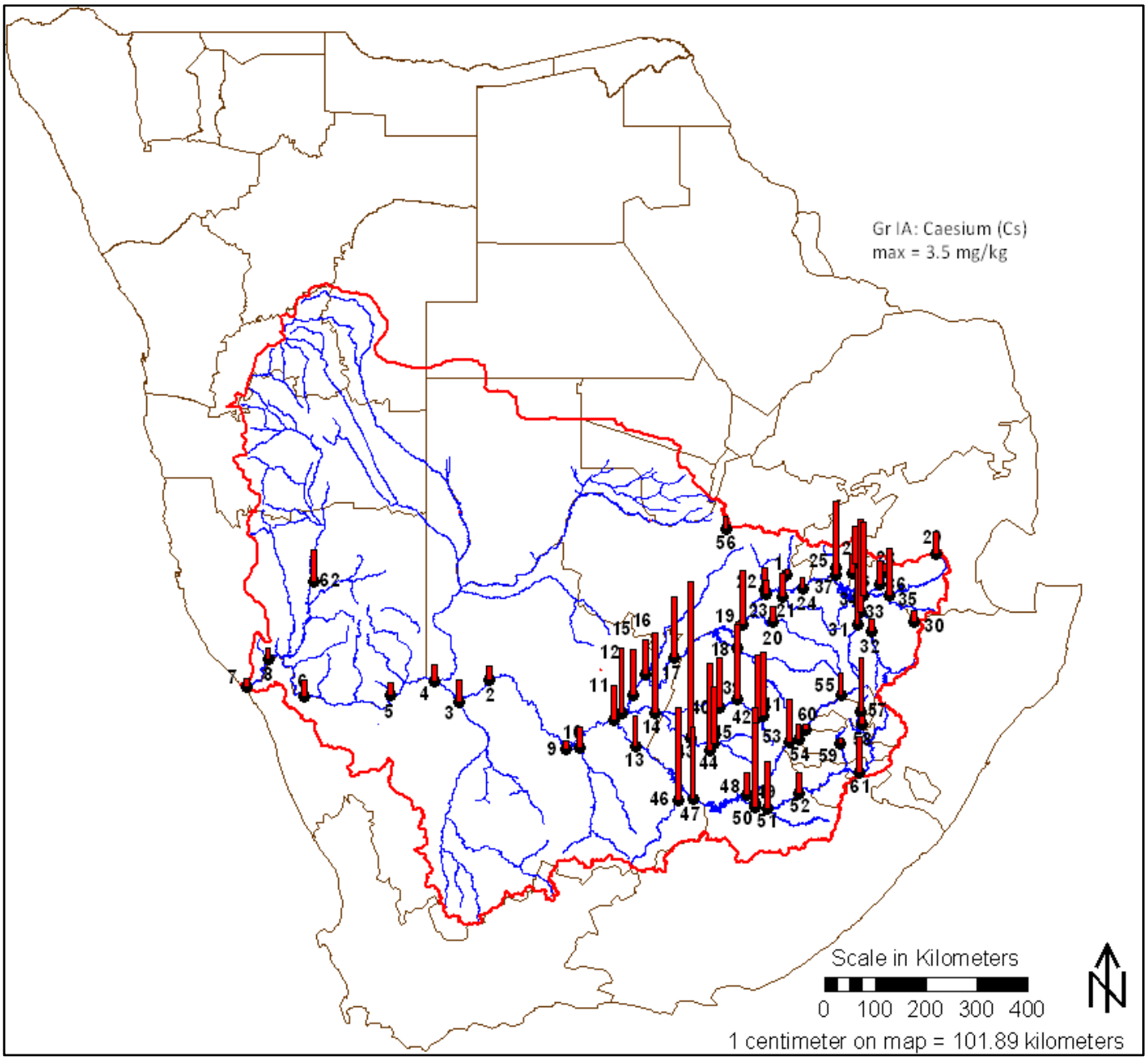

Figure 3.2.4: The Group IA elements are represented by Cs

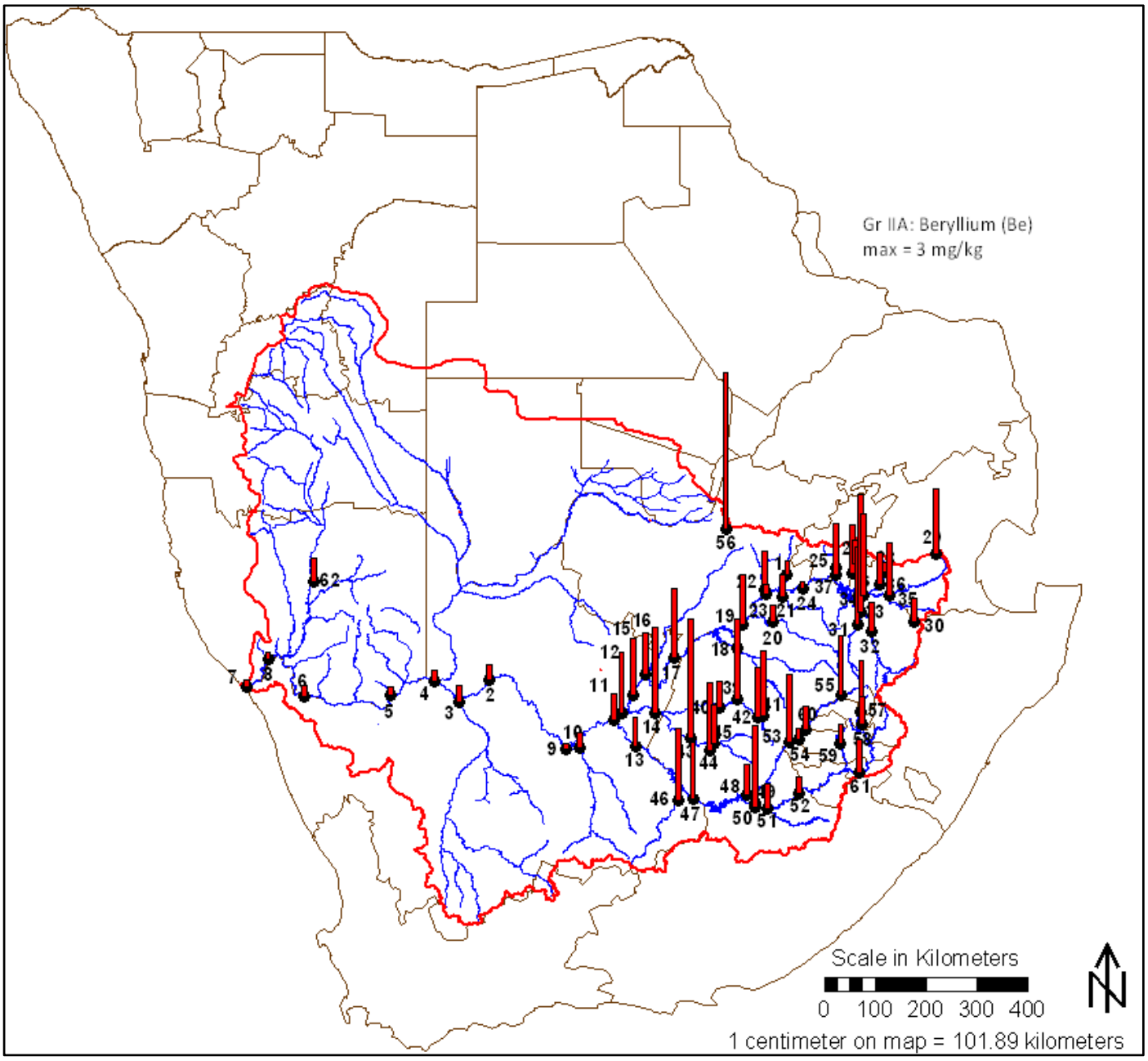

Figure 3.2.5: The Group IIA elements are represented by Be

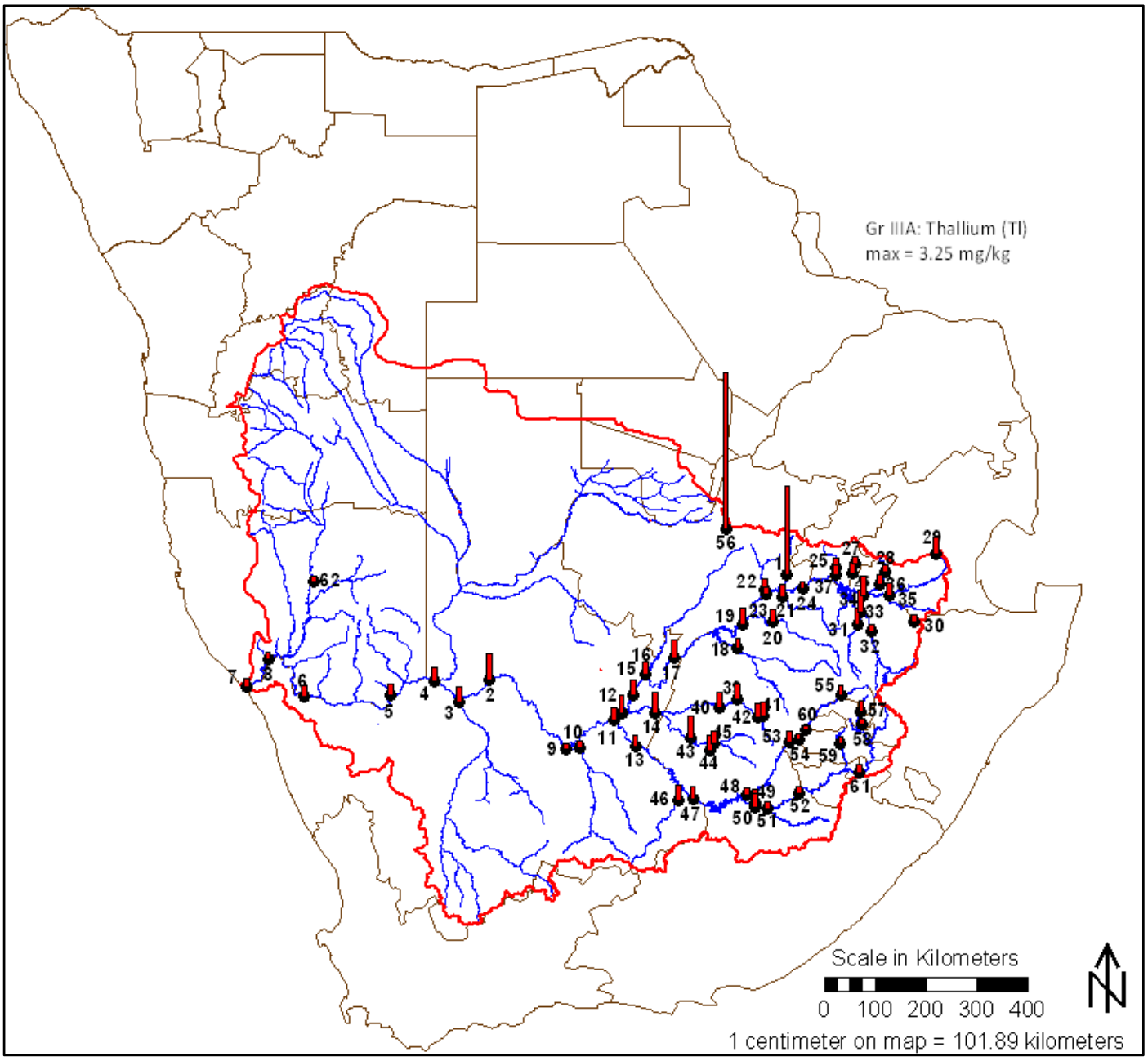

Figure 3.2.6: The Group IIIA elements are represented by Th

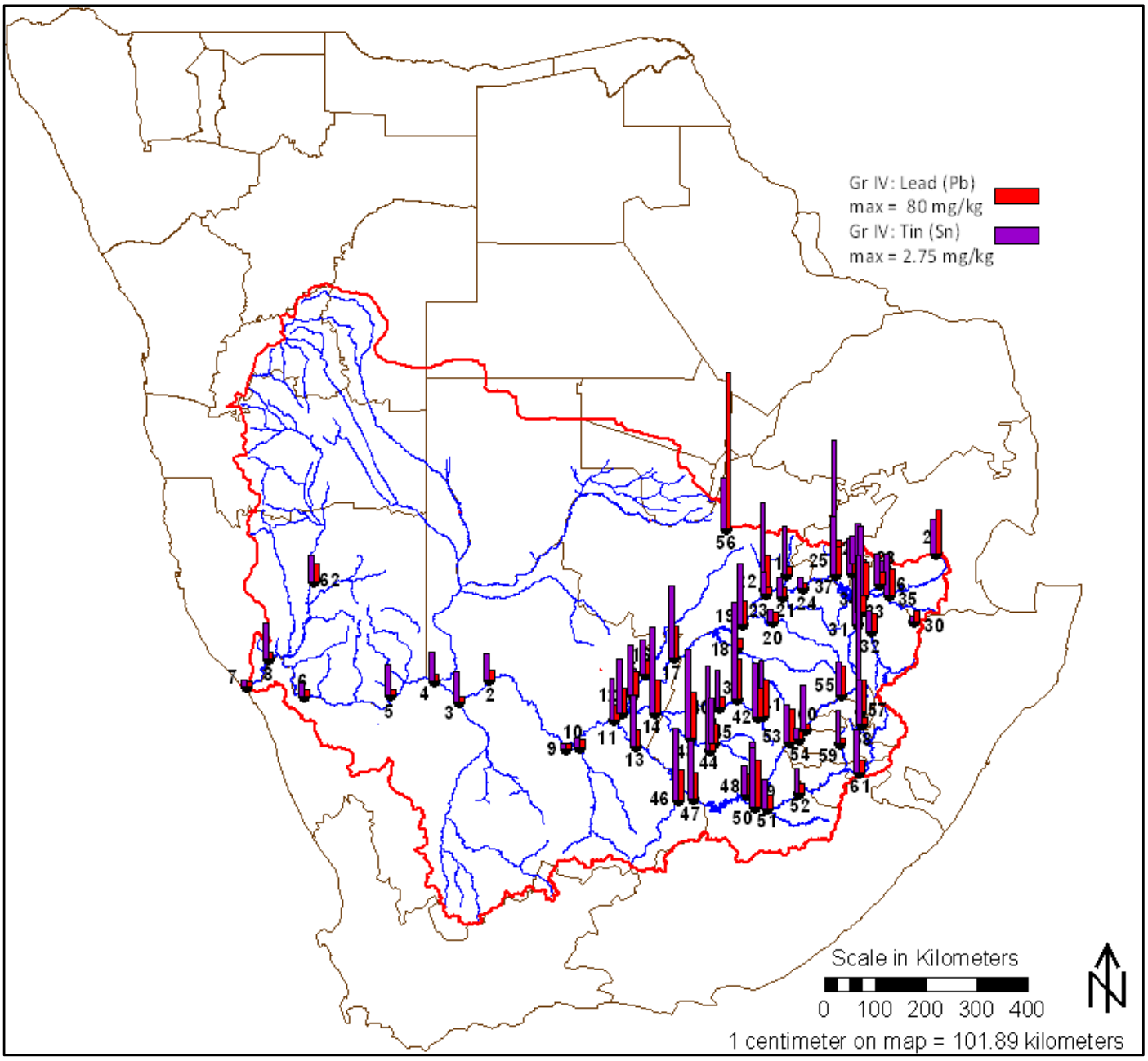

Figure 3.2.7: The Group IVA elements are represented by both Pb and Sn

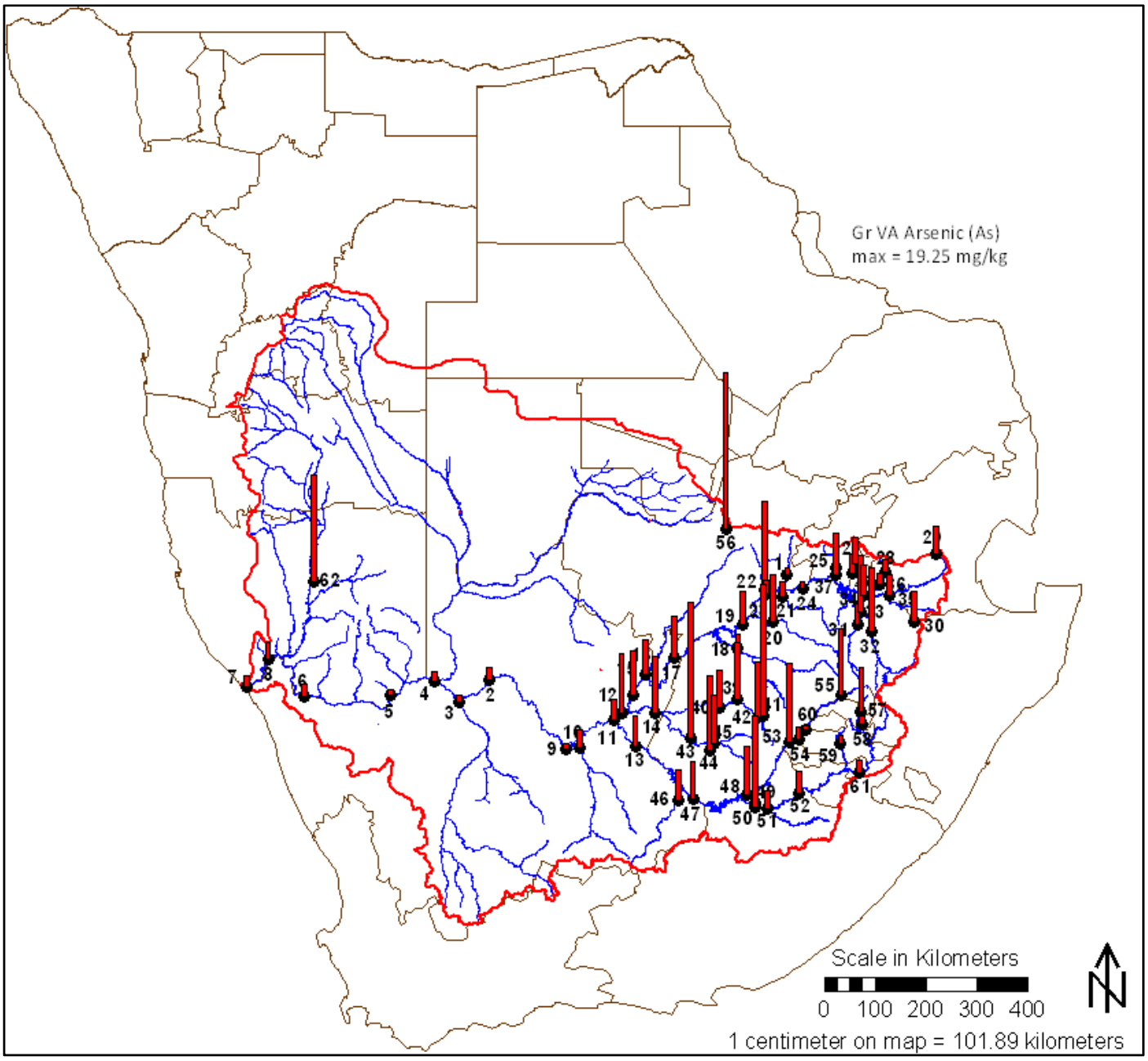

Figure 3.2.8: In Group VA As was the only element analysed for.

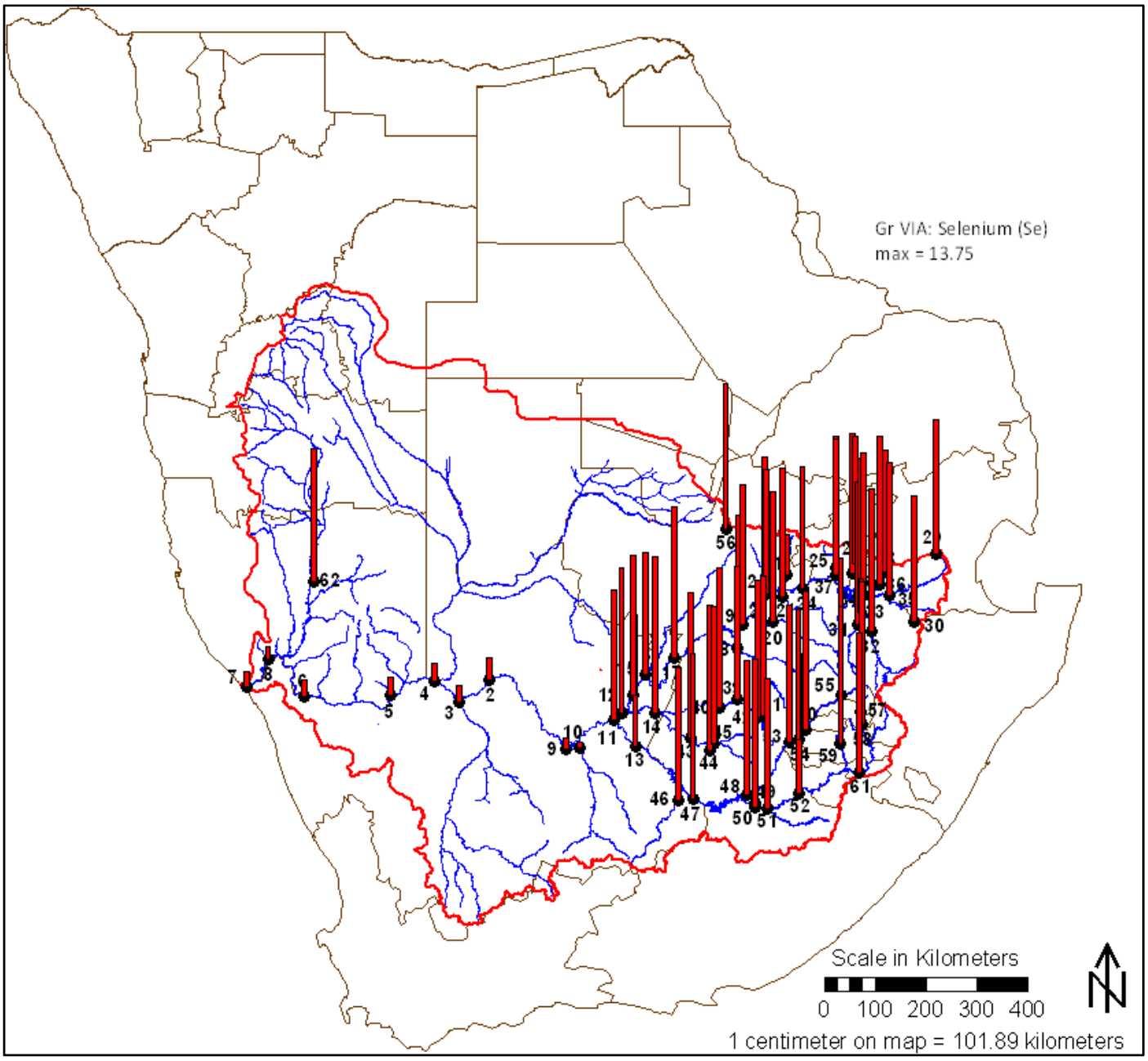

Figure 3.2.9: In Group VIA Se was the only element analysed for.

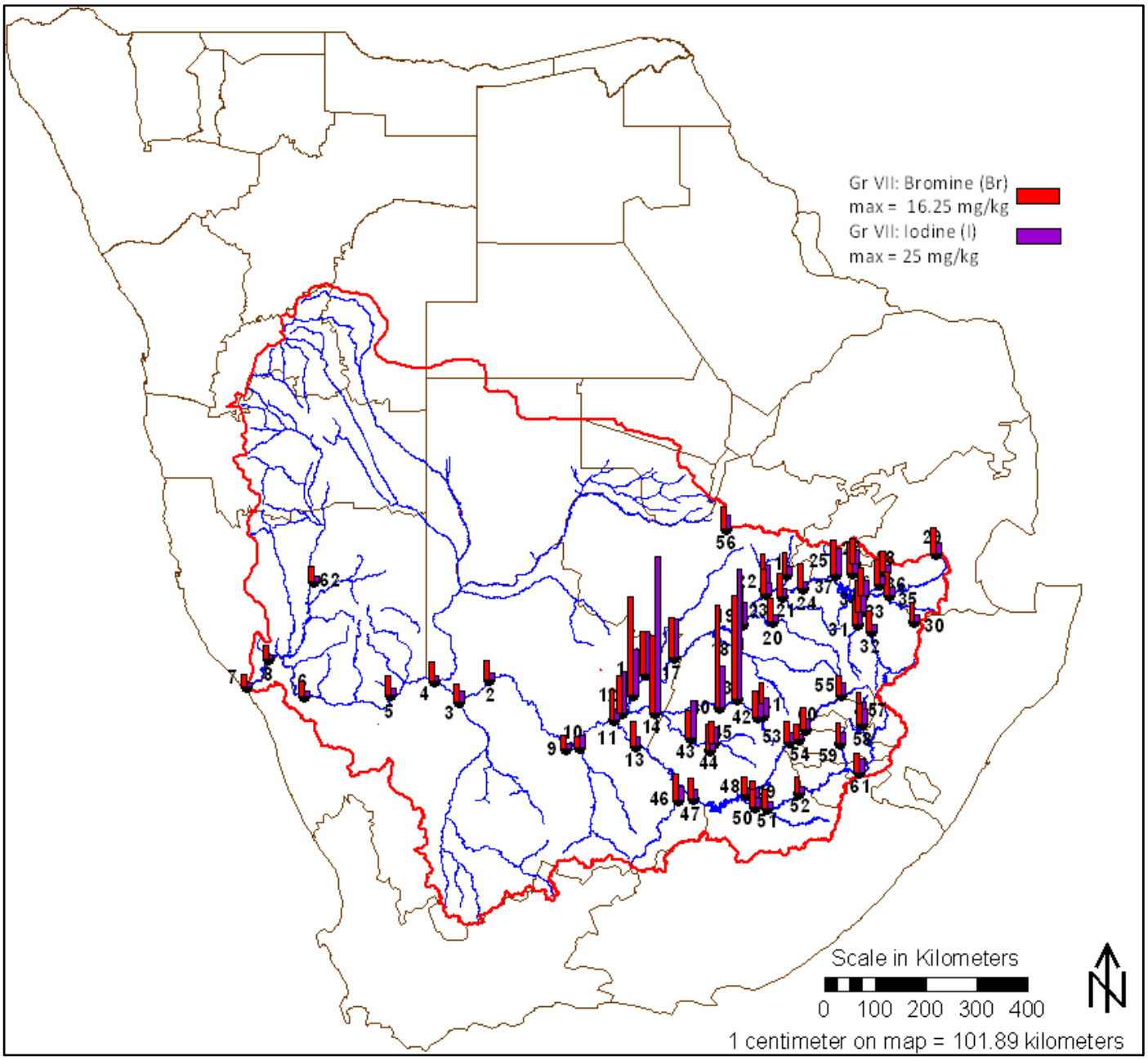

Figure 3.2.10: In Group VIIA only Br and I were analysed for.

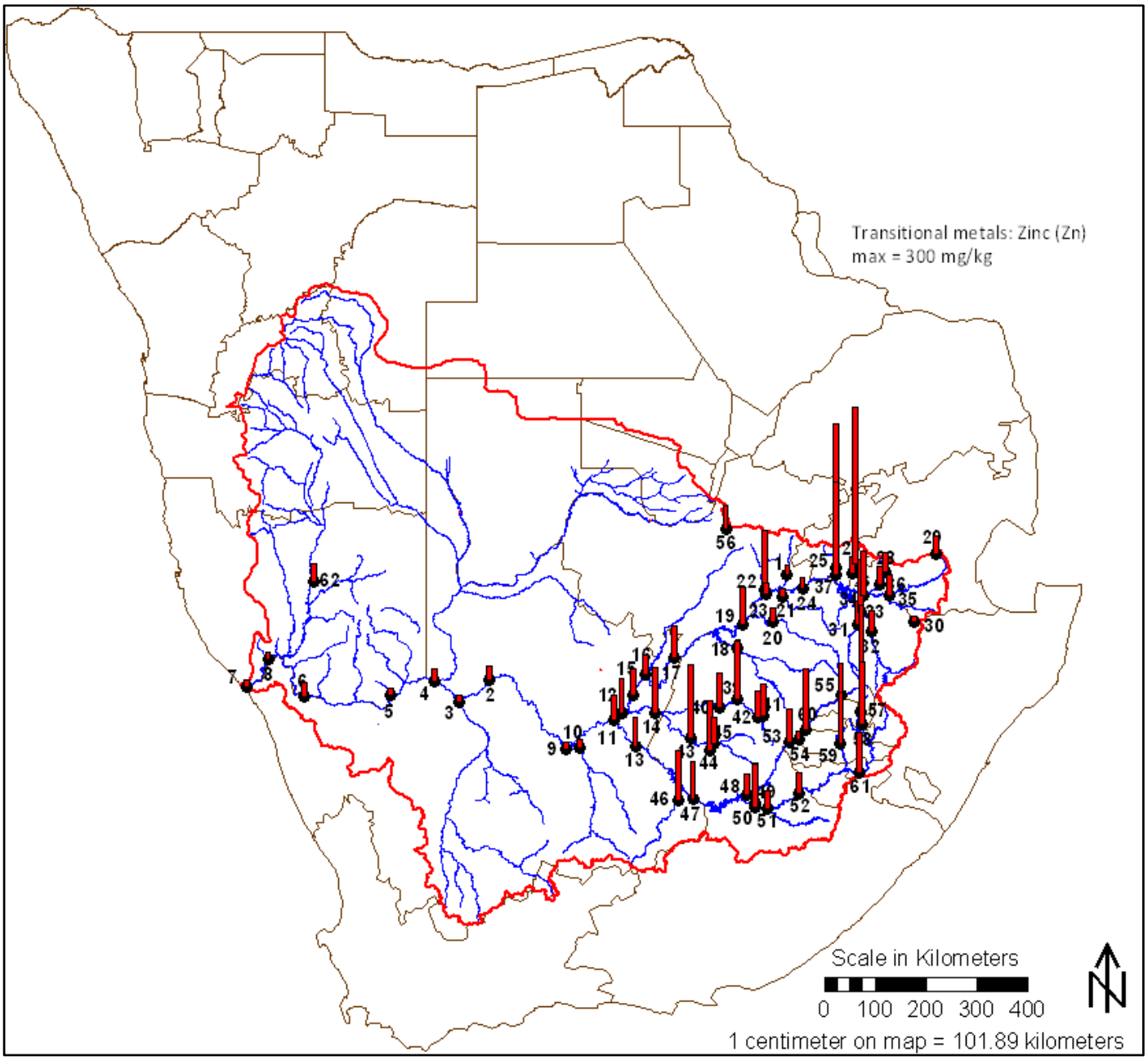

Figure 3.2.11: Zn was selected as the representative of all of the transitional metals analysed for.

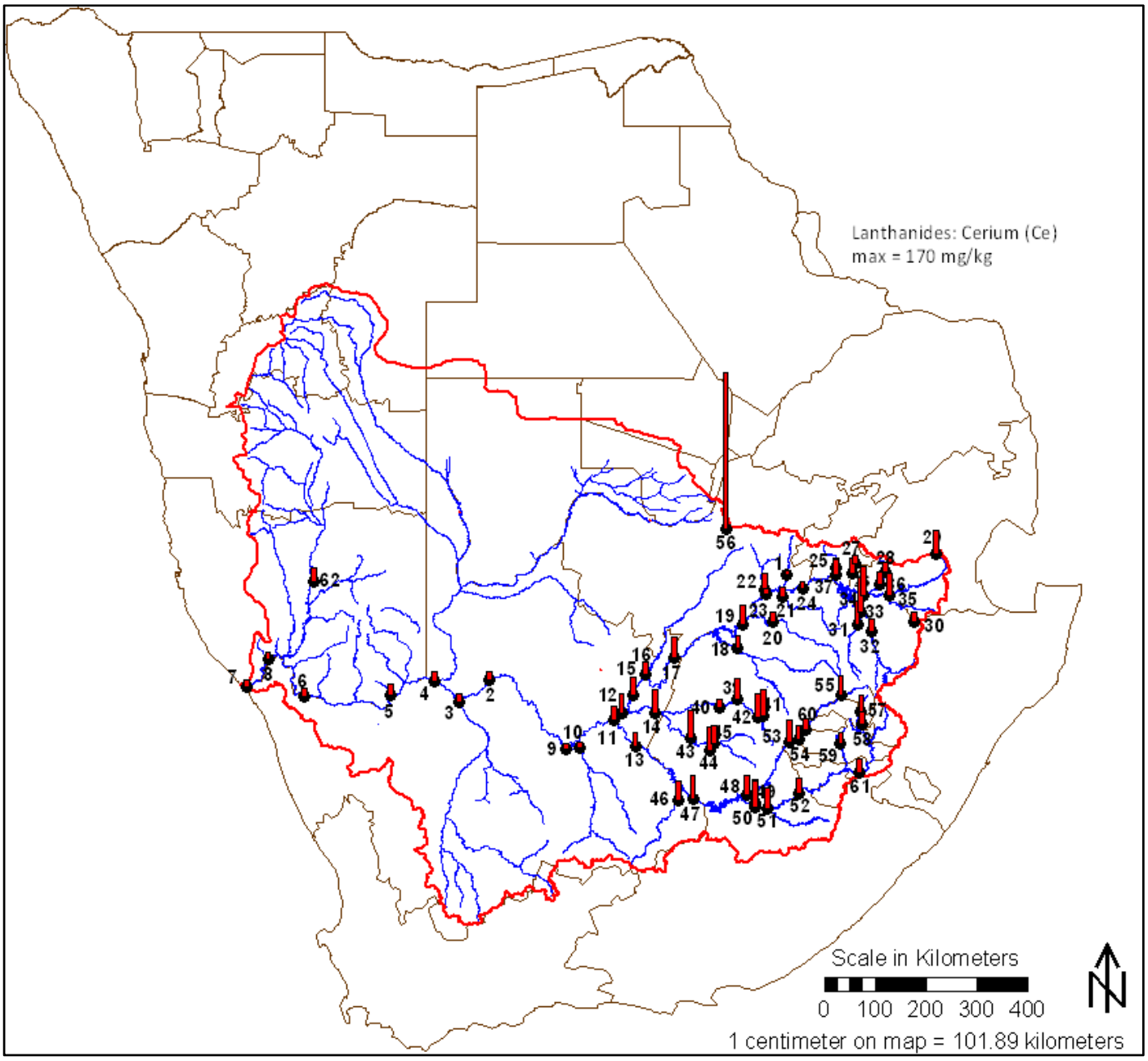

Figure 3.2.12: Ce was the only lanthanide analysed for.

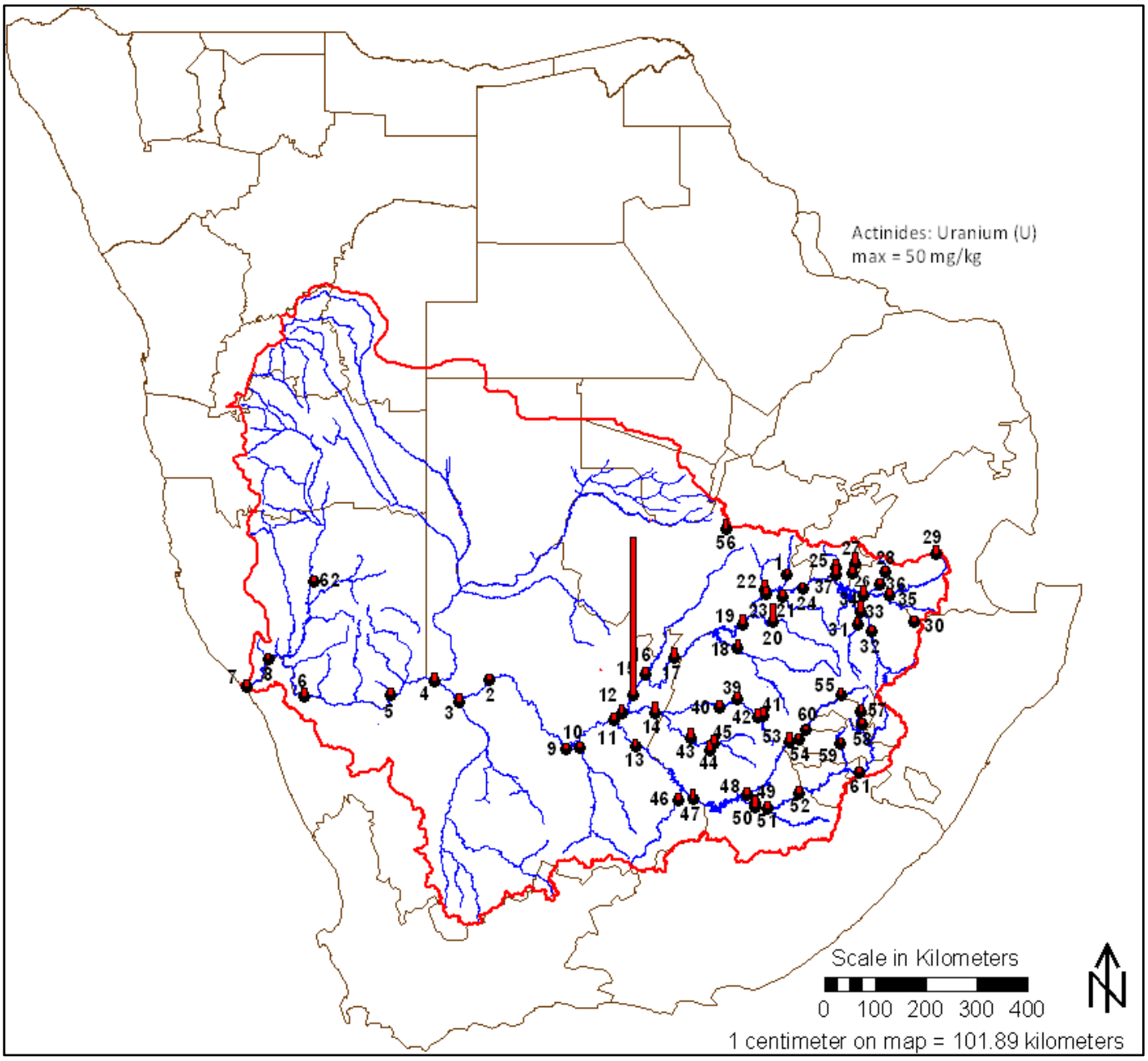

Figure 3.2.12: U was the only actinide analysed for.

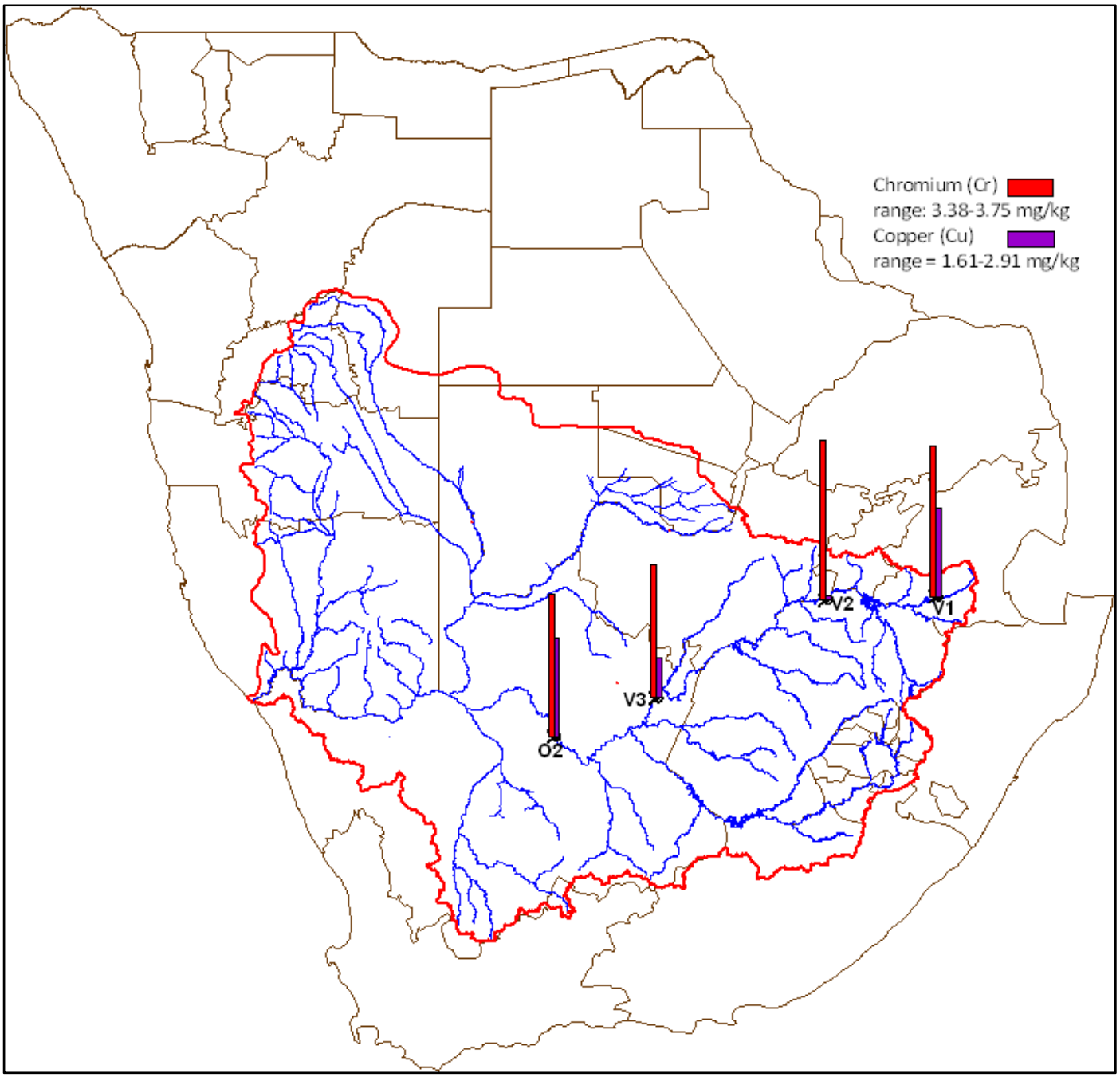

Figure 3.2.13: Cr and Cu levels in the fillets of the Sharptooth Catfish.

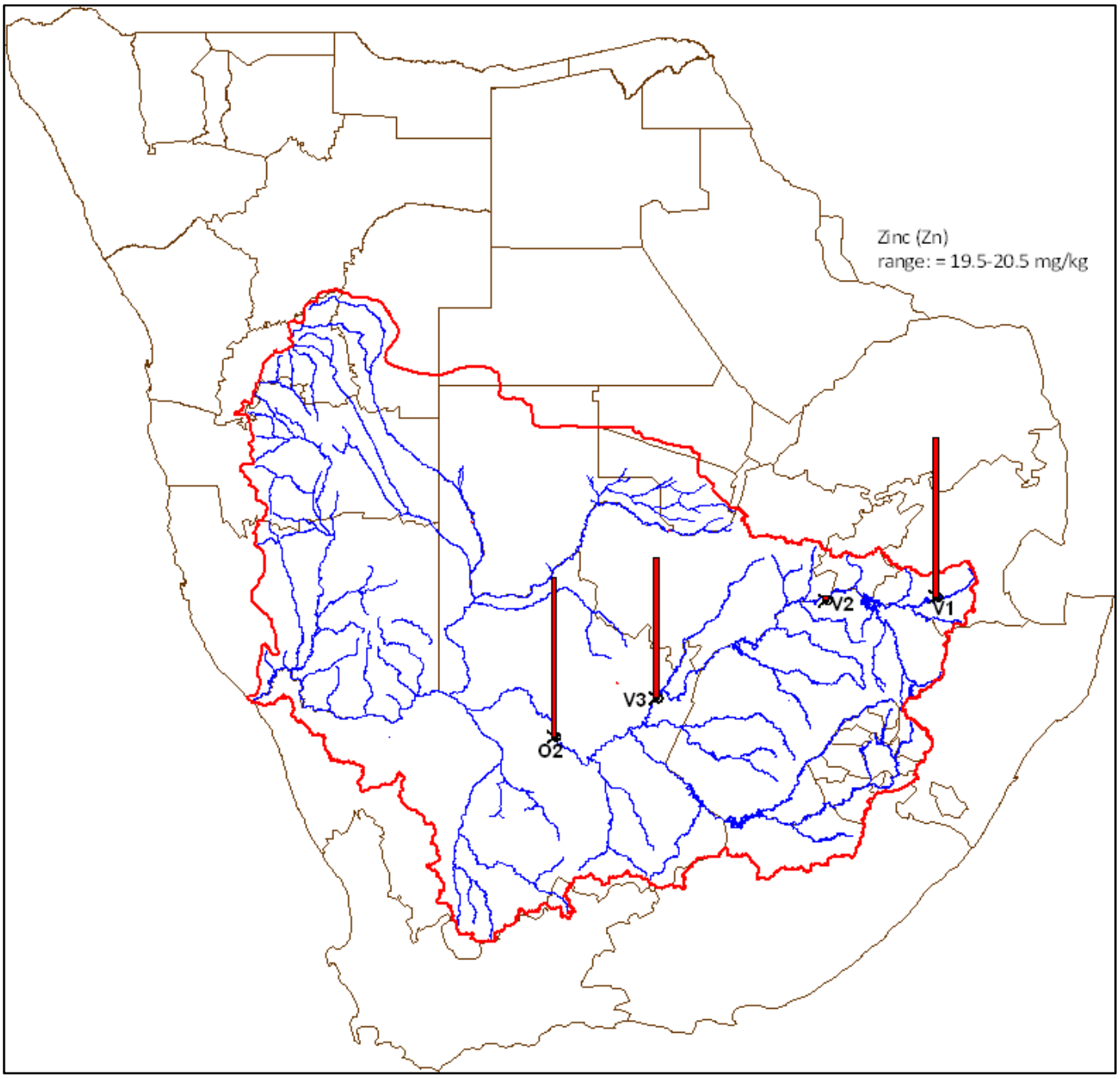

Figure 3.2.14: Zn levels in the fillets of the Sharptooth Catfish.

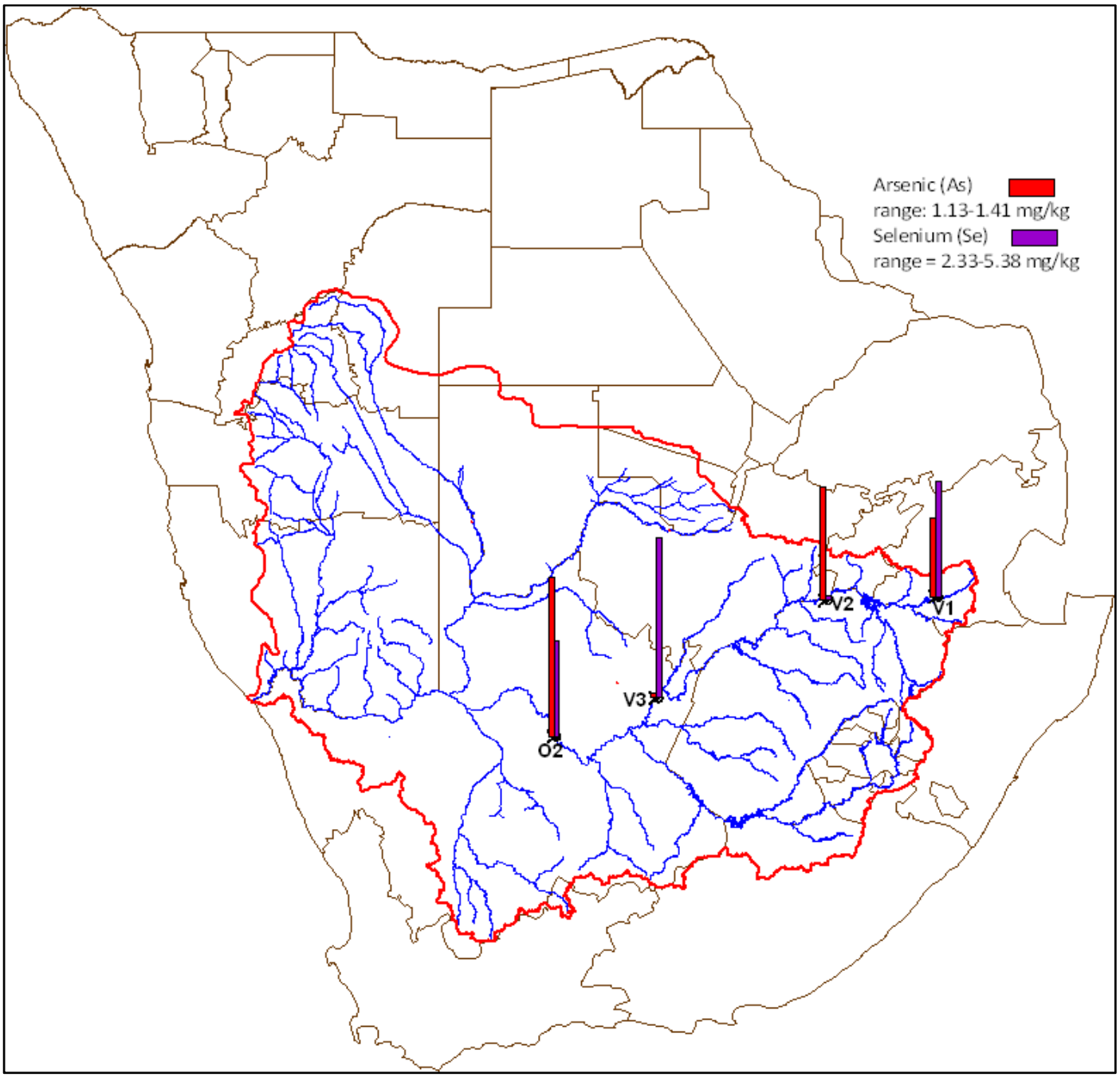

Figure 3.2.15: As and Se levels in the fillets of the Sharptooth Catfish.

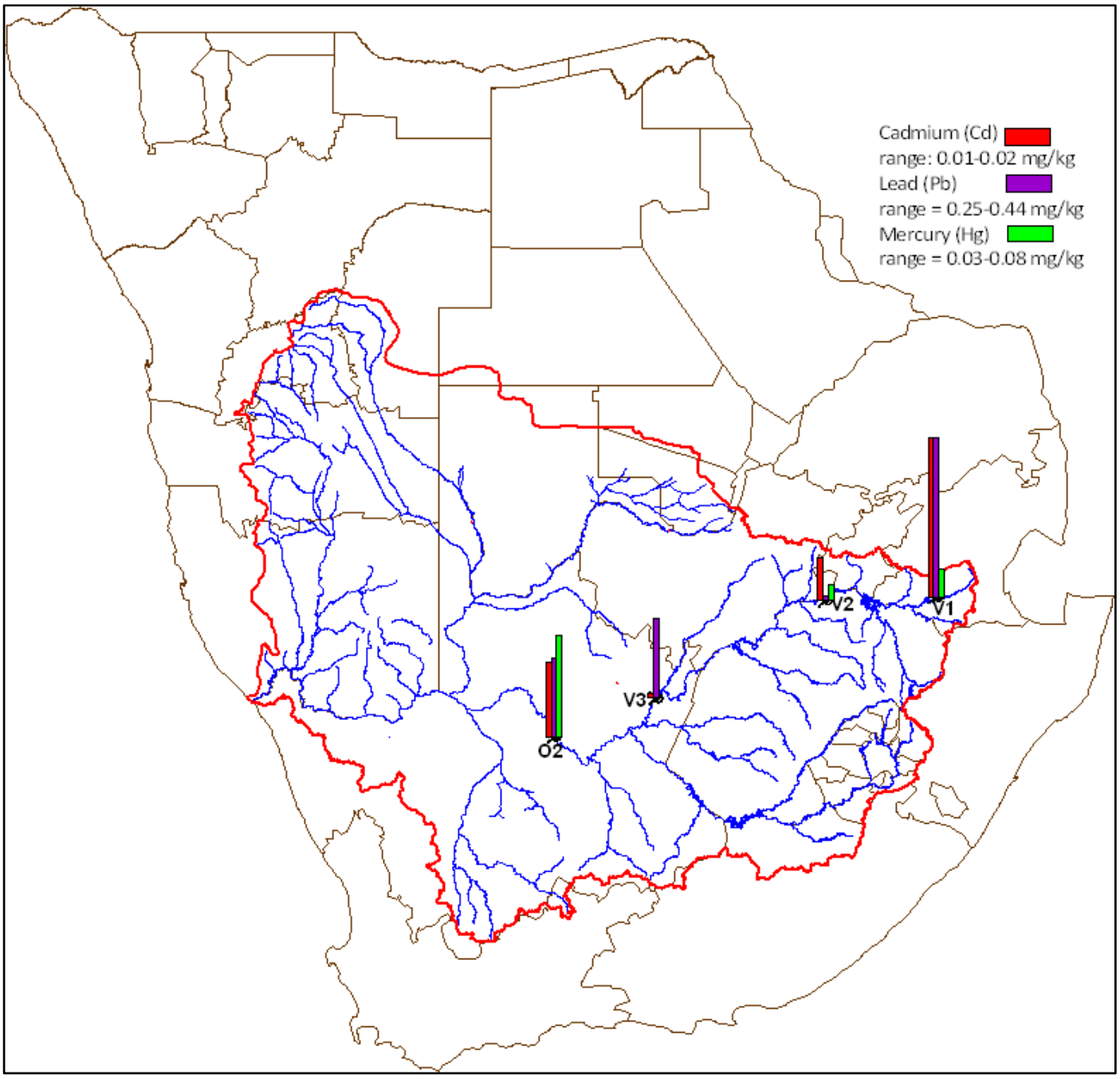

Figure 3.2.16: Cd, Pb and Hg levels in the fillets of the Sharptooth Catfish.

4 Conclusion

4.1 Persistent Organic Pollutants

4.1.1 Dioxin like TEQ

In general, dioxin like TEQ levels was low in all media, but indications of bioaccumulation were seen in from sediment (Figure 3.1.1) to fish (Figure 3.1.4) and from there to birds (Figure 3.1.8). TEQ levels were higher in sediment from the stern side, and seemed to become less towards the mouth. However, the TEQ levels in fish from Rooipoort need further investigation, and a species specific analysis is needed for birds. It needs to be pointed out though, that we have not sampled fish from the Gauteng region, and it would be very instructive to do some investigations here as well.

4.1.2 PCBs

PCBS in sediment (Figure 3.1.2), as for the dioxin TEQs (Figure 3.1.1) were higher towards the eastern than the western parts of the catchment, and then more into Gauteng. In biota, however (Figure 3.1.5 and 3.1.9) it seems as if fish and birds had higher levels towards the west. This pattern needs more investigation, as appreciable levels were found in some bird eggs, especially at Bloemhof Dam.

4.1.3 Organochlorine compounds

In sediments, OCs were mostly found in Gauteng, very little downstream from there (Figure 3.1.3). The picture in biota, again, differed from the sediment distribution pattern. Although the highest OC levels in fish were from Parys (Figure 3.1.6), in birds (Figure 3.1.10), the highest levels were from Bloemhof Dam. It would have been very instructive to sample the fish and sediments from Bloemhof Dam as well. However, the colony at Bloemhof Dam was only located after the fish sampling was completed. It would appear as if Bloemhof Dam could act as a biological retainer of some compounds.

4.1.4 PFOS

Although none of the sediments had detectable levels of PFOS, they were quantified in fish (Figure 3.1.7) and bird eggs (Figure 3.1.11). For both fish and bird eggs, concentrations seem to increase downstream. Although a more in-depth species specific assessment needs to be done. The surprisingly high levels of PFOS needs further exploration, as so little is known about this compound in Africa. Again, the area near Bloemhof Dam could do with some concentrated investigations.

4.1.5. Synthesis

Sediment had higher levels of POPs towards the east, decreasing drastically downstream towards the west, while the picture in biota seems almost the opposite. It does show that sediment analysis alone will not provide enough information on biotic levels and exposure. Levels below detection limits in sediments also will not allow human health risk assessments. In this study, we have shown that POPs are difficult to measure and more difficult to interpret, but that pollution distribution patterns on a catchment scale is very instructive in assessing the overall pollution picture and to derive some ideas of where hotspots or areas of interest might be.

To clarify some aspects it would be very instructive to sample fish from a number of additional areas including between Bloemhof Dam to Boegoeberg, Upington, Modder River, Klerksdorp, Potchefstroom, in or near Lesotho,

and Gauteng, while bird eggs from the colony at Upington would also be extremely helpful, especially regarding PFOS.

4.2 Heavy metals and trace elements

The levels of the elements in the sediment warrants further investigation, especially in the light of the I_{geo} values for Se, As and Hg. The geology of Orange/Senqu River basin needs to be considered. This assessment will be included in the final report.

When the sediment levels are compared to sediment quality guidelines for The Netherlands, all of the sites had a value less than 0.5, which is considered to be a low probability of being toxic. It was only the site at the Molopo eye that had a value of 1.6. This is regarded as having a high probability of being toxic to the biota in the system. Those elements for which the Dutch published guidelines, are As, Ba, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, and Zn (Adriano, 2001). The levels for U and Se were published elsewhere (Hamilton, 2004; Sheppard et al 2005).

An in depth comparison of the elemental levels in the sediment and the fish will also be included in the final report. At this stage it is already clear that most of the elements had higher levels in the sediment than in the fish fillet. Some of the elements had similar levels in both the sediment and the fish fillet, such as Br, Ag, and Sn. Those elements with higher levels in the fish fillet than in the sediment were K, Br, Rb and Pt. The levels of K in the fish fillets were almost five times that of the sediment. The levels of Br, Rb and Pt were barely higher in the fish than in the sediment. Proper statistical analysis still needs to be done.

The possible impacts of these pollutants on human health still need to be investigated. This will also be included in the final report.

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