Orange-Senqu River Basin

Orange-Senqu River Commission Secretariat
Governments of Botswana, Lesotho, Namibia and South Africa

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POPs, PAHs and Elemental Levels in Sediment, Fish and Wild Bird Eggs in the Orange-Senqu River Basin

Final Report

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POPs, PAHs and Elemental Levels in Sediment, Fish and Wild Bird Eggs in the Orange-Senqu River Basin
Final Report

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Contents

Executive summary

Study design

Four southern African countries, Lesotho, South Africa, Botswana, and Namibia share the basin of the Orange-Senqu River and are Parties to the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs). Currently, the SC targets 21 chemicals and classes of chemicals. Previously, the research in the Orange-Senqu Basin on POPs concentrated on pesticide POPs such as DDT. Only recently has more attention been given to POPs such as dioxins and PBDEs. Almost nothing is known about PAHs in the catchment, except for a recent Water Research Commission survey. There are also very few studies available on elemental levels in sediments. This study undertook a survey and assessment of POPs and heavy metals in water bodies and riverine sediments as contribution to the Transboundary Diagnostic Analysis (TDA) of the orange-Senqu River Basin. During the study, polycyclic aromatic hydrocarbons (PAHs) were added as additional research topic.

The entire Orange-Senqu River catchment was targeted for sediment collection and 61 sites were South Africampled in September 2010. Of the 61 sites, 33 were in the Vaal River catchment. The remaining 28 sites were Orange-Senqu River sites that did not drain into the Vaal River (Table 1). One site was in Namibia from and five from Lesotho. These sites largely conform to the sites used by other components of the TDA. Fish and wild bird eggs were South Africampled to investigate the levels of the compounds and elements in the biota of the Orange-Senqu River Basin.

Figure 1: Sediment South Africampling sites (left) and fish and bird egg South Africampling sites (right).
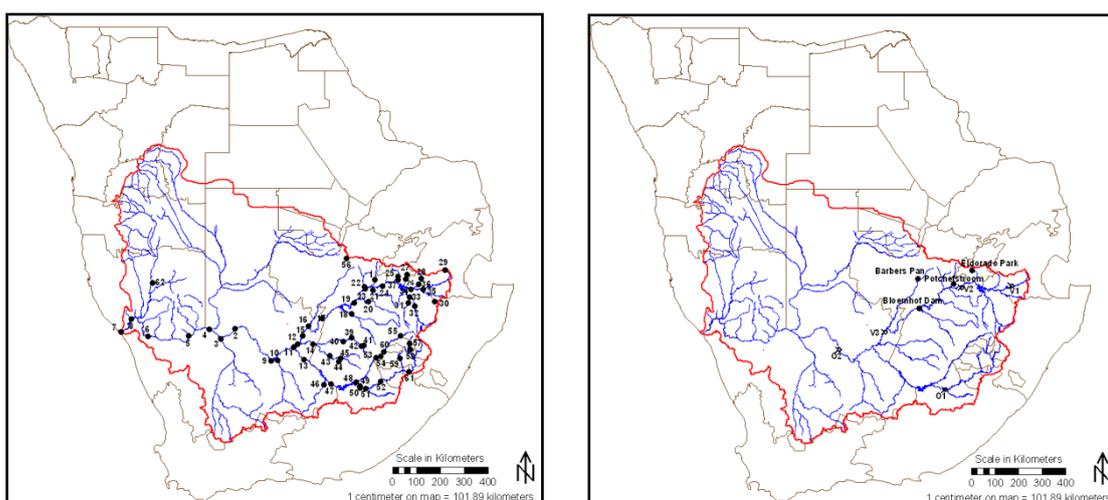
South Africamples were prepared and sent to Germany for analyses for POPs and PAHs. South Africamples were also analysed for complete elemental composition at Potchefstroom.

Results and discussion

Organic compounds

Dioxin like TEQ: In general, dioxin like TEQ levels was low in all media, but indications of increase in TEQ (possibly due to bio-accumulation) were seen from sediment to fish and birds. TEQ levels were higher in sediment from the east, becoming less towards the mouth. However, the relatively higher TEQ levels in fish from Rooipoort need further investigation, and a species-specific analysis is needed for birds.

PCBs: PCBS in sediment, as for the dioxin TEQs, were higher towards the eastern than the western parts of the catchment, and then more into Gauteng. In biota, however, 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.

Organochlorine compounds (OCs): In sediments, OC levels were higher in Gauteng, and less downstream. The picture in biota differed from the sediment distribution pattern. Although the highest OC levels in fish were from Parys, in birds the highest levels were from Bloemhof Dam. It would have been very instructive to South Africample fish and sediments from Bloemhof Dam as well. It would appear as if Bloemhof Dam could act as a retainer of some compounds coming from upstream.

PFOS: Although none of the sediments had detectable levels of PFOS, they were quantified in fish and bird eggs. 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.

PAHs: The three sediment sites with the highest ∑PAH levels were downstream of both urban and industrial areas in South Africa and Lesotho. The source for the PAHs were pyrogenic in nature, often due to the combustion of coal or smelters. The most common PAH was fluoranthene, followed by phenanthrene and benzo(b+k)fluoranthene.

Synthesis of organic compounds: 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 in sediment are difficult to measure and more difficult to interpret. However, using pollution distribution patterns on a catchment scale assists in assessing the overall pollution picture and to identify hotspots and areas of interest.

Elements

The Metal Pollution Index for sediment site 56, the Molopo Eye, was the highest and when the Igeo-values were determined, the South Africame site had the most elements with Igeo-values regarded as polluted. The South Africame site was also among the 25% sites with the most elements with the highest levels. A cluster of sites in the Riet and Modder Rivers also belonged to this 25% sites with the most elements with the highest concentrations. Shared geology between some of the sites could only partially explain this phenomenon, but in-depth investigation of the area is deemed necesSouth Africary to determine the exact cause. Two sites in Lesotho (58 and 57) with high levels of elements are likely to be due to geology rather than mining activities or any other anthropogenic activities. The levels of the elements in the sediment warrant further investigation, especially in the light of the Igeo values for Se, As, and Hg. However, intensive investigation into the natural background levels for these elements is needed to clarify this observation.

When the sediment levels are compared to sediment quality guidelines for The Netherlands (for As, Ba, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Zn, U and Se), all sites had levels less than half the sediment quality guidelines, which is considered to be a low probability of being toxic. It was only the site at the Molopo Eye (56) that had a value of 1.6. This is regarded as having a high probability of being toxic to the biota in the system.

The levels of Cu, Cr, Zn, As, Se, Cd, Pb and Ag in the fish fillets were compared to international guidelines deemed South Africafe for human consumption. It was only the Se levels that were higher than the guideline levels. At site V3 it was twice as high as the highest allowable level. Those elements that seemed the most likely to bioaccumulate in the fish, should exposure to sediment be their only exposure pathway, and all of elements were to be bioavailable, were Pt > Rb . > Au > Sn > Ag > Rh. None of the other elements had bioaccumulation factors greater than 1. Further assessment is needed on the bio-available fractions of the elements at the sites identified.

Sn had the highest level in bird egg, followed by Fe. Sn, Fe, B, and Zn had the highest levels at each of the bird egg collection sites. All elements had bioaccumulation factors greater than 1, except for Cs, but this is only a broad indication of possible bioaccumulation in the catchment as these calculations were done under a number of assumptions.

Health risk assessment

The health risk assessment examined whether possible human health effects might be anticipated based on chemical contaminants detected in sediment, wild bird egg and fish South Africamples. In order to determine whether this is possible, a human health risk assessment was conducted modelling the chemical contaminant concentrations expected in fish based on levels detected in sediments. Trans-media calculations (sediment to fish) were conducted based on individual chemical parameters.

The screening risk assessment identified the chemicals that could be responsible for adverse health effects if fish were to be eaten, over a 30 year period. The contaminants over the risk threshold were identified as arsenic, benzo(a)pyrene, PCBs, chromium and selenium. The type of adverse effect that might result was also identified as predominantly carcinogenic associated with arsenic, benzo(a)pyrene and PCBs exposure, with other toxic effects being anticipated from heavy metal exposure to chromium, arsenic and selenium.

This screening risk assessment has highlighted that possible health risks can be anticipated resulting from ingestion of fish or eggs on a regular basis. There are many uncertainties in any health risk assessment, and this study presents a screening or rapid human health risk assessment. This was used to provide an indication of potential health risks and should be investigated in more detail. In addition to South Africample variation, dose calculations also represent uncertainty, based on the assumption of the number of times a year that people eat fish and the amount of fish eaten. The identified human health hazard will have to be evaluated in more detail before interventions are planned.

Beryllium, and especially arsenic, in all media investigated, presented high risks of developing cancer. The risk of developing cancer from the consumption of wild bird eggs, is as high as 1 in a 1000. PAHs were only measured in sediment and the following pose between a 2 in 100 000 and 5 in 100 000 risk for the development of cancer; indeno(1,2,3 –cd) pyrene, benz(a)anthracene, benzo(b) fluoranthene and benzo(k)fluoranthene. Benzo(a)pyrene in sediment poses an "unacceptable" cancer risk of 1 in 10 000. This sediment South Africample was collected from site 64 which also had significant pyrene, benz(a) anthracene, chrysene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene and pyrene concentrations. Of the persistent organic pollutant, PCBs in wild bird eggs pose a 2 in 10 000 cancer risk. This wild bird egg South Africample was taken from Bloemhof Dam which also posed a significant arsenic cancer risk.

High toxic health risks (HQ) were found for arsenic in the wild bird eggs and fish. These HQ values exceed 3 which suggest a serious health risk posed. The chromium and selenium HQ value in the wild bird eggs also exceed 1, and pose a possible health risk.

Areas of concern

Organic compounds in sediments

In general, the levels of all compounds except PAHs were fairly low, but with strong indications that industrial activities and combustion (pyrogenic) processes contribute. The levels of higher benzo(a)pyrene were deemed to pose unacceptable high cancer risks. The highest concentrations (and therefore the higher risks) were found at sites 16, 17, 22, 54, 60 and 64. The sources of the PAHs at all these sites were pyrogenic in nature, but the exact type of activity needs further on-site investigation. Dioxin TEQ and indicator PCBs were associated with industrial activities in Gauteng and possibly mining or residential combustion in the North-West Province. The relatively high

levels in and close to Lesotho cannot be explained as we have very little knowledge of any activities or conditions that could explain such quantities. The generally low levels of organochlorine pesticides found in sediment is a positive finding. However, detectable levels found at Blesbokspruit, Suikerbosrand, Potchefstroom, and Klerksdorp needs careful monitoring.

Organic compounds in biota

Our results show that the levels of organic compounds do not reflect the levels in sediments. Care should be taken with interpretation as the biota were not collected at sites that were South Africampled for sediments. The low number of available sites for fish and bird eggs South Africampling hinders interpretation. However, the patterns do not quite agree with what is seen in sediment. Except for organochlorine pesticides, the highest levels of dioxin TEQ, PCBs and PFOS were from isolated sites, far removed from industrial areas. The high levels of PFOS in fish at Boegoeberg and Rooipoort, and in bird eggs from Bloemhofdam and Barberspan suggests sources other than industry. It might be linked to unknown releases from agriculture (although it should then be similar to OC distribution), or unknown uses in mining in the drier, central parts of the country. There are no indications from literature on this. The high levels of PFOS in bird eggs from a dam and a pan suggest that impoundments be act as a trap for PFOS. The levels of PFOS are quite high compared to European levels. Although a health risk could not be assessed due to lack of supporting data, PFOS sources and environmental distribution needs much scrutiny. Consumption of PFOS via fish by humans could be a serious concern.

Elements in sediment

The elemental composition of sediments was difficult to associate with sediment source geology due to the very complex geology of the system, the huge drainage area covered, and the numerous tributaries and flood events. It must be noted that this assessment is based on complete digestion of the sediment and does not imply that these elements will be in water or bio-available. It has however, found areas of concern where more in-depth assessments should be done to determine whether the levels are higher than other areas because natural background or due to disturbance, agricultural run-off, industry, urbaniSouth Africation, mining, or a combination. The health risk assessment found concerns for arsenic, chromium, and selenium. Based on elemental analyses and risk assessment of sediments from 61 sites, the areas in the Orange-Senqu basin that were deemed to be of concern are:

- Molopo Eye (56) due to Ga, Cr, Mn, Ni, Ag, and Se,
- Vaal River at Schmidtsdrift (15) due to uranium,
- The areas associated with the Riet River and Koranna Spruit (12, 14, 39, 41, and 44) due to a combination of higher than average levels of several elements,
- The Caledon and Makbomatso Rivers draining into the Senqu and Orange-Senqu Rivers (49, 50, 55, 57, 58, and 60) due to a combination of higher than average levels of several elements,

- Skoon Spruit (22) due to higher than average levels of Fe, Ni, and other elements,
- Fish River, due to higher than average levels of As.

Elements in biota

The major activity of this survey was on sediment levels of compounds. Bio-availability can be ascertained by looking at elemental levels in biota. The elements in biota are derived from the environment and are therefore taken up by fish and birds as they are bio-available. Fish and bird eggs were collected from four sites each. Arsenic and beryllium was found to pose significant cancer hazard in bird eggs and fish. This aspect needs further investigation as the sites with higher levels in eggs and fish were mostly far away from industry and it was not possible to determine the sources. The levels in bird eggs in particular needs closer scrutiny, as very little data is available on the impacts of these elements on biota and the humans and other organisms that consume them.

Recommendations

Organic compounds

- Communities potentially exposed to hazardous levels of PAHs should be identified and investigated as to sources of pyrogenic composition. Interventions can then be proposed to reduce PAHs emissions. Such interventions would also reduce releases of dioxins and PCBs.
- The probability exist that there are more sites and communities that may experience hazardous exposures from PAHs than was covered by this system-wide survey. This study has identified both pyrogenic and petrogenic sources, and additional areas can now be identified from activities alone. Concentrations of industry, mining and residential areas seem to characterise areas with high PAHs levels in sediment.
- The dynamics and sources that resulted in the higher than expected levels of certain organic compounds (especially PFOS) in biota in isolated areas need to be better understood. The risks these compounds pose to biota needs to be better understood as the number of South Africamples that could be analysed were restricted.
- A monitoring programme should be instituted to track changes.
- Historic South Africamples should be stored, as more compounds are likely to be added to the Stockholm Convention. Collections then need not be repeated, as South Africamples will be available.

Elements

- Now that specific areas of concern have been identified, more attention should be targeted on these areas on determining sources and processes, as well as the bio-availability of these elements in water and sediment.

- Attention should be given to identify communities that may be exposed to higher than recommended levels of elements in water and water-associated food. Water used for irrigation for instance, may contaminate produce.
- Historic background levels seemingly have never been collected on this scale before, and the data collected should be curated such that future comparisons and trend monitoring can be made.

1. Introduction

1.1 Study background and aim

The Orange-Senqu River originates in the Lesotho Highlands, from where it flows westwards to its mouth at Alexander Bay/Oranjemund on the Atlantic West Coast. The river basin is the third largest in southern Africa, after the Zambezi and the Congo, covering a total area of 1,000,000 km2. Four countries – Botswana, Lesotho, Namibia, and South Africa - share the basin.

Lesotho, the upstream country falls entirely within the basin and contributes over 40% of the stream flow from only 5% of the total basin area, but is one of the smallest users of water from the basin. South Africa, with some 60% of the basin area is by far the biggest user of water, this use drives the economic heartland of South Africa. The Botswana part of the basin is entirely covered by the Kalahari Desert with very little surface runoff, but groundwater contributes to the water demands in this portion of the basin.

The water requirements in the lower reaches of the river are driven primarily by irrigation demands from both Namibia and South Africa, and the need to maintain environmental flows to the estuary. As the most downstream portion of a heavily used basin, water quality in this stretch is a concern. Similarly, the middle and lower reaches of the river are subject to periodic and often devastating floods. The Orange-Senqu River estuary is ranked as one of the most important wetland systems in southern Africa, but has experienced environmental degradation. The wetland system was designated as a RamSouth Africar Site, but because of its threatened status was placed on the Montreux Record.

The effective management of the Orange-Senqu River Basin is therefore particularly complex, but is also vital to the economy of the region. As a result, the riparian States prioritised this basin for the establishment of a Shared Watercourse Institution under the revised Southern African Development Community (South AfricaDC) Protocol on Shared Watercourses. The Orange-Senqu River Commission (ORASECOM) established in 2000 was one of the first of the joint basin commissions to be established under the Protocol. The Orange-Senqu River Basin Environment Programme (also the ORASECOM Programme), agreed at the Council Meeting in April 2007, brought the various ICP supporting ORASECOM under one umbrella. The Programme includes six thematic areas: Institutional and organiSouth Africational strengthening; Capacity building on shared watercourse management; Information System; Communication and awareness building; Trans-boundary projects and studies; and Conservation and environmental strategies and policies.

The preliminary Trans-boundary Diagnostic Analysis (TDA) of the Basin, compiled during the preparation of the UNDP GEF Orange-Senqu Strategic Action Programme and adopted by ORASECOM in April 2008 noted several knowledge gaps, among them the lack of basin wide and

consitent information on persistent organic pollutants (POPs) and heavy metals. These areas were addressed in this study. During the course of the work, polycyclic aromatic hydrocarbons (PAHs) and a human health risk assessment were added to the study's scope.

1.2   POPs, PAHs and heavy metals

Four southern African countries, Lesotho, South Africa, Botswana, and Namibia share the catchment of the Orange-Senqu River System and are Parties to the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs). 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 South Africa 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 South Africa 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.

Polycyclic aromatic hydrocarbons (PAHs) are composed of carbon and hydrogen atoms arranged in the form of fused benzene rings (Sims & Overcash, 1983). The widespread occurrence of PAHs is largely due to their formation and release in all processes of incomplete combustion of organic materials such as: production of coke and carbon, petroleum processing and aluminium sintering, furnaces, fireplaces, gas and oil burners, coal power plants and mobile sources like cars, lorries and trains (Maliszewska-Kordybach, 1999). Releases from petroleum and coal are also possible. Natural

sources such as volcanic activity contribute only slightly to environmental PAH levels. However, the releases from vegetation fires are unknown in southern Africa. All of these sources occur in Southern Africa (Nieuwoudt et al., 2011).

Of the thouSouth Africands of PAH compounds, the United States Environmental Protection Agency (US EPA) has classified 16 of them as priority pollutants based on toxicity, potential for human exposure, frequency of occurrence at hazardous waste sites, and the extent of information available (ATSDR, 2005). The emphasis of this propoSouth Africal is on these 16 PAHs naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorene, fluoranthene, *benzo(a)anthracene, chrysene, pyrene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene,* benzo(g,h,i)perylene, indeno[1,2,3-cd]pyrene. [The compounds in italics in the list are regarded as human carcinogens (NTP, 2005)].

It is known that PAHs are present in the South African environment, specifically in sediment from the Vaal River catchment of the Vaal Triangle (Nieuwoudt et al., 2011). The total concentration of PAHs (Σt-PAH) ranged between 44 and 39,000 ng/g, dw and the concentration of carcinogenic PAHs (Σc-PAH) ranged between 19 and 19,000 ng/g, dw. Pyrogenic processes (burning processes) were the most likely sources, with minimal petrogenic (derived from fuels and oils) contributions. PAH levels were in the South Africame range as levels reported from other countries. In a parallel study completed for the Water Research Commission on freshwater sites throughout the entire country, the PAHs had the highest levels of all of the organic pollutants analysed for. One of the sites with the highest PAH levels, was in Soweto/Lenasia with ΣPAHs of 5,528,000 ng/kg (Roos et al, in press).

One of the main mineral commodities mined in South Africa, 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 also releases from the mine tailings dumps. 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, impacting 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 have been conducted. Studies carried out on the Vaal River have shown that fish accumulate heavy metals released by industries and other sources (Crafford, 2000; Groenewald, 2000; Kotze, 2003; Retief, 2006). 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

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 were in the Vaal River catchment. The remaining 28 sites were Orange River sites that did not drain into the Vaal River. One site was in Namibia from and five from Lesotho (Table 1 and Figure 3).

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

Site number	River	Coordinates longitude	latitude	Country	River system
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

Site number	River	Coordinates		Country	River system
		longitude	latitude		
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

Site number	River	Coordinates		Country	River system
		longitude	latitude		
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). 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).

Figure 1:   A diagrammatic representation of the Orange-Senqu Rivers Basin without the Vaal River Catchment (cf Fig 2) ⊗ *= city/town, R = River, D = Dam (not to scale).*
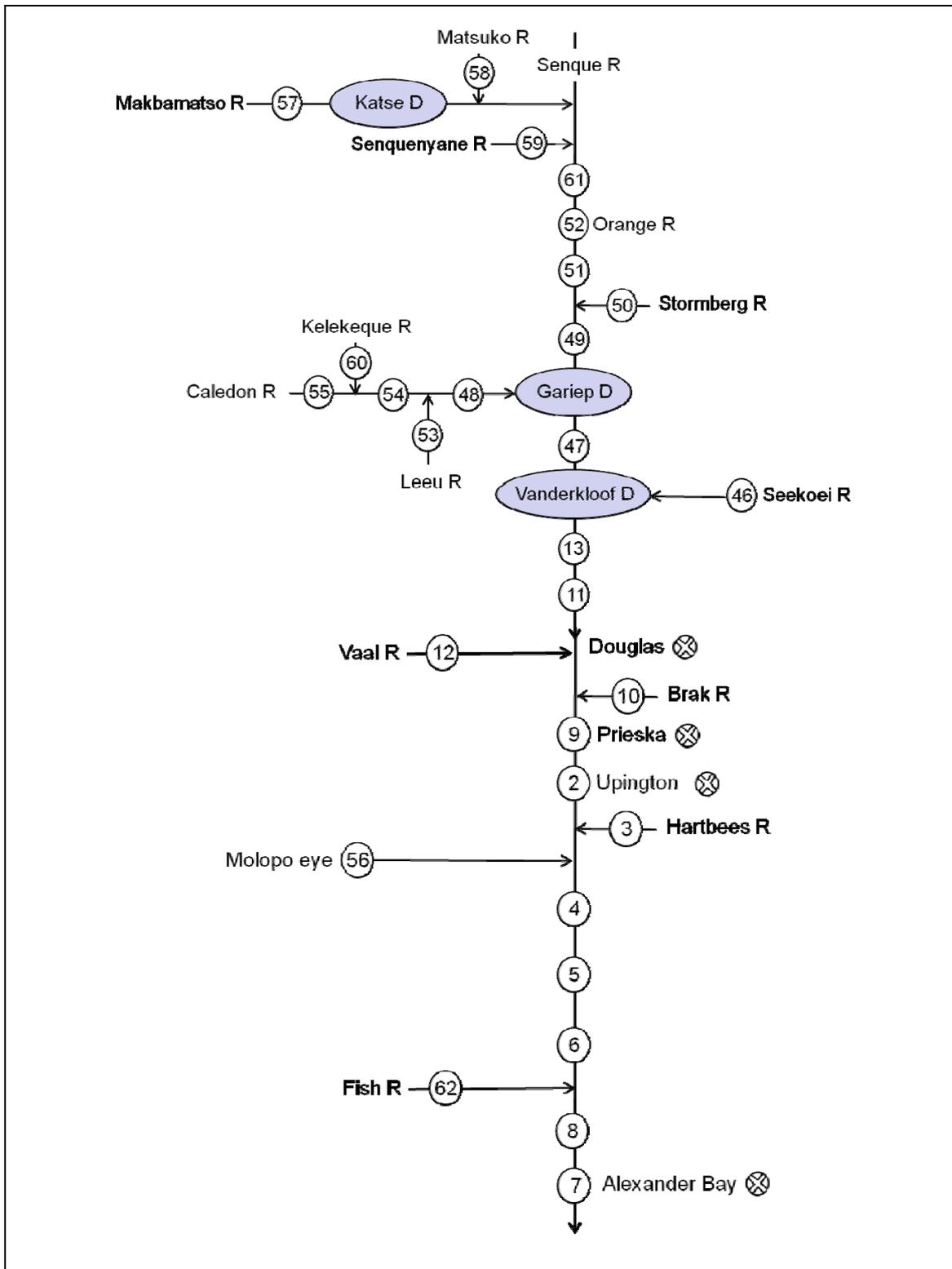
Figure 2: A diagrammatic representation of the the Vaal River Catchment (cf Fig 2) ⊗ = *city/town, R = River, D = Dam (not to scale).*
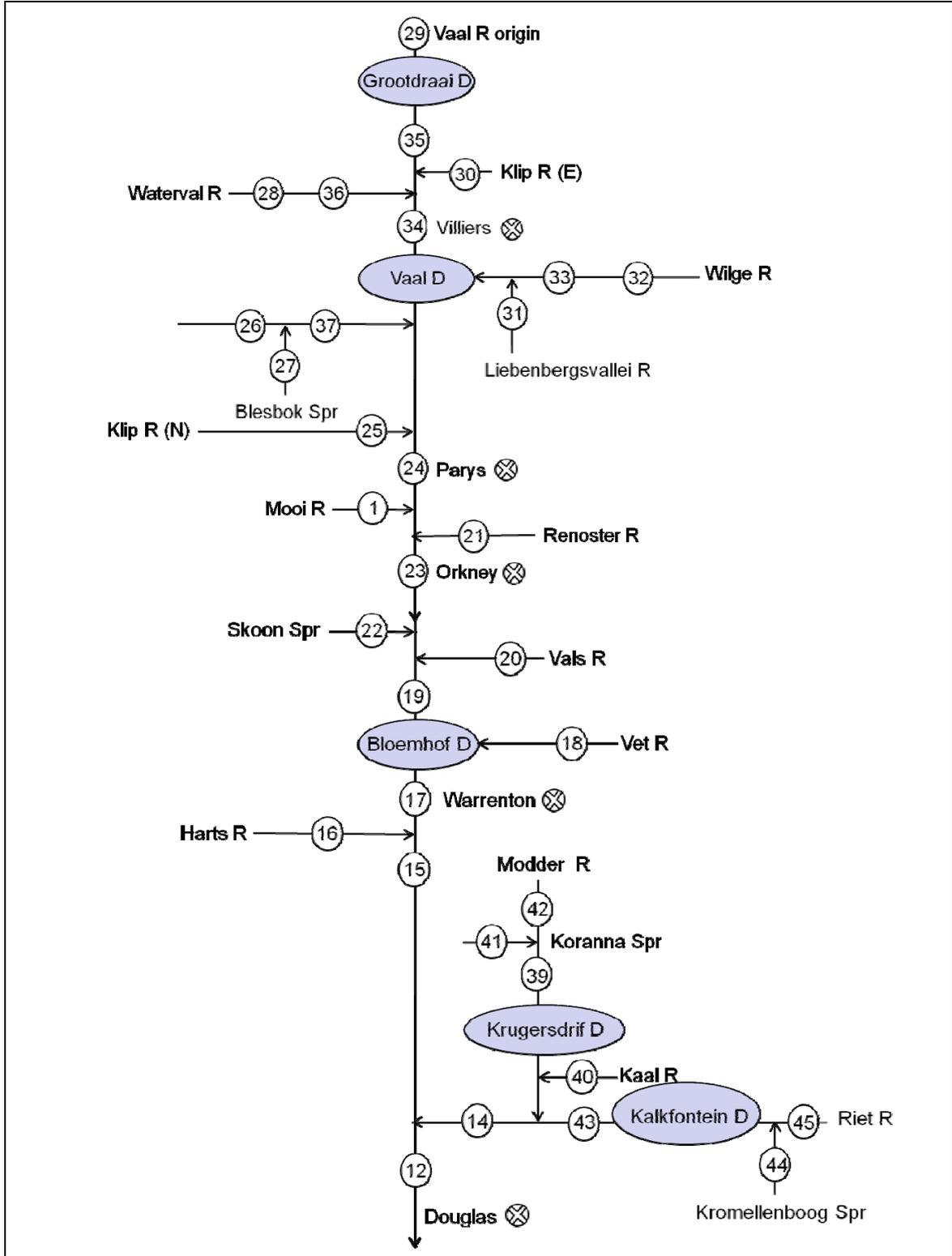
Figure 3: Sediment sampling sites
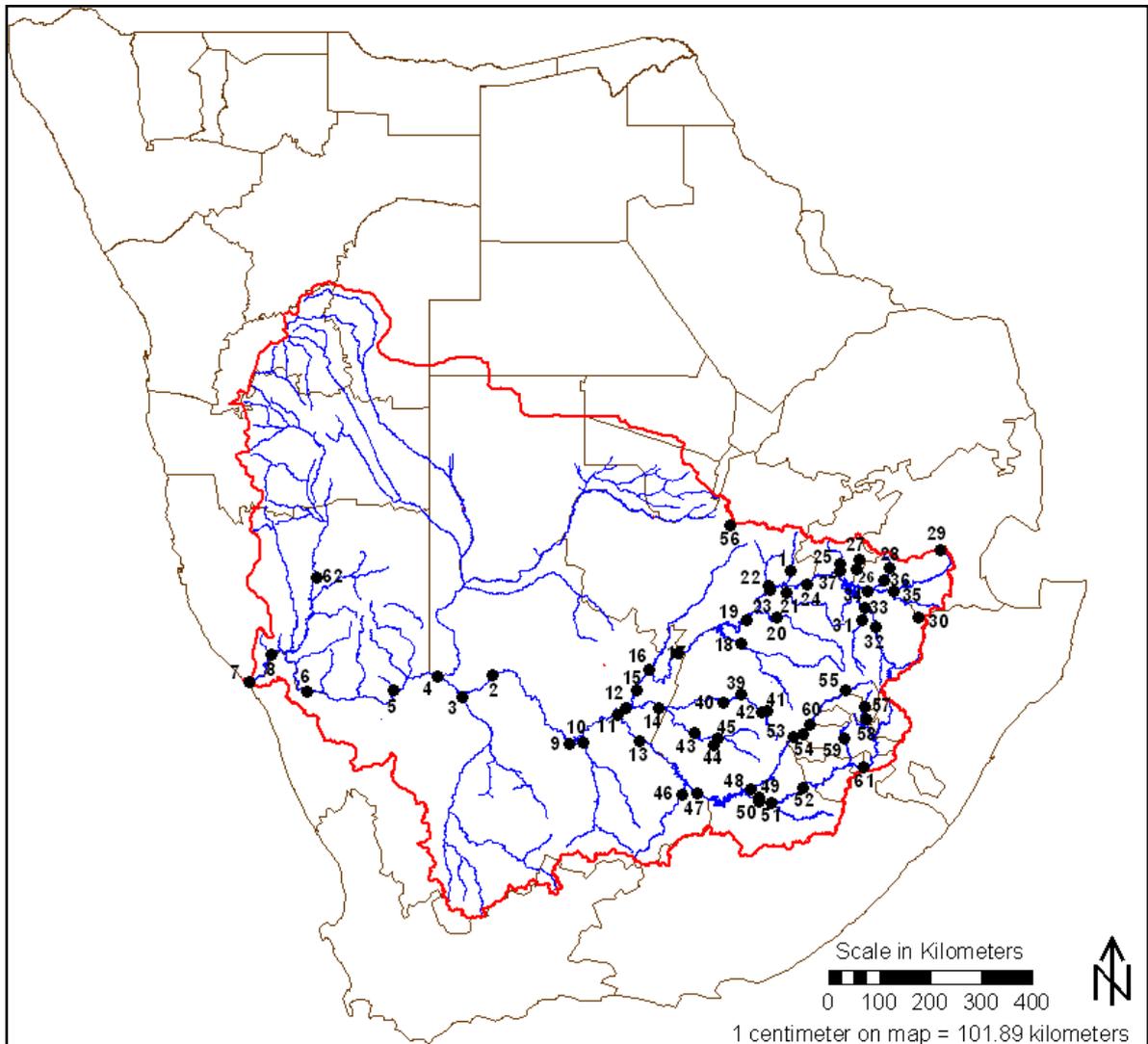
Fish and bird egg collection sites

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

Although five fish sampling sites were initially targeted, we were successful at only four. As the main tributary, and a known polluted river, the Vaal River was targeted for fish sampling (V1 and V2; Figure 3). V1 is at Standerton in Mpumalanga 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. A comparison between V1 and V2 would 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 an up-stream and downstream site in the Orange River could not be done.

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

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 (Medvedev & Markove, 1995; Lebedev et al., 1998) since eggs:

- 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; and
- can be sampled randomly.

Table 2:   Fish and wild bird egg sampling sites

Sample type	Site name/label	Coordinates longitude	latitude	Location name	River
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

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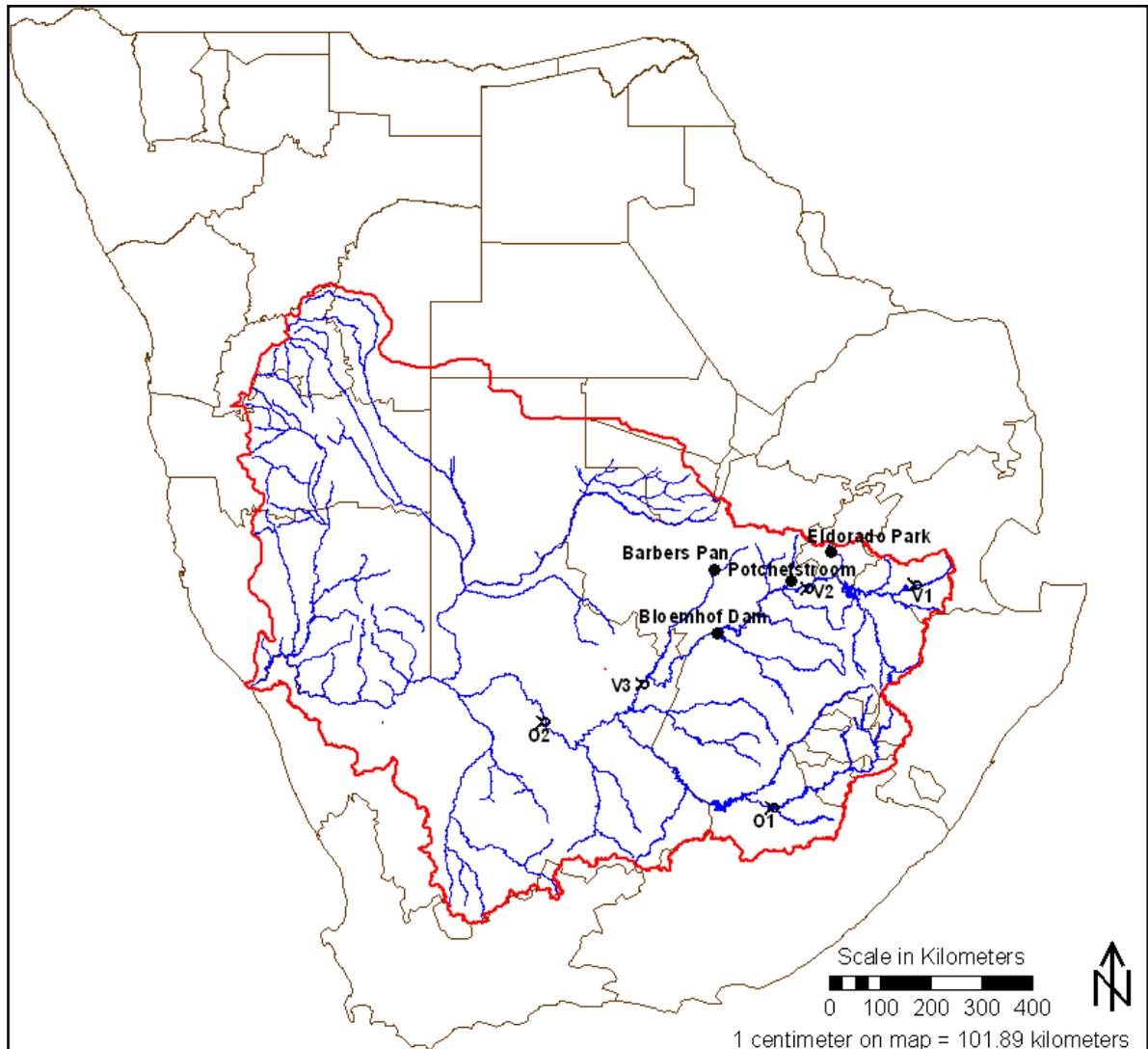
2.2   Sampling and sample preparation

Sediment sampling

All sampling equipment was 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 and non-polar contaminants and prevent cross-contamination.

Sediment samples were prepared at each site by collecting the top 5 cm of five collection points within a 10 m radius and stirring the pooled 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 campaign. The sediment pH of the remaining samples was determined after thawing of the sediment in the laboratory at the NWU.

The sediment was air-dried, ground, 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 21 POPs. The sediment was also analysed for the 16 polycyclic aromatic hydrocarbons (PAH's) deemed of concern by the USEPA.

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 completely digested with concentrated HNO3 at 50-60 °C and allowed to evaporate to 5 ml. The samples were further treated with H2O2 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. Complete digestion was chosen as an exhaustive search of the literature revealed very little knowledge of elemental bio-available levels in the Orange-Senqu basin. Since sediments are derived from the rock and soils from particular drainage areas, no knowledge exists on what the basic elemental composition of sediments at each site should be. Exceedence of levels of certain elements due to pollution or disturbance will therefore not be possible to determine. To determine the basic elemental composition of each site, complete digestion was done and the elemental levels compared with the geology of the area.

Figure 5:   The elements analysed are highlighted

Fish sampling

After obtaining the necessary provincial permits, 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 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 inhospitable to many other fish species. Thus, they survive long enough so that, if bio-accumulation occurs, 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.

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 for two pools per site (Table 3). Approximately the same mass of fillet was 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.

Table 3:   Dimensions and gender of the Clarias gariepinus individuals that constituted the pools (*Length from the tip of the head to end of peduncle, i.e. where the tail starts.)

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
		2 240		700	640	300
Pool 2		1 300	Female	570	530	255
		2 340		730	680	300
		2 740		710	640	320
		2 240		740	670	295
		3 160		780	690	340
Pool 3	V1	2 950	Male	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 no	Site label	Body mass (g)	Gender	Total length (mm)	Standard length (mm)	Girth (mm)
Pool 5		4 200	Male	800	730	345
		4 340		790	700	350
		4 140		850	770	350
		4 700		790	760	340
	V2	3 520		720	660	320
		3 960		760	690	340
Pool 6		4 140	Female	770	700	340
		4 150		770	750	330
		3 560		750	660	320
		4 560		830	760	340
		3 660		820	740	370
Pool 7		9 060	Male	1 070	980	505
		12 380		1 200	1 060	555
	V3	11 000		1 200	1 070	560
		2 960		745	660	335
		7 560		980	890	500
Pool 8		2 940	Female	750	670	335
		3 860		840	760	370

Aquatic bird egg sampling

Bird eggs were collected at four breeding colonies. Attempts were made to locate more colonies but this failed. The two breeding colonies at Upington were washed away by the floods during the study. 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 thawed. Eggs from the same species from different localities were pooled to obtain a large enough sample volume, 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 various laboratories with all necessary permits.

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	Black-headed 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*
	7	Reed Cormorant	*Microcarbo africanus*
Potchefstroom	9	Glossy Ibis	*Plegadis falcinellus*
	12	Black-headed Heron	*Ardea melanocephala*
	13	Black-headed Heron	*Ardea melanocephala*
	15	Cattle Egret	*Bubulcus ibis*

3. Results and discussion

The results of the analyses completed will be discussed below. All data and maps are available on the ORASECOM Water Information System (wisp.orasecom.org). The maps also includes overlays of the geology and land-use, for further interpretation and assessments.

3.1 Persistent Organic Pollutants

Sediment

Figure 6: 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.
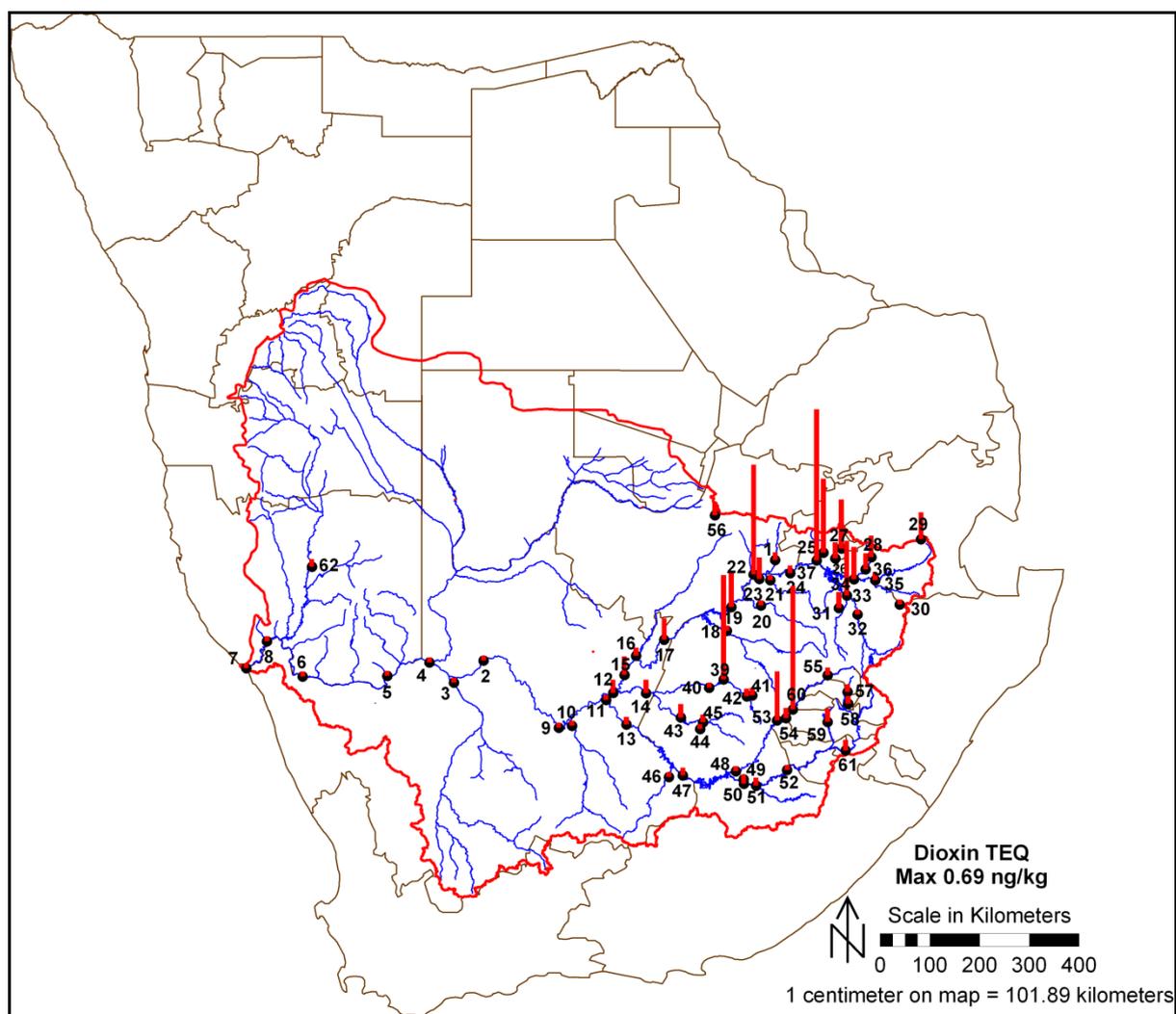
In general, the levels detected were quite low. Figure 6 shows levels of TEQ above detection limits in Gauteng, Klerksdorp, Orkney, Modder River, and Kelekeque River. The first three sites can be associated with industry, urban activities, and mining, while the sources for the last two are unknown. The last two may be associated with smaller industry and urban activities. The general interpretation 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 7: Distribution of indicator PCBs in sediment. Sites indicated with small red dots have PCB levels at or below detection limit. Bar scale is relative.
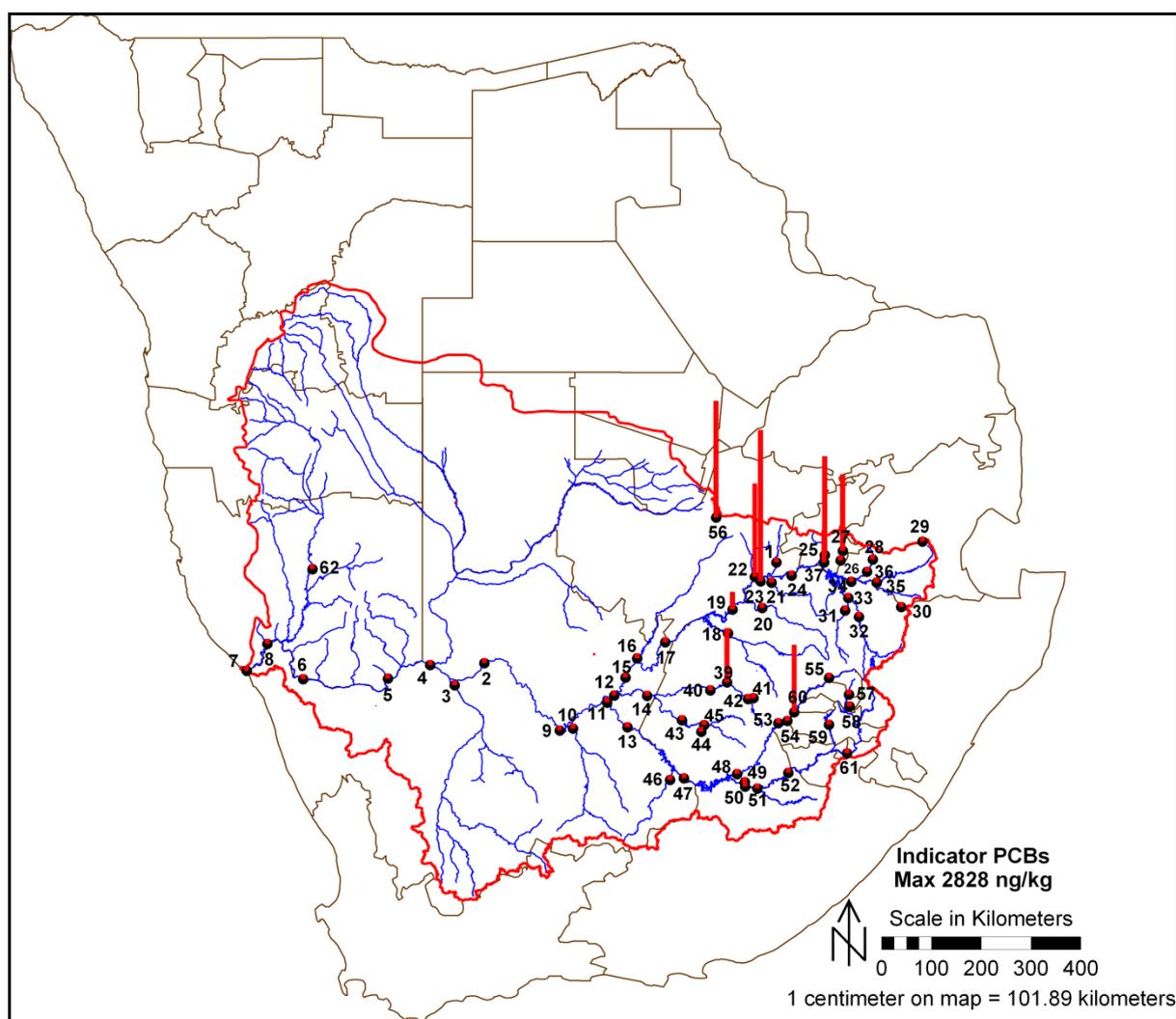
The PCB distribution (Figure 7) reflects the TEQ distribution (Figure 6). It is presumed that the same sources are involved as for the dioxin TEQ, and therefore the same concerns apply. Site 56,

however, differs from the pattern in Figure 6 in that it had relatively high PCBs when compared with dioxin TEQ. This difference cannot yet be explained.

Figure 8:   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.
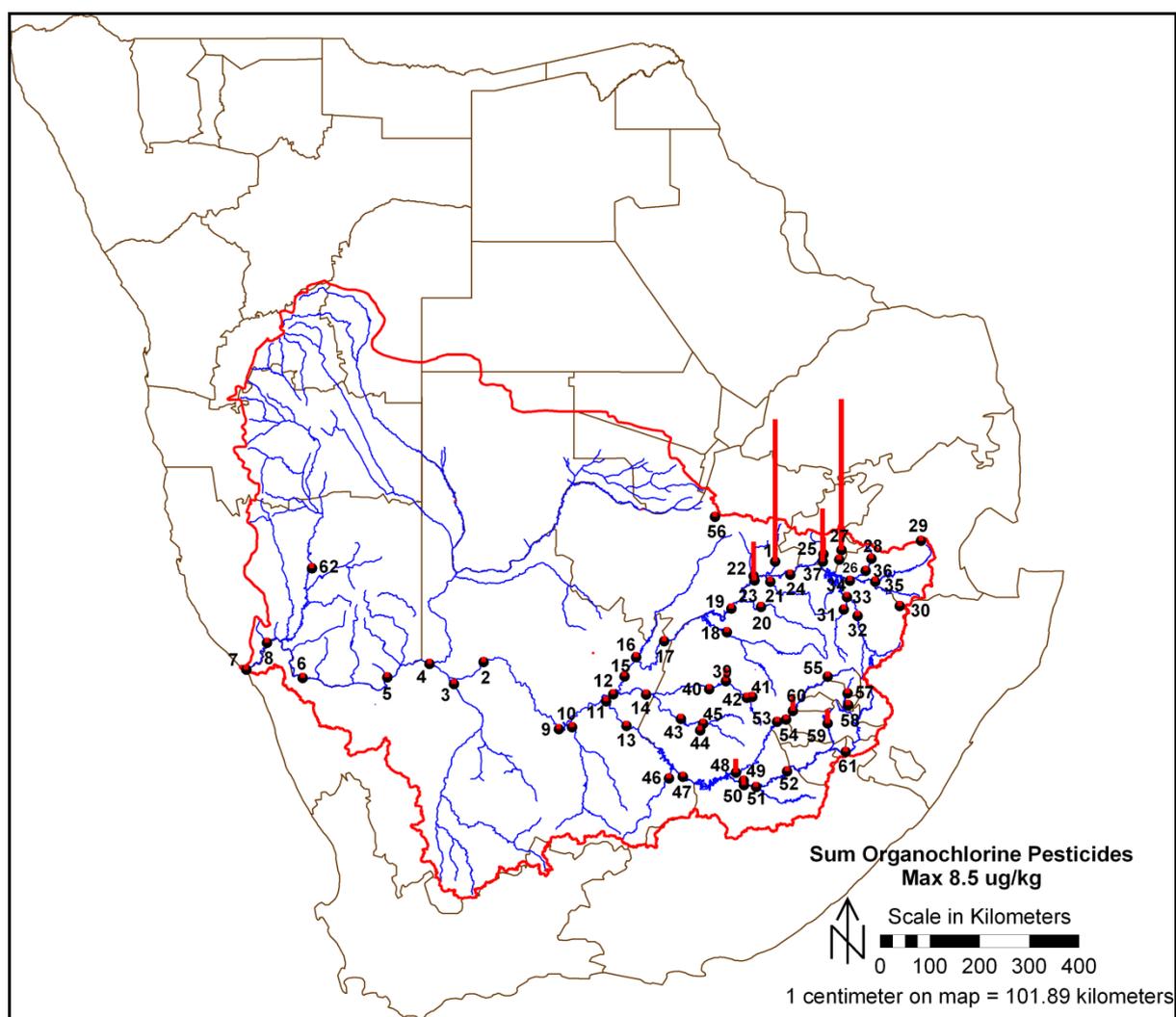
Blesbokspruit, Suikerbosrand, Potchefstroom, and Klerksdorp had the highest levels of organochlorine compounds (OCs), mainly in the form of legacy DDT. Again, it seems that pollution remains isolated and does not travel downstream, or is diluted or broken down quickly.

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 14 and 17).

Figure 9:   Distribution of summed PAHs in sediment from the sampling sites. The bar scale is relative.
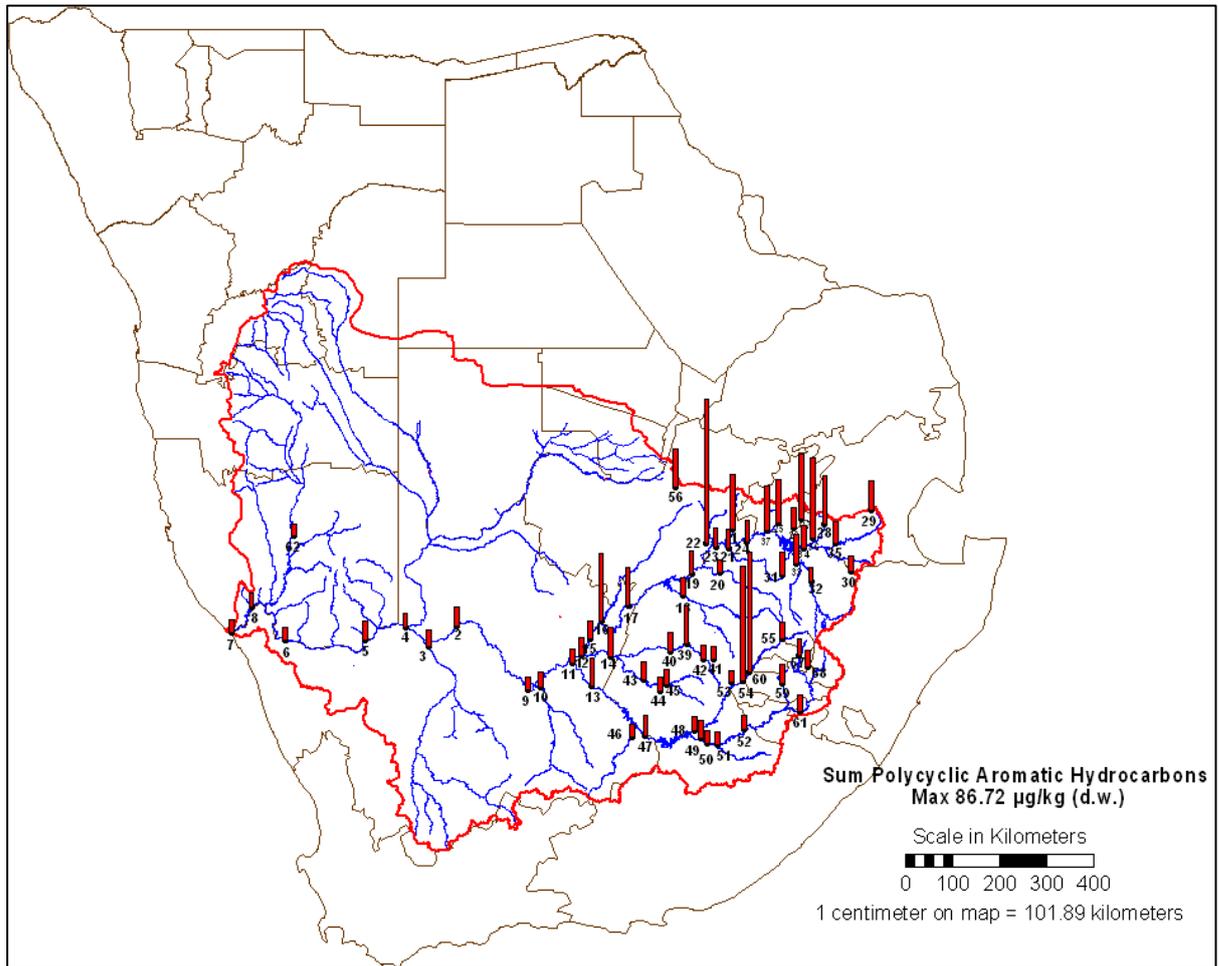
The highest ∑PAH concentration (867 µg/kg dw) was measured at sediment site 22 (Figure 9) which is downstream of urban and industrial development of the town of Klerksdorp in South Africa, followed by site no 60 (711 µg/kg dw) and 54 (673 µg/kg dw). The latter are both downstream of a large city in Lesotho (Figure 9). The most common PAH was fluoranthene, a four ring PAH followed by phenanthrene a three ring PAH and phenanthrene a five ring PAH (Table 5). The highest concentrations of the carcinogenic benzo(a)pyrene (and therefore the higher risks) were found at sites 16, 17, 22, 54 and 60. 16, 17, 22, 54 and 60. The sources of the PAHs at all these sites were pyrogenic in nature (Table 6).

Table 5:   The mean concentrations of the various PAH's in sediment and the number of benzene rings each PAH consists of.

Name	No of rings	Mean (μg/kg (d.w.))
Fluoranthene	4	16.4
Phenanthrene	3	15.2
Benzo(b+k)fluoranthene	5	13.3
Naphthalene	2	12.8
Pyrene	4	12.4
Benz(a)pyrene	5	7.4
Acenaphthene	3	7.3
Chrysene	4	7.2
Benzo(ghi)perylene	6	6.9
Indeno(1,2,3-cd)pyrene	6	6.1
Benz(a)anthracene	4	6
Fluorene	3	2.9
Anthracene	3	2.3
Acenaphthylene	3	1.3
Dibenz(ah+ac)anthracene	6	1.2

To determine the petrogenic or pyrogenic origin of the PAHs (Culotta et al., 2006), the ratios of selected isomers were determined and origin assigned according to:

- If fluoranthene (flu)/pyrene (pyr) >1 and phenanthrene (phe)/anthracene (ant) < 30 = pyrogenic origin
- If fluoranthene (flu)/pyrene (pyr) < 1 and phenanthrene (phe)/anthracene (ant) > 1 = petrogenic origin
- If indeno(1,2,3-cd)pyrene (ind)/benzo(ghi)perylene (ben) > 1 = coal/coke sources or smelters.

Table 6: *The PAH ratios of the sediment sites according to pyrogenic or petrogenic origin. The shaded cells in columns 1 and 2 indicate predominant pyrogenic origin, and shaded cells in column 3 indicate contributions from and coal/coke sources or smelters. Further analyses are provided in Figure 10.*

Site no	Flu/Pyr >1	Phe/Ant <30	Ind/Ben >1
1	1.3	5.8	1.0
2	1.5	10.5	1.0
3	1.9	14.0	1.0
4	1	11.3	1.0
5	1.3	8.3	1.2
6	1	16.3	1.0
7	1	9.3	1.0
8	1	14.7	1.0
9	1	11.7	1.0
10	1	7.9	1.3
11	2.7	9.5	1.0
12	1.3	10.9	1.1
13	1.6	10.9	1.2
14	1.5	14.1	1.1
15	1.3	8.9	1.0
16	1.3	3.6	1.0
17	1.1	5.9	0.9
18	2.3	37	1.0
19	1.3	7.1	1.0
20	1	12.3	1.0
21	1	9.0	1.1
22	1.3	6.4	0.8
23	1.3	7.2	1.5
24	1.3	5.8	1.2
25	0.9	4.3	1.0
26	1.9	10.3	1.8
27	1.3	6.3	0.9
28	1.3	3.2	0.8
29	1.3	8.2	0.8
30	1	17.0	1.0
31	1.8	11.3	1.7
32	1	8.3	1.0
33	1.6	8.8	0.9
34	1.2	10.7	1.0
35	1.6	11.6	1.1
36	1.5	6.4	0.7
37	1.3	5.5	1.0
38	1.3	10.8	0.7
39	1.2	5.5	0.8
40	1.4	7.0	1.3
41	1	8.3	1.0
42	1	7.7	1.0
43	1.2	8.8	1.0

Site no	Flu/Pyr >1	Phe/Ant <30	Ind/Ben >1
44	1	6.3	1.0
45	1.8	10.0	1.0
46	1	4.3	1.0
47	1.5	7.2	1.4
48	1	7.0	1.0
49	1.8	5.3	1.1
50	1	7.3	1.0
51	1	1.0	1.0
52	1	1.0	1.0
53	1	1.0	1.0
54	1.2	3.4	0.8
55	1.6	8.7	0.9
56	0.8	5.6	1.3
57	1.3	6.3	2.2
58	2.1	7.2	2.0
59	1.1	6.3	0.7
60	1.5	8.2	0.9
61	1.6	7.4	1.4
62	1	2.3	1.0

Judging by the large number of shaded cells in Table 6, the conclusion is that the main origin of PAHs were pyrogenic for two thirds of the sediment sites (see also Figure 10), specifically those sites with shaded cells in both the first and second columns of Table 6. These sites are 1-3, 5, 11-19, 22-24, 26-29, 31, 33-40, 43, 45, 47, 49, 54, 55, 57-61. Of these sites, the specific pyrogenic origin was likely to be coal/coke sources or smelters for sites 5, 10, 12-14, 21, 23, 24, 26, 31, 35, 40, 47, 49, 56-58, and 61.

The PAH origin for the three the sites with the highest levels were pyrogenic (Table 6), but only at site 60 was the pyrogenic origin predominantly coal or smelter related.

Figure 10: The PAHs from most of the sediment sites were calculated to be dominated by pyogenic origin. The labels for some of the overlapping sites were removed for clarity.
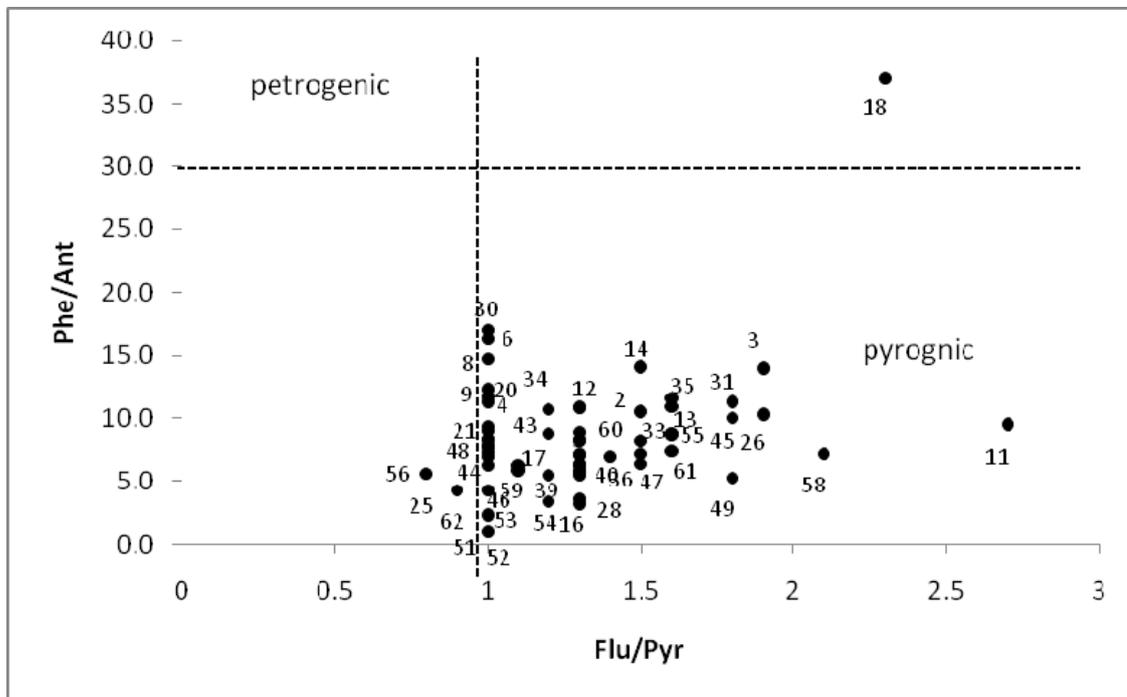
Fish

Figure 11: Distribution of dioxin-like TEQ in fish from the sampling sites. Sites indicated with small red dots had TEQ levels at or below detection limit. Bar scale is relative.
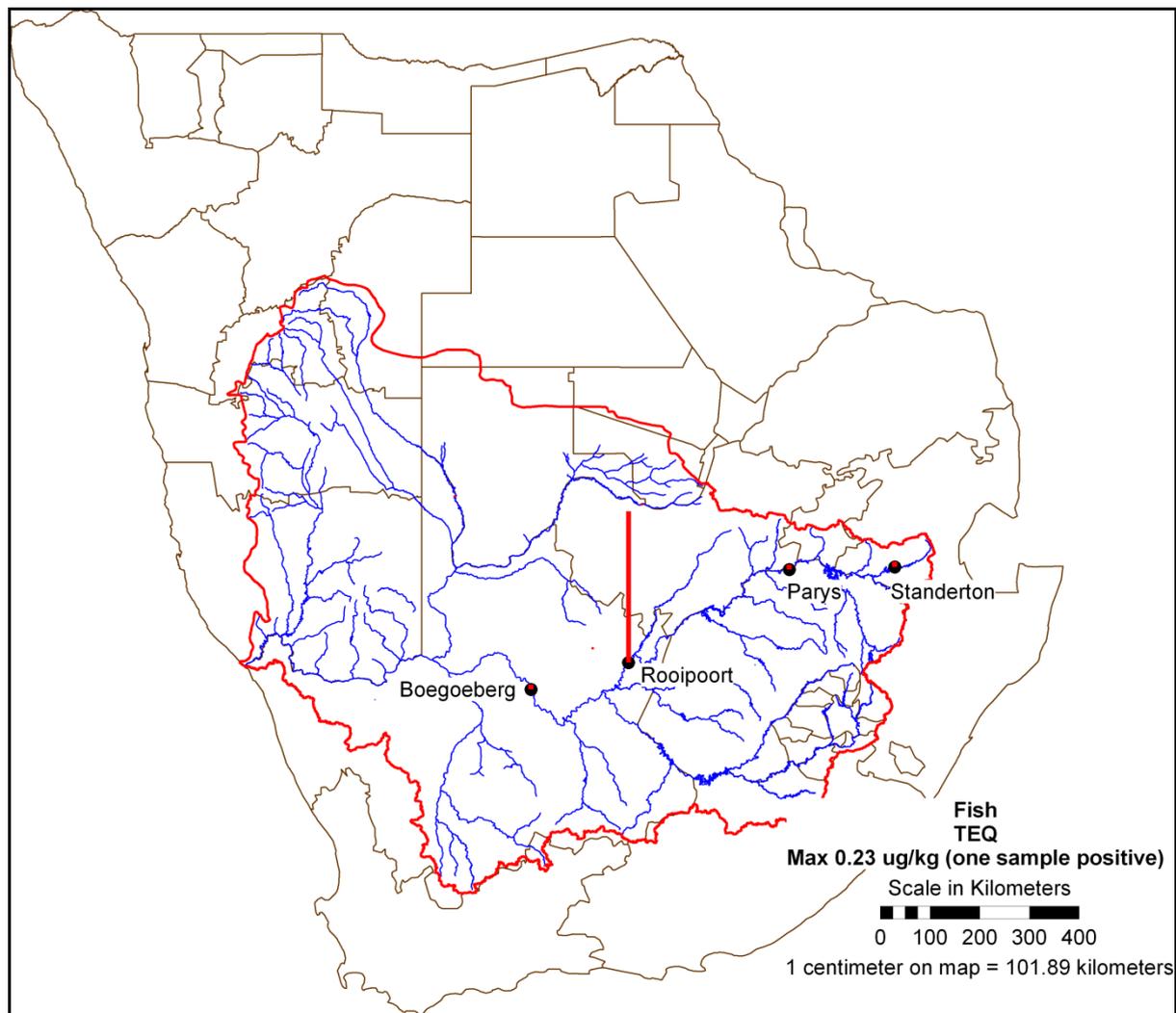
TEQ was detected in *Clarias gariepienus* (sharptooth catfish) from only one of the four collection sites, namely Rooipoort (Figure 11). Why this site would have the higher levels is not known. Potential upstream sources associated with this site include mining, urban, industrial, and sewage associated with Kimberly and the smaller urban and rural areas. However, since Figure 6 indicates no apparent down-stream movements of dioxin TEQ in sediment, the relatively higher level in fish indicates a potential local source of TEQ. It also shows the need to sample and analyze fish closer to Soweto and Lenasia and downstream of Orkney since the sediment TEQ distribution (Figure 6) showed hotspots there as well.

Figure 12: 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.
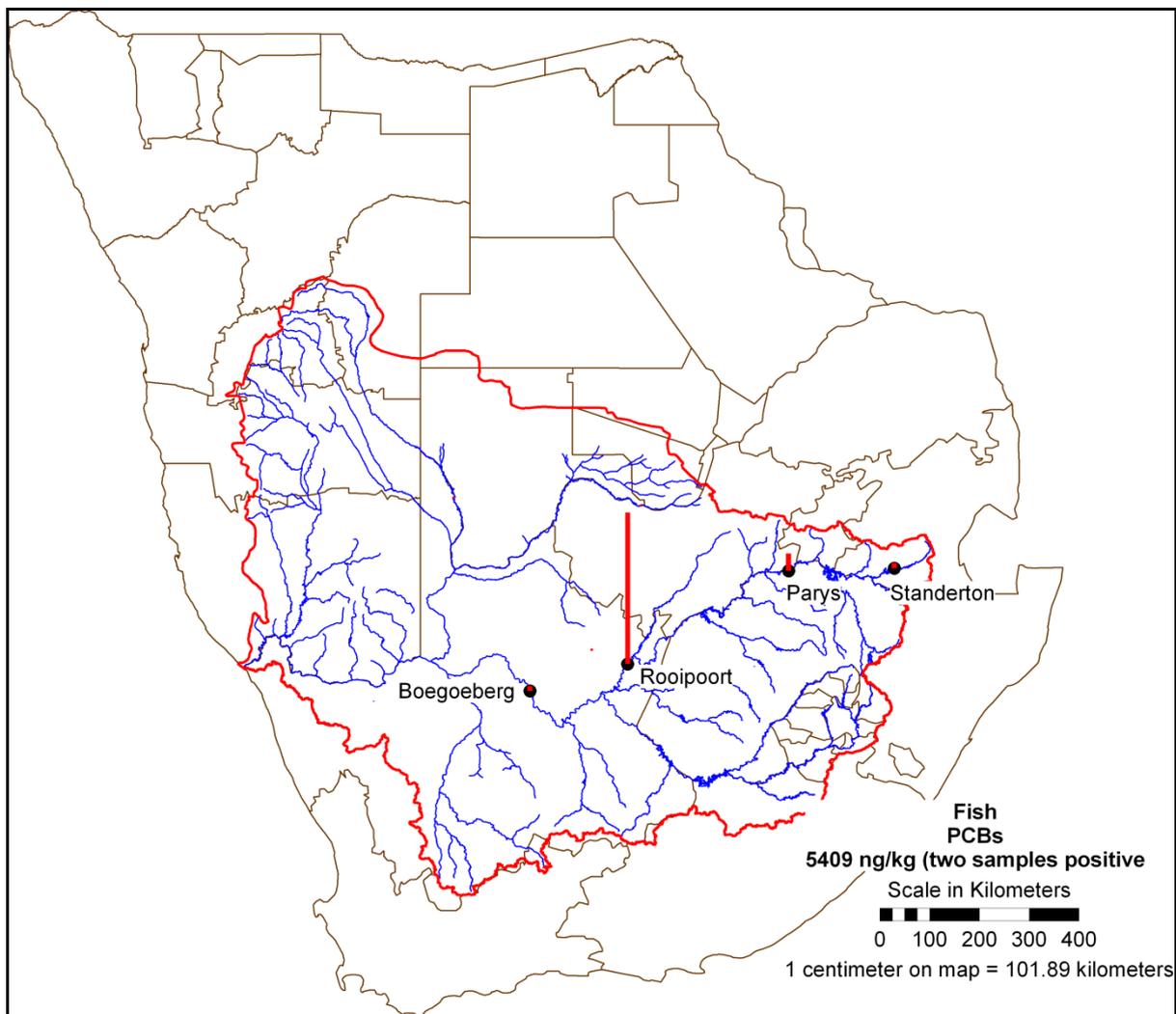
As for sediment TEQ (Figure 6) and PCB (Figure 7) distributions, the fish PCB distribution (Figure 12) reflects the TEQ distribution (Figure 11). The same sources and concerns are therefore applicable. It does show however, that sediment levels do not always reflect levels in biota in this system.

Figure 13: Distribution of organochlorine pesticides (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.
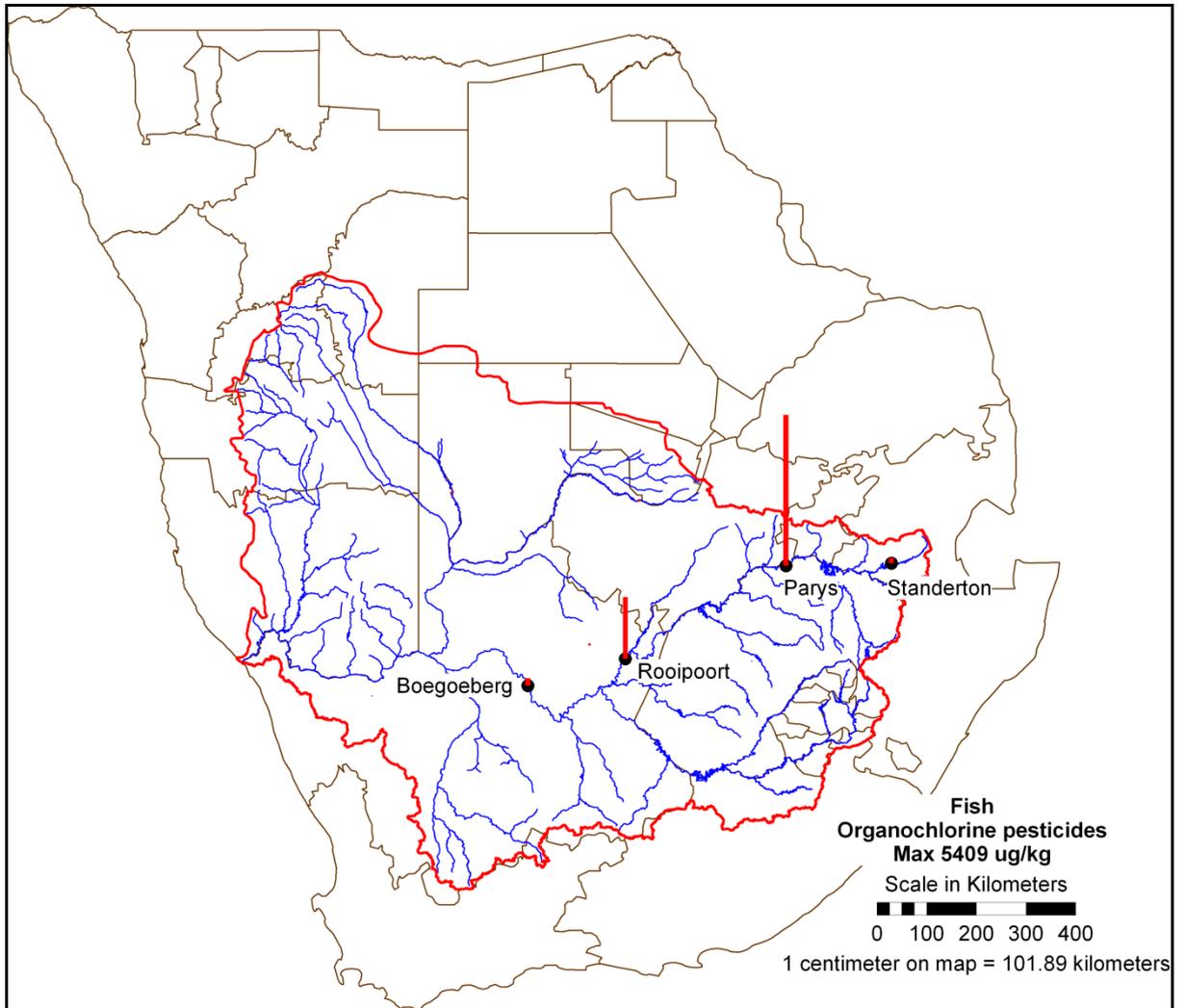
Parys and Rooipoort had the highest levels of OCs, again mainly DDT and metabolites (Figure 13). How and where these metabolites come from is not known, and needs further investigation. Since there is intensive recreational and subsistence fishing along these rivers, the health risks needs assessment.

Figure 14: 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.
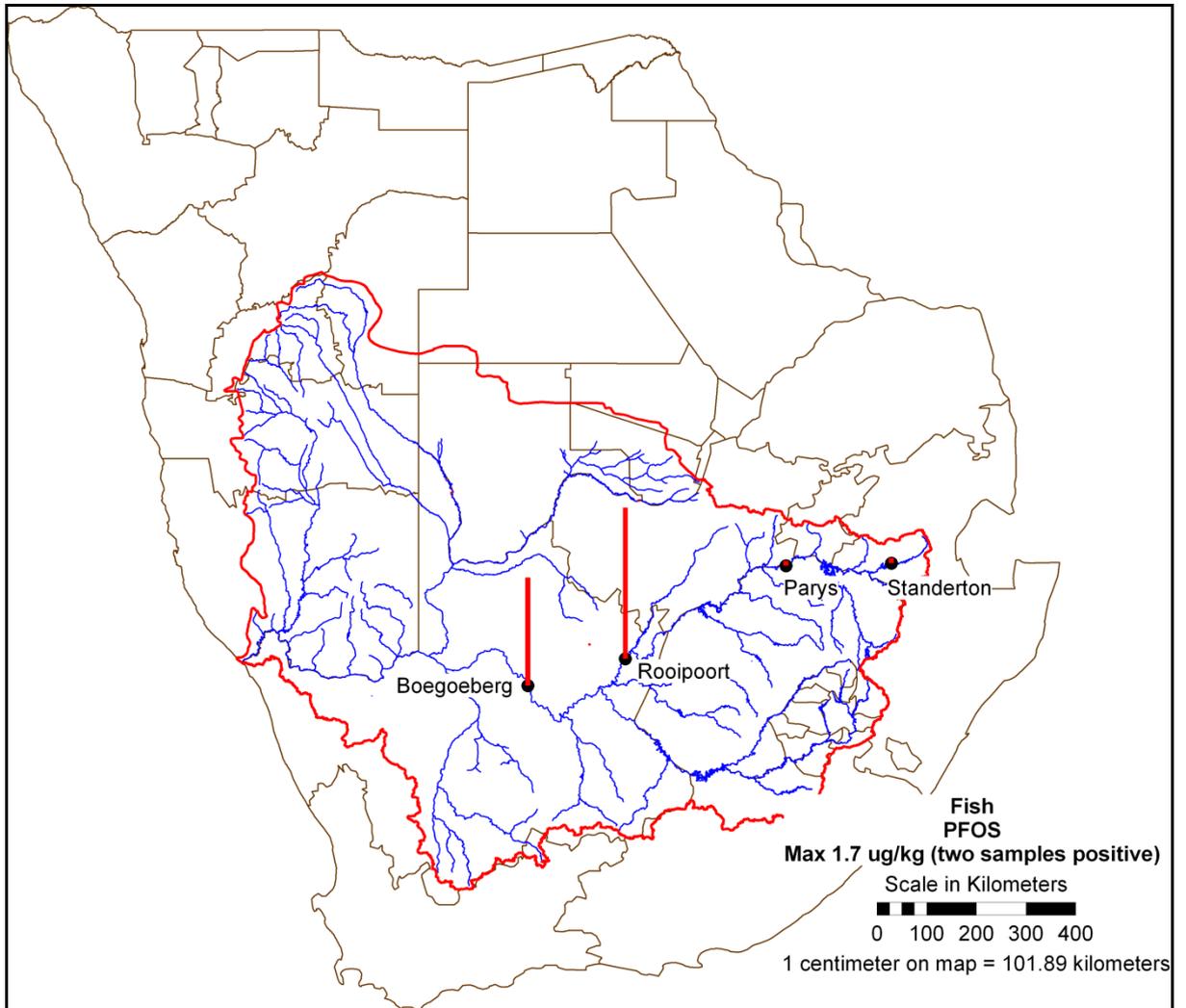
This surprising distribution (Figure 14) cannot be explained. PFOS is an industrial and consumer chemical and it would have been expected at higher concentrations near industrial centres and cities. PFOS is also very persistent. The pattern we see might be due to past use whereby residues have now found 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 and implications for this distribution pattern need further investigation.

Wild bird eggs

Figure 15: Distribution of maximum dioxin TEQ in bird eggs from the sampling sites. Bar scale is relative.
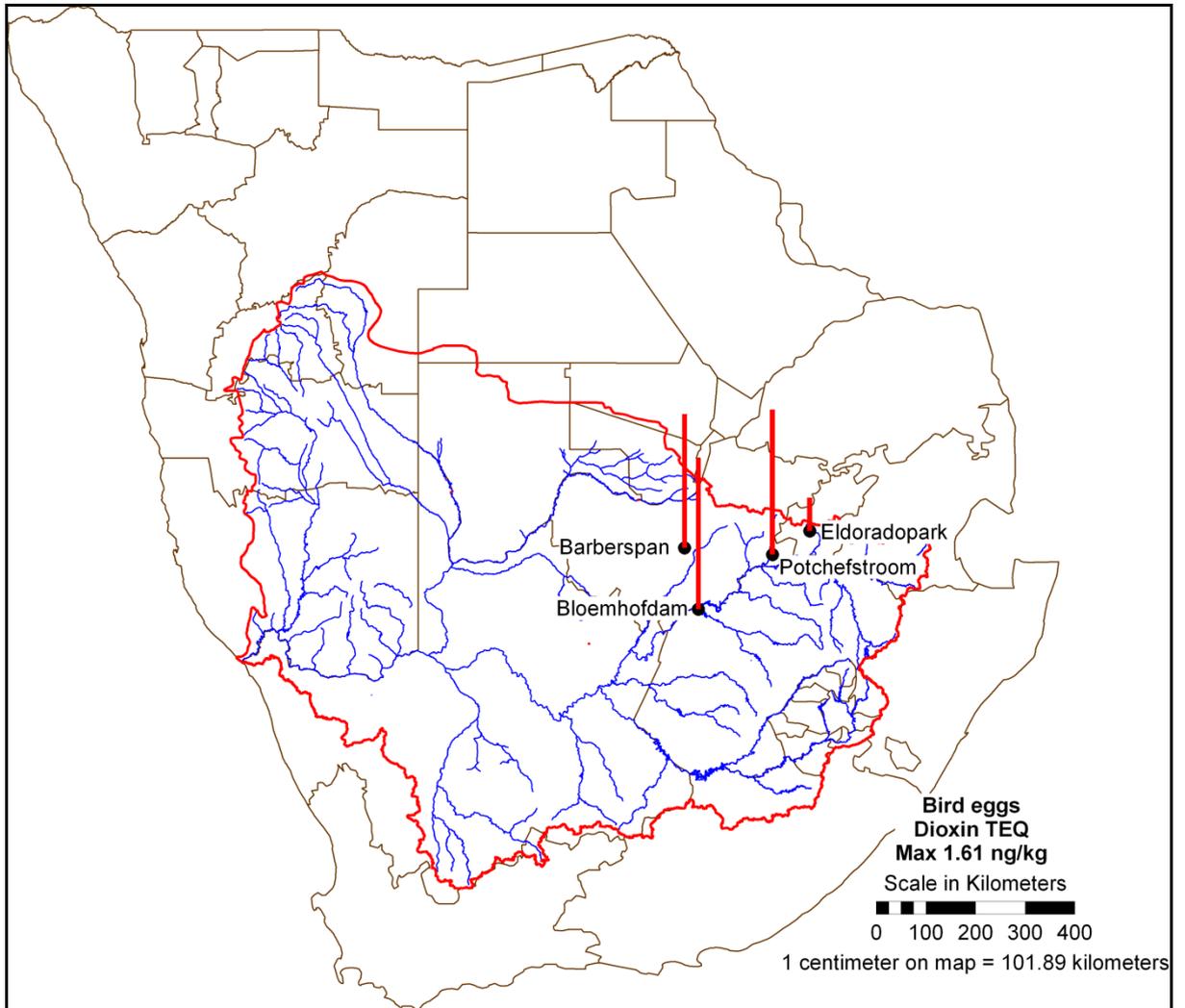
This surprising map indicates widespread distribution of TEQ (Figure 15). The levels were and order of magnitude higher than the single positive fish value (Figure 11). We expected higher levels in eggs from birds from Eldoradopark, but here it is much lower. Birds also move around quite a bit; the distribution 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 16: Distribution of PCBs in bird eggs from the sampling sites. Bar scale is relative.
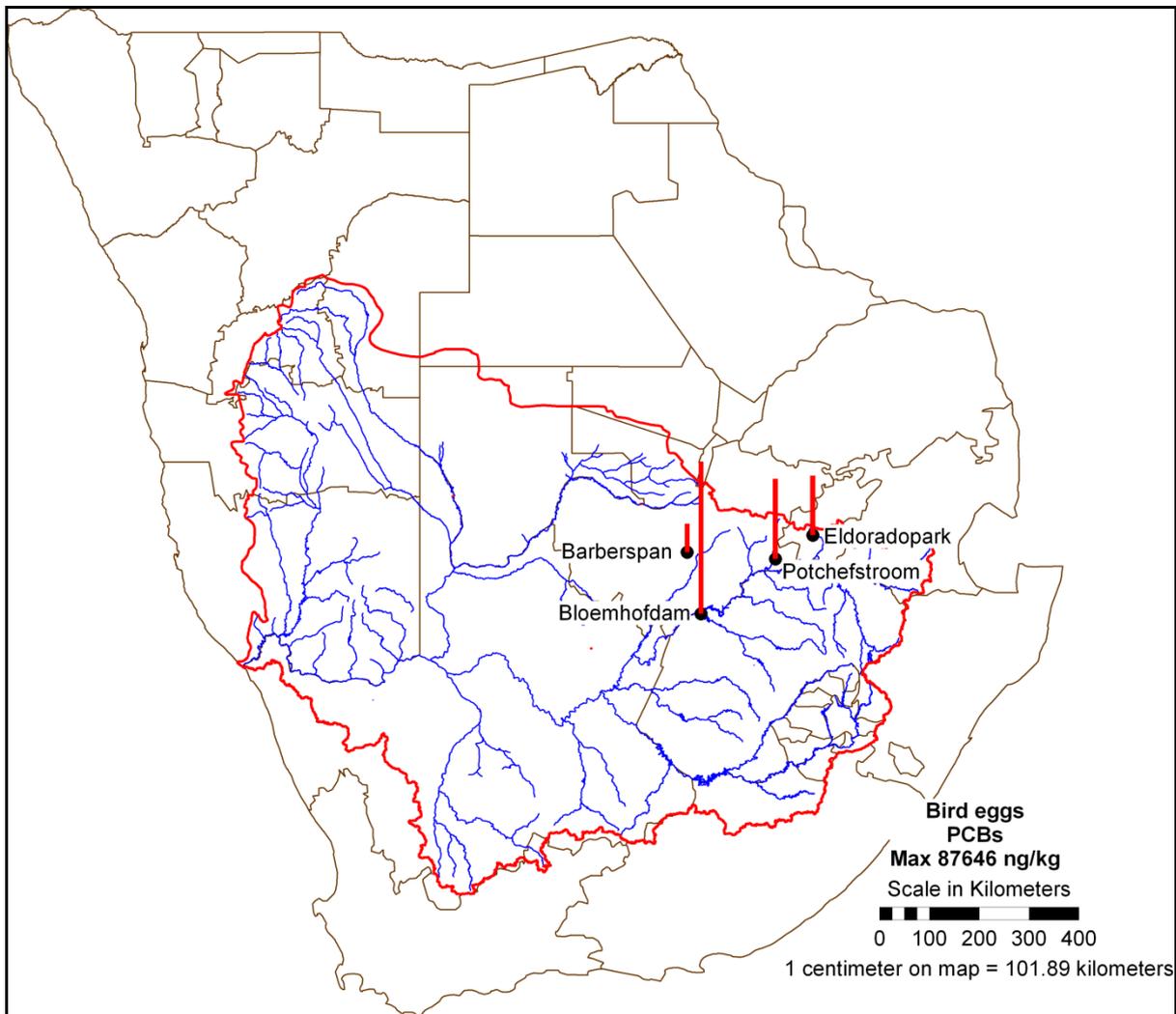
There seems to be an increase in levels from Eldoradopark towards Bloemhof Dam along the Vaal River (Figure 16). Bloemhof Dam may represent a retaining effect of PCBs in biota, but not in sediment (Figure 7). Confirmation is needed, as well as a more in-depth species assessment.

Figure 17: Distribution of OCs in bird eggs from the sampling sites. Bar scale is relative.
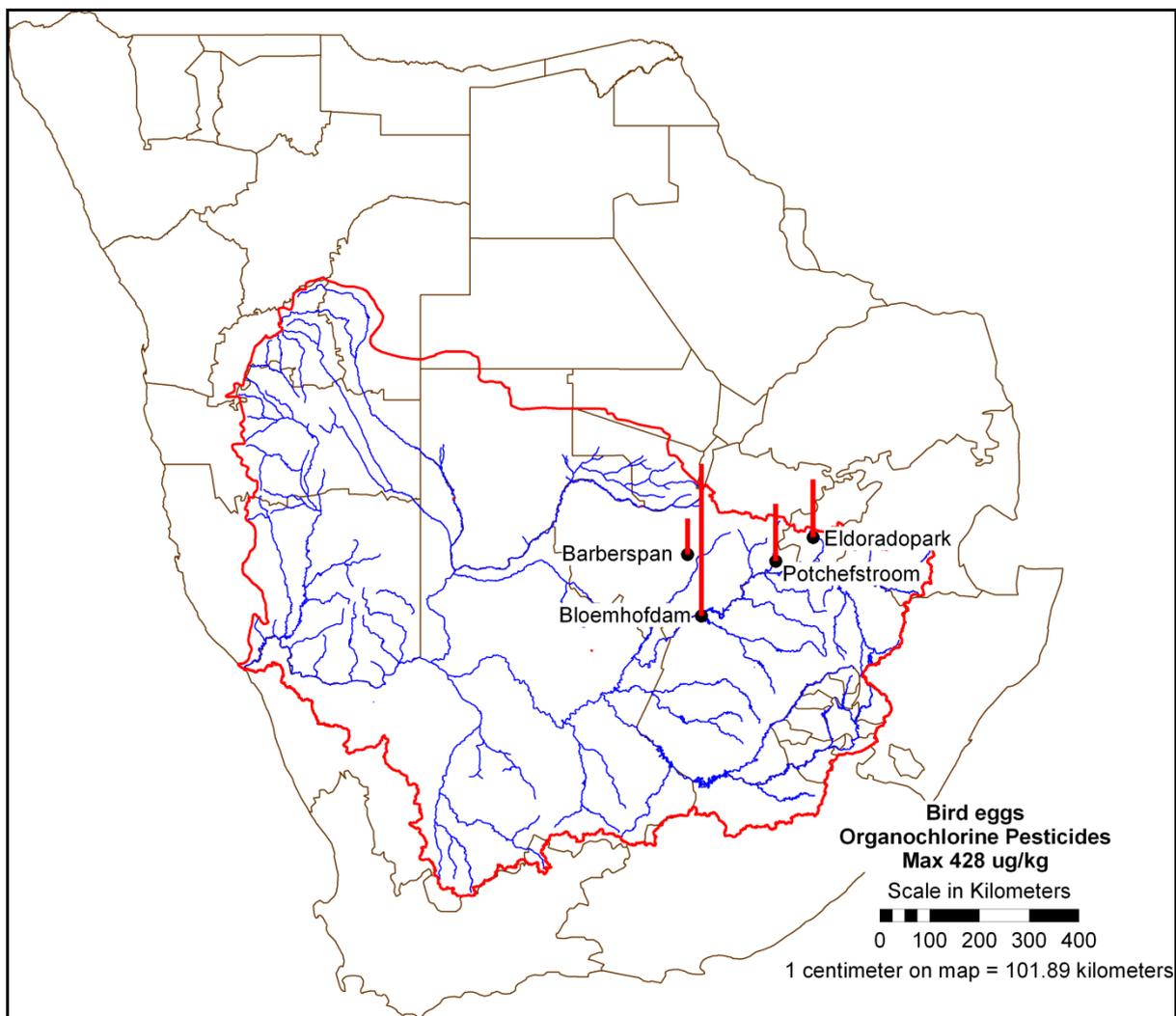
The relatively higher levels of OCs in the bird eggs were expected, but that the highest was from Bloemhof Dam was not (Figure 17). Just as with PCBs (Figure 16) it seems that Bloemhof Dam might retain OCs as it does with PCBs. However, a careful species assessment needs to be done.

Figure 18: Distribution of PFOS in bird eggs from the sampling sites. Bar scale is relative.
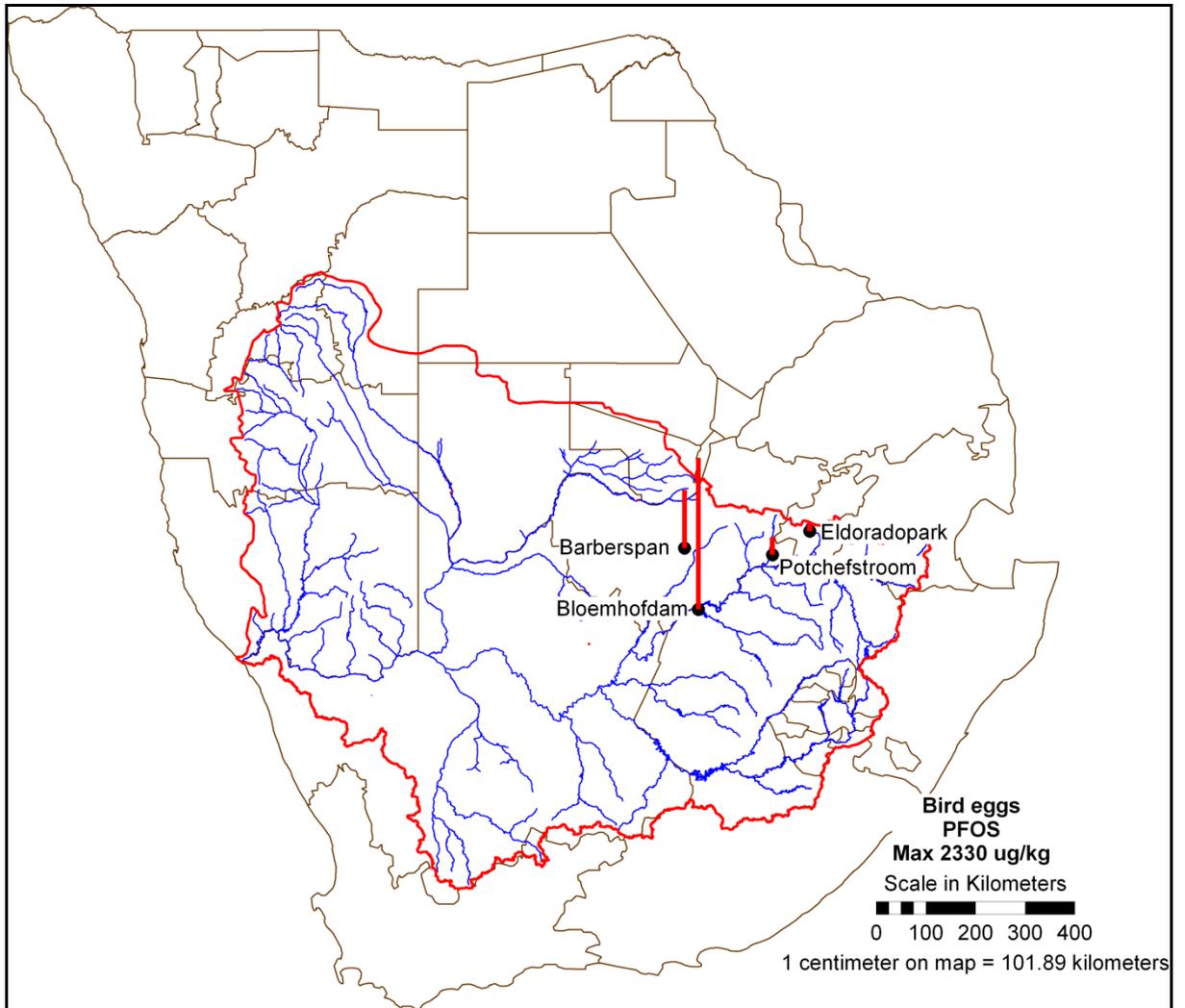
The levels of PFOS are relatively high, higher than the OCs represented in Figure 17 and not much less than the PCB levels represented in Figure 16. We expected higher levels at Eldoradopark and less at Bloemhofdam. Again, it might be that Bloemhof Dam acts as a retainer of pollutants, but species assessments and a more careful analysis of the data is required. It was a pity that we were not able to collect eggs at Upington, as this would have indicated if aquatic transport of PFOS was indeed involved. 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. The PFOS levels at Bloemhof Dam is of the highest levels measured anywhere in the world, and need much closer scrutiny as to source and impact.

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 Figures 19 and 20. Iron (Fe) and aluminium (Al) had the
highest means of all of the 42 elements analysed for (Table 7).

Figure 19: Mean concentrations for the majority of the heavy metals and trace elements in the sediment.
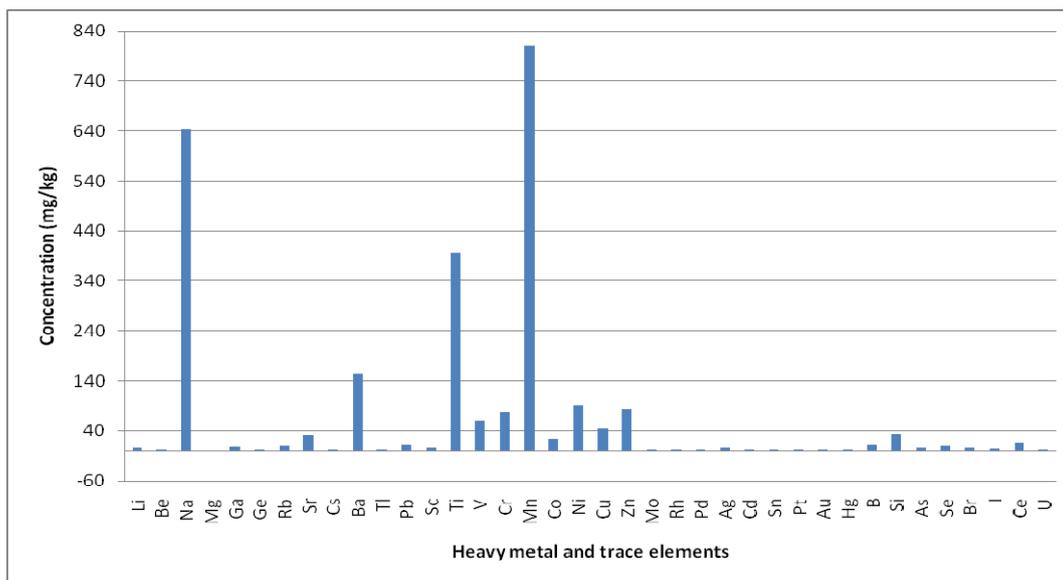
*Figure 20: Mean concentrations for Al, K, Ca and Fe in the sediment. Their concentrations were two orders of
magnitude higher than the elements in Figure 19.*
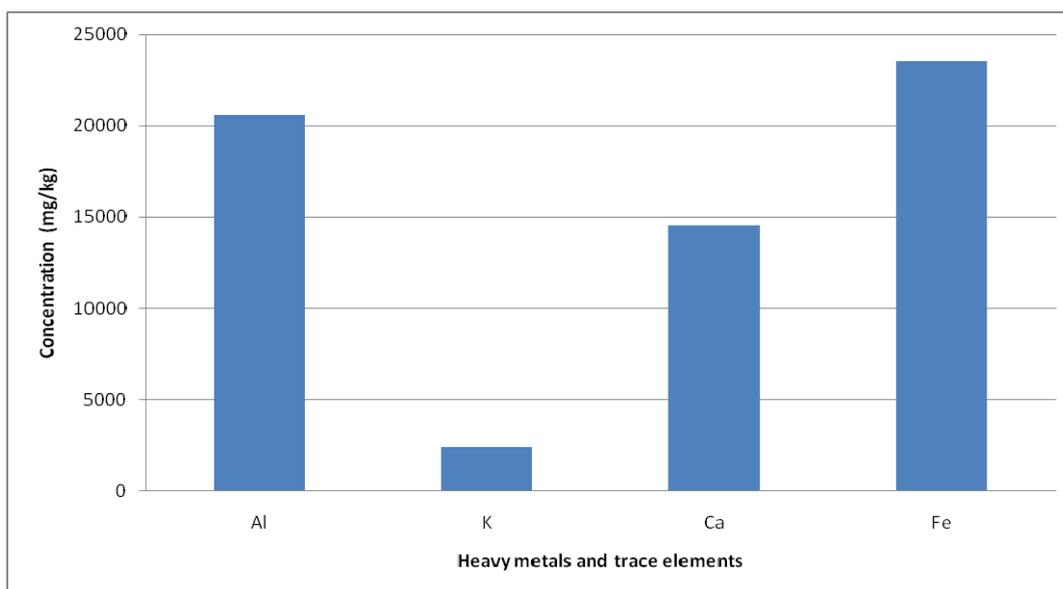
Table 7: The means and other summary statistics of the elements detected in the sediment. Units are mg/kg d.w.

	Mean	Standard deviation	Minimum	Maximum	Median
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

	Mean	*Standard deviation*	*Minimum*	*Maximum*	*Median*
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 calculated for each of the sediment sites. The MPI is the geometric mean of all of the elements (Figure 21).

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).

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 were general, global values for crustal shale (Wedepohl, 1995). The Igeo could be interpreted from a pollution point of view, according to the scale below. The results can only be used as an indication of possible pollution as local geological variations would have 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 are summarised in Tables 8 and 9.

The highest I_{geo} value was calculated for site 56 at the origins of the Molopo River, also known as the Molopo Eye. This finding is difficult to explain because this is a rural area with only agricultural activities in its immediate vicinity. 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 found its way to underground caverns from which the Molopo eye originates.

Figure 21: The Metal Pollution Index (MPI) for the sediment sites. Bar scale is relative.
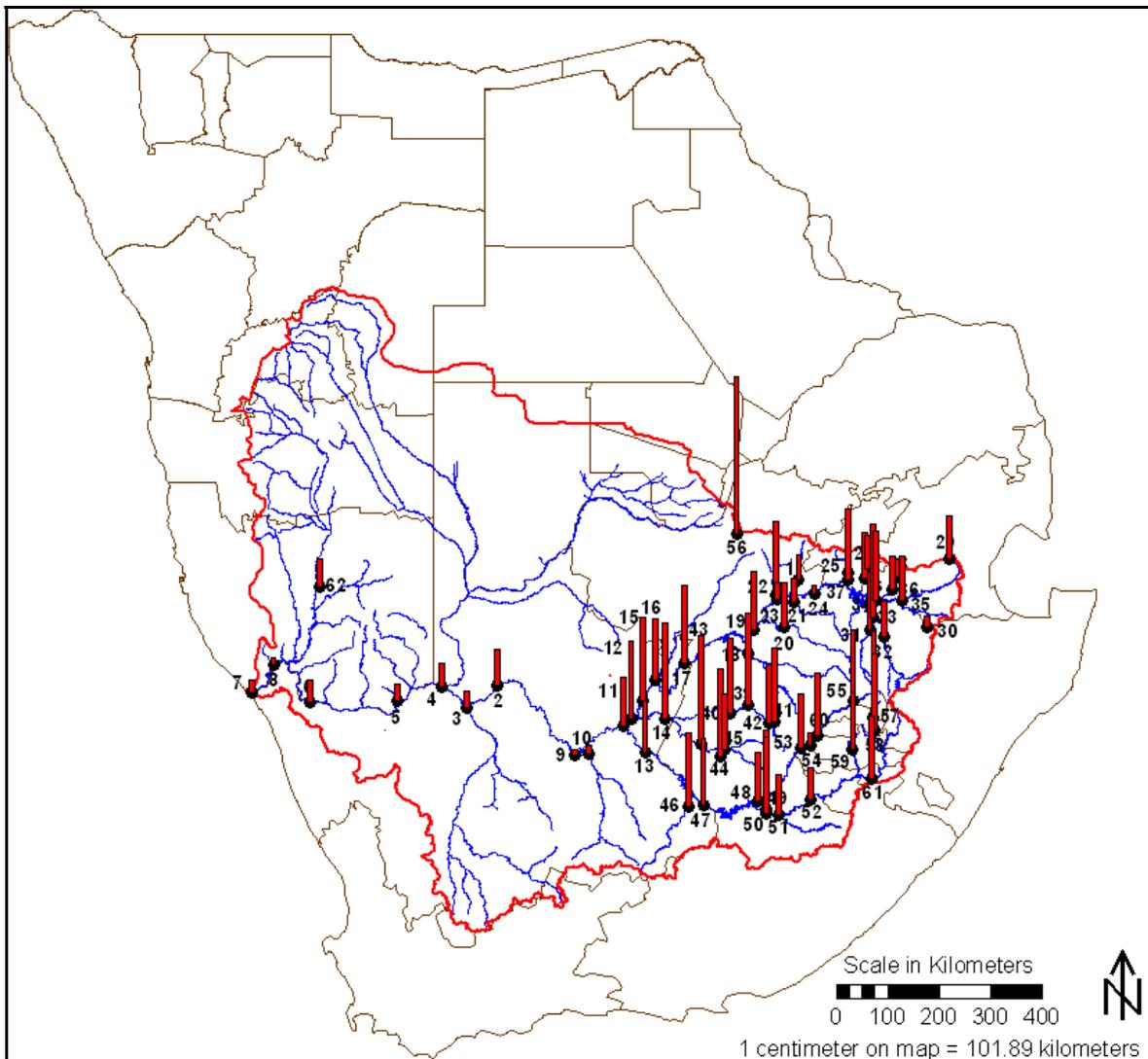
Table 8:   Possible pollution levels of the elements at the sites in the Vaal River catchment as indicated by the geoaccumulation index (I_{geo})

		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 9: 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 Southern

Africa, because it is difficult to assume that both Se and Ag would be at such high pollution levels throughout the entire Basin, even in the remote areas (Tables 8. and 9). The possible pollution due to Hg has a more expected pattern. Much better understanding of these results will be possible if the minerals from the geology of the sites would be considered in the future.

A third approach was followed to identify sediment sites of concern. For every element, the 25% of sites with the highest concentrations were determined. The sites were ranked according to the percentage elements they had in the upper 25% (Table 10). I, Br, Li, Ca, K, Na and Mg were not considered because they form part of the salts usually measured in water quality determinations and as such their influence on the state of the basin would be measured there. Si was also removed as the element is integral in all minerals and its level will most likely not indicate increased anthropogenic activities. The geology of the sites was included in the ranking table to interpret its contribution to the measured elemental levels.

Site 43 in the Riet River in the Free State Province had the highest ranking (Table 10). Sites 12, 14, 39, 41 and 44 are sites in the in the Modder and Riet River systems and are sites that ranked within the upper 25% having elements with the highest levels (Figure 22). 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 had similar high levels of elements. Site no 34 (Figure 22) also has the same geology, but is geographically far from sites 39, 43 and 44. Sites 12, 14, 39, 41, 43 and 44 (Figure 22) also have battlegrounds of the Second Anglo-Boer war in common. This is also the situation for sites 49 and 50. In the light of the lack of obvious reasons for these high levels of elements at all of these sites (only some share similar geologies), such as mining activities, it may be worthwhile to investigate the possible legacy of conflict 111-113 years ago. Sites 33 and 41 also share the same geology (Table 10)

Two sites inside Lesotho (Figure 23), sites 57 and 58 were also in this upper 25% ranking (Table 10) but there is no mining, agriculture or other obvious activities that might have caused this; the deduction is that these are naturally high levels. They do however have the same geology (Table 10). Other sites on this in Table 10 that share the same geology, and therefore might explain their high levels of many elements, are sites 49, 50 and 55.

The only site prominent in any of the three assessment methods, is site 56, which is the Molopo eye. In Table 9 it is also the site with the most elements with an $I_{geo} > 1$.

Table 10: The 25% sites with the highest 25% concentration of the elements analysed for in the Orange-Senqu catchment.

Site rank	Site no and name	Geology	Similar geologies = same pattern*
1	43 Riet River	Karoo Supergroup, Ecca Group, Volksrust Formation: argillaceous rocks - clay minerals, quartz; thin phosphate and carbonate layers – siderite.	
2	33 Wilge River (up-stream of Frankfort)	Karoo Supergroup, Beaufort Group, Adelaide Subgroup, Normandien Formation: mudstone, lithofeldspathic sandstone - quartz, feldspar, clay minerals.	
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	
6	50 Stormberg River	Karoo Supergroup, Beaufort Group, Tarkastad Subgroup: sandstone and mudstone - quartz, clay minerals.	
7	58 Matsuko River	Karoo Igneous Province, Drakensberg Group: basalt - ferromagnesian minerals and plagioclase feldspar.	
8	57 Makbamatso River	Karoo Igneous Province, Drakensberg Group: basalt - ferromagnesian minerals and plagioclase feldspar.	
9	39 Modder River	Karoo Supergroup, Ecca Group, Volksrust Formation: argillaceous rocks - clay minerals, quartz; thin phosphate and carbonate layers - siderite.	
10	34 Vaal River (in Villiers)	Karoo Supergroup, Ecca Group, Volksrust Formation: argillaceous rocks - clay minerals, quartz; thin phosphate and carbonate layers - siderite.	
11	55 Caledon River	Karoo Supergroup, Beaufort Group, Tarkastad Subgroup: sandstone and mudstone - quartz, clay minerals.	
12	49 Orange River (up-stream of Gariep Dam)	Karoo Supergroup, Beaufort Group, Tarkastad Subgroup: sandstone and mudstone - quartz, clay minerals.	
13	60 Kelekeque 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.	
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 22: A diagrammatic representation of the sites in the Vaal River catchment. The highlighted sites (dark circles) are sites containing the 25% highest concentration of measured elements (Table 10).
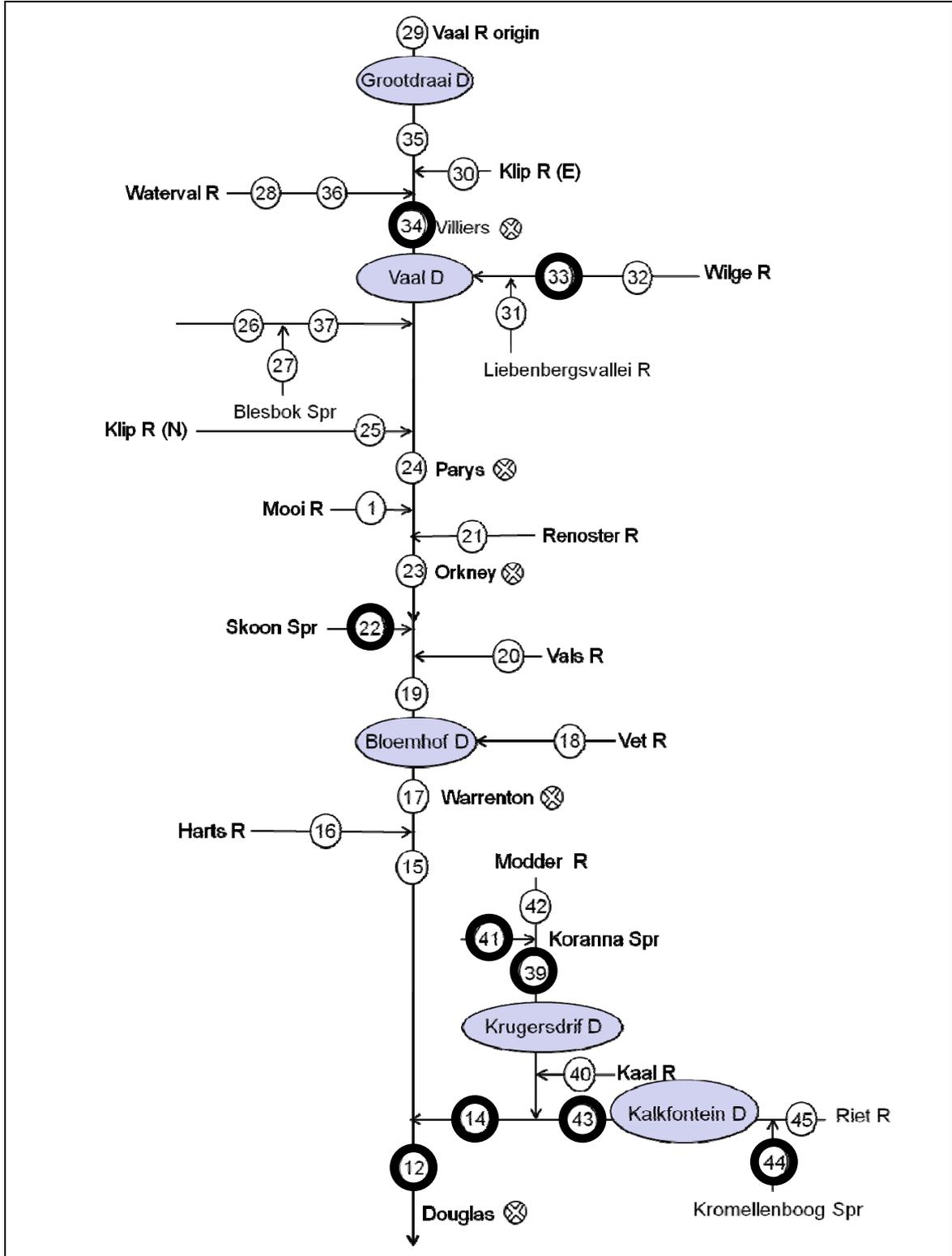
Figure 23: A diagrammatic representation of the sites in the Orange River catchment. The highlighted sites (dark circles) are sites containing the 25% highest concentration of measured elements (Table 10).
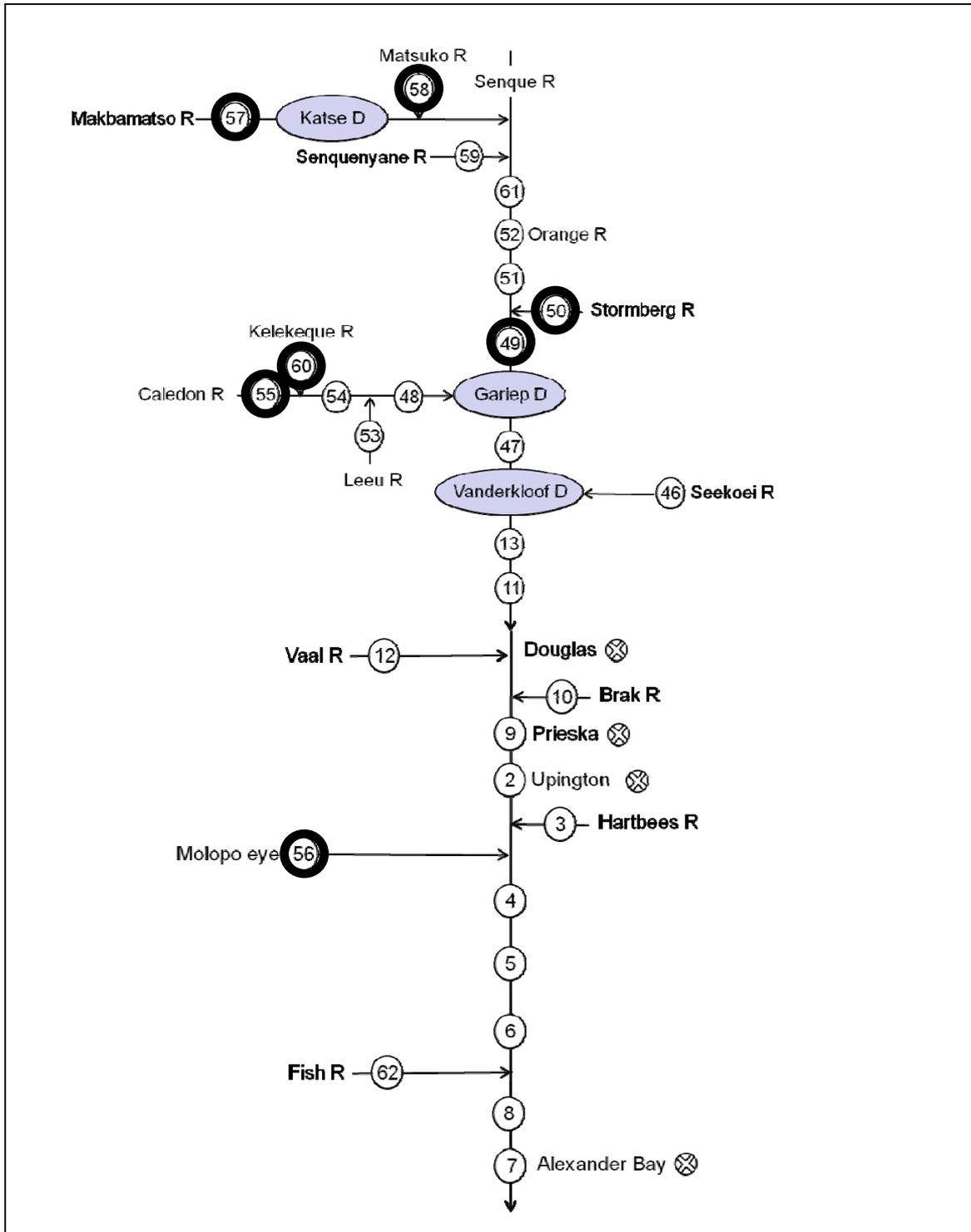
In the following section, maps are presented of the relative distribution patterns of various elements between sites. These graphs occur at the end of this section. At least one representative of the major groups, e.g. GrIA, on the Periodic Table or category of elements such as the transitional metals 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 (Figures 22 and 24). It seems as if the relatively higher levels were from Free State and Mpumulanga sites (Figure 24).

The highest level for the representative of the Group IIA elements , Be, was found at the Molopo Eye, site 56 (Figure 25). Again, the relatively 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 (Figure 26).

The only two elements in Group IV that were analysed for, were Pb and Sn in Figure 27. Their concentrations are not presented 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 (Figure 28). 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 62 in the Fish River.

Selenium was the only element of the Group VIA elements 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 throughout all of the sites in the Basin (Figure 29). Most of the sites in the Lower Orange River (sites no 2 to 10) had low Se levels, but when their Igeo values are considered (Table 9), they too could be regarded as highly polluted by Se.

Of the halogens (Group VIIA elements), only Br and I were analysed (Figure 30). 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, a site in the Riet River, downstream of its confluence with the Modder River (Figure 2).

Zn was selected as the representative of all of the transitional metals analysed because it correlated significantly with all of the transitional metals that were analysed in this study. The highest level was found at site 27 (Figure 31), which is a site in the Blesbok Spruit. This river receives effluent

from mines on the East Rand and has previously been recognised 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 in the Suikerbosrand River. The Suikerbosrand River receives water from the Blesbok Spruit (Figure 2).

Ce was the only lanthanide analysed and again the highest level was found at the Molopo Eye, at 170 mg/kg (Figure 32).

U was the only actinide analysed and the highest level (50 mg/kg) was found at site 15 in the lower catchment of the Vaal River (Figure 33). At this point the river also receives drainage from lime mining activities to the North. This site is at a small town called Schmidtsdrift where there is ongoing alluvial diamond mining (CMR, 2008). In 1974 the South African Defence Force (SADF) acquired the Schmidtsdrift farms and established a military training base. Schmidtsdrift was occupied by the SADF for the next 20 years (Kleinbooi, 2007). Since no other site in the lower Orange River had similarly high levels of U, even though there are many diamond mines based in the river, the U levels at site 15 might be associated with military activities.

Figure 24: The Group IA elements are represented by Cs. Bar scale is relative.
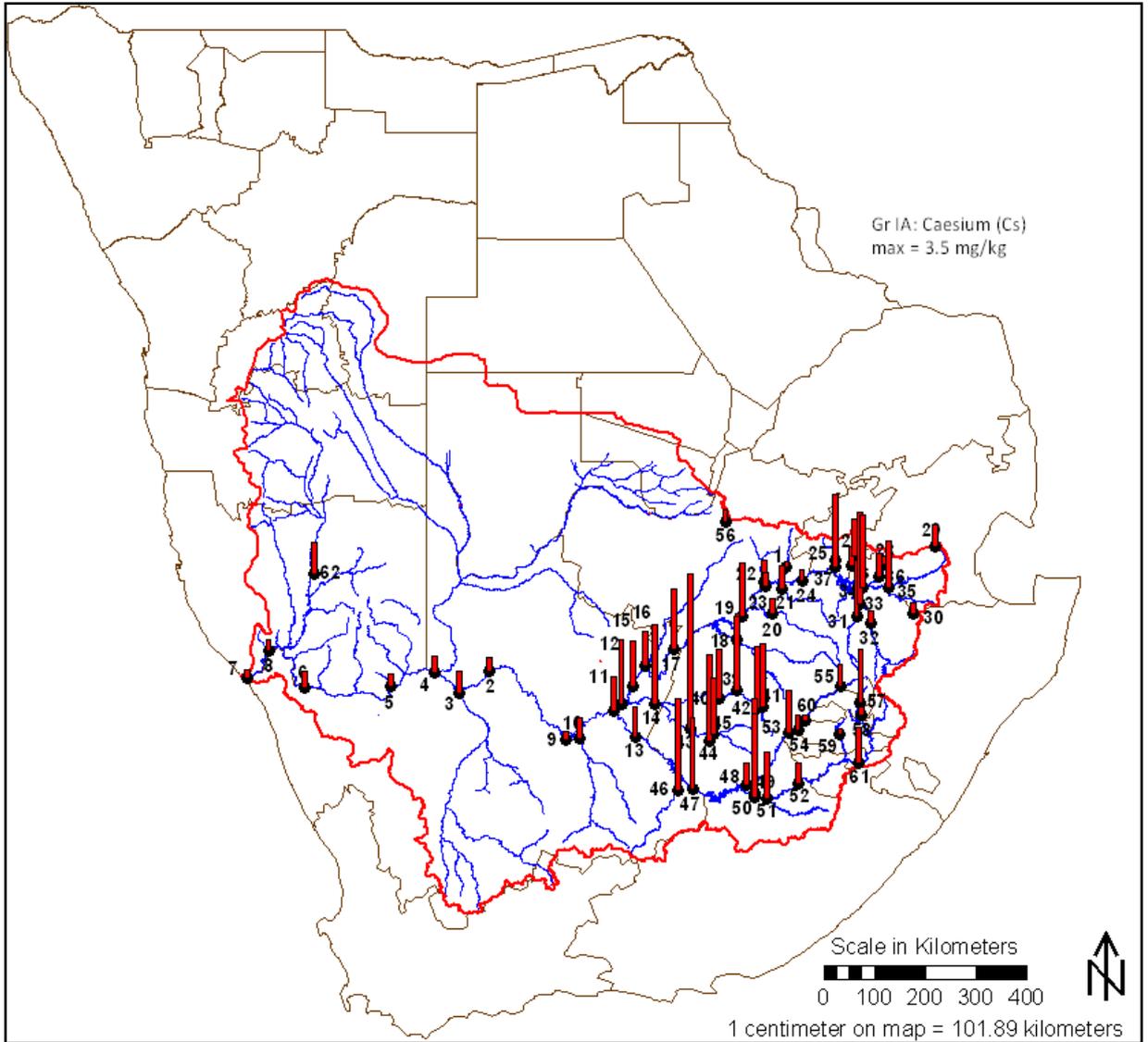
Figure 25: The Group IIA elements are represented by Be. Bar scale is relative.
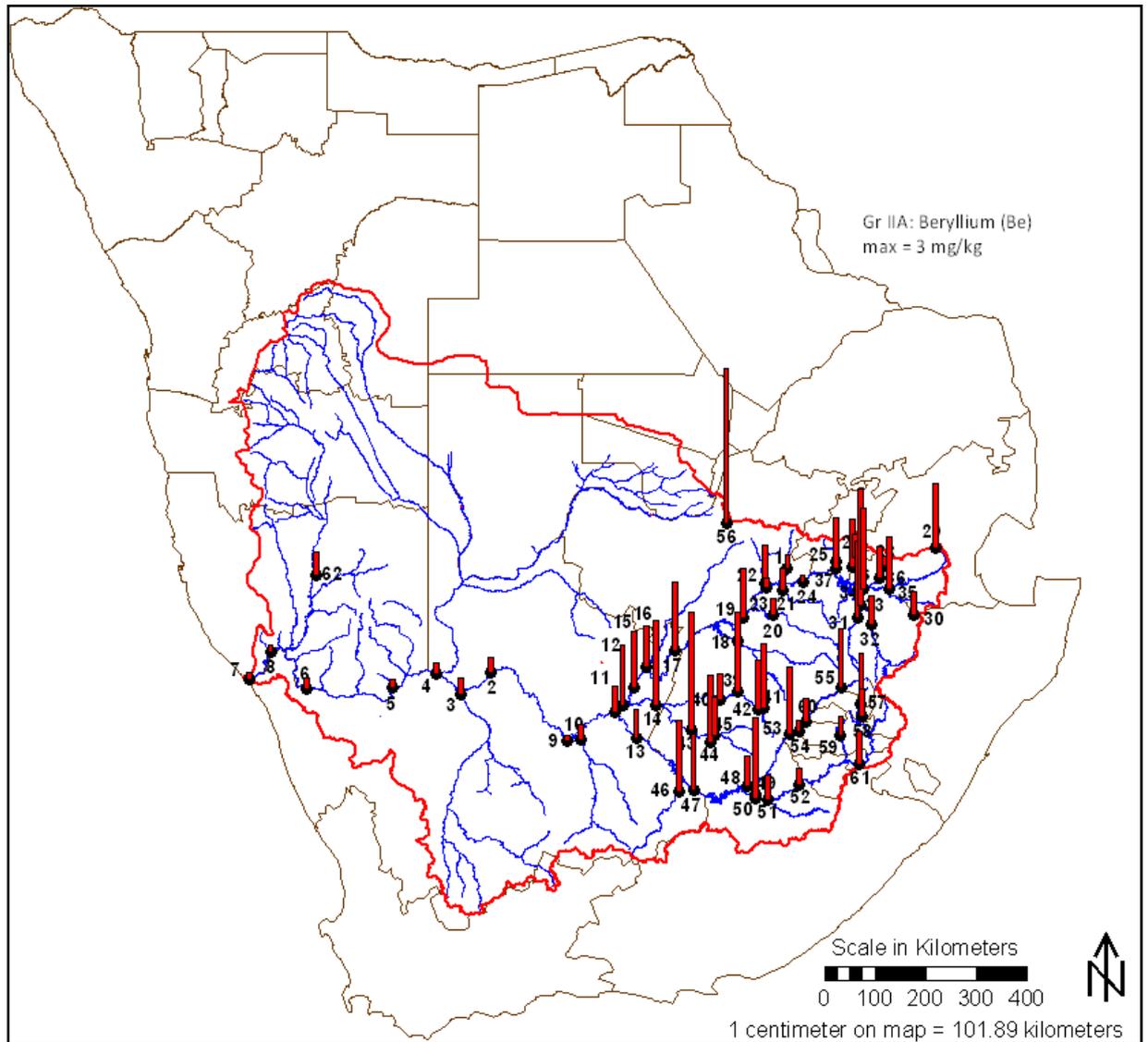
Figure 26: The Group IIIA elements are represented by Th. Bar scale is relative.
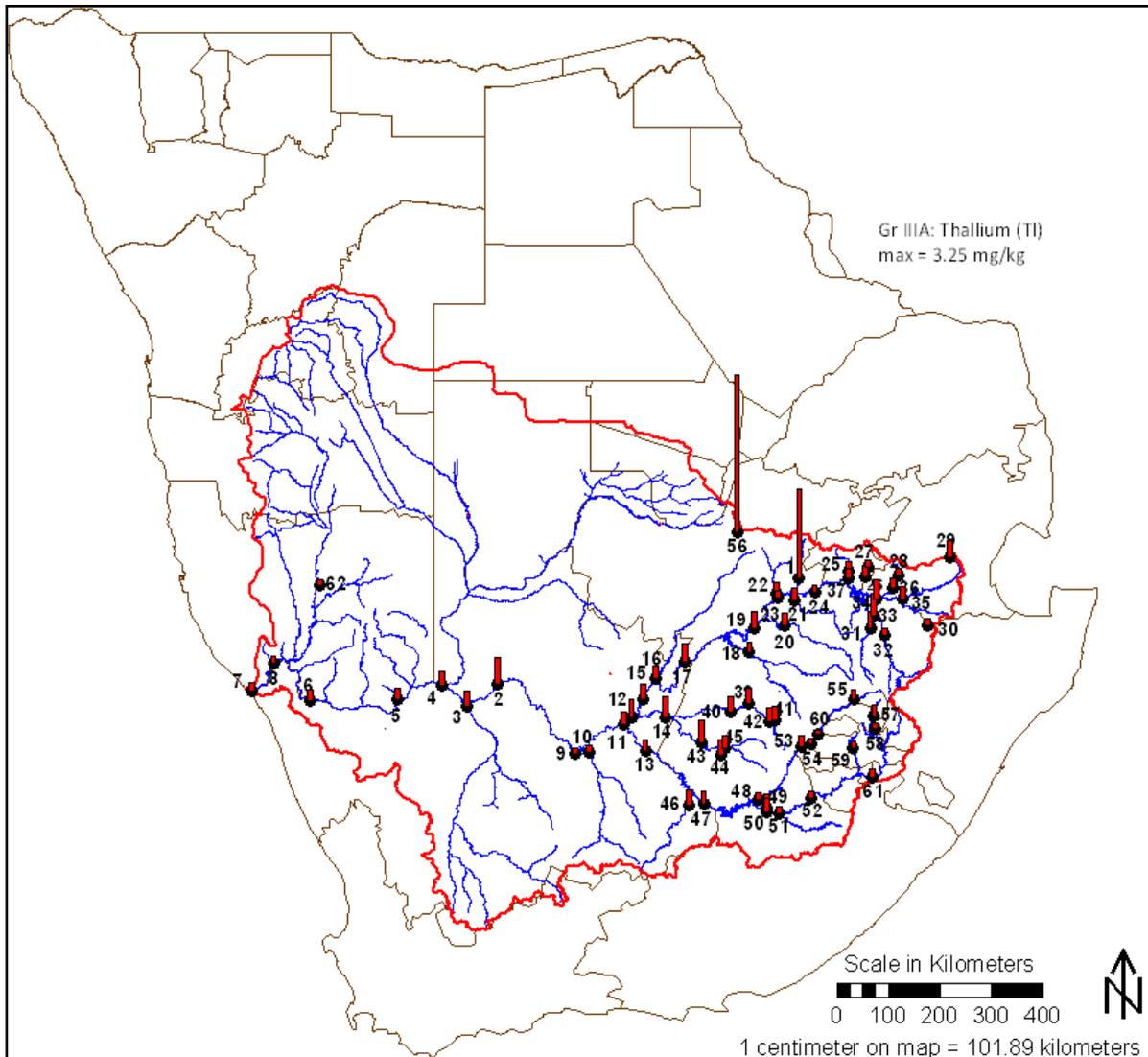
Figure 27: The Group IVA elements are represented by Pb and Sn. Bar scale is relative for each element, but not between elements.
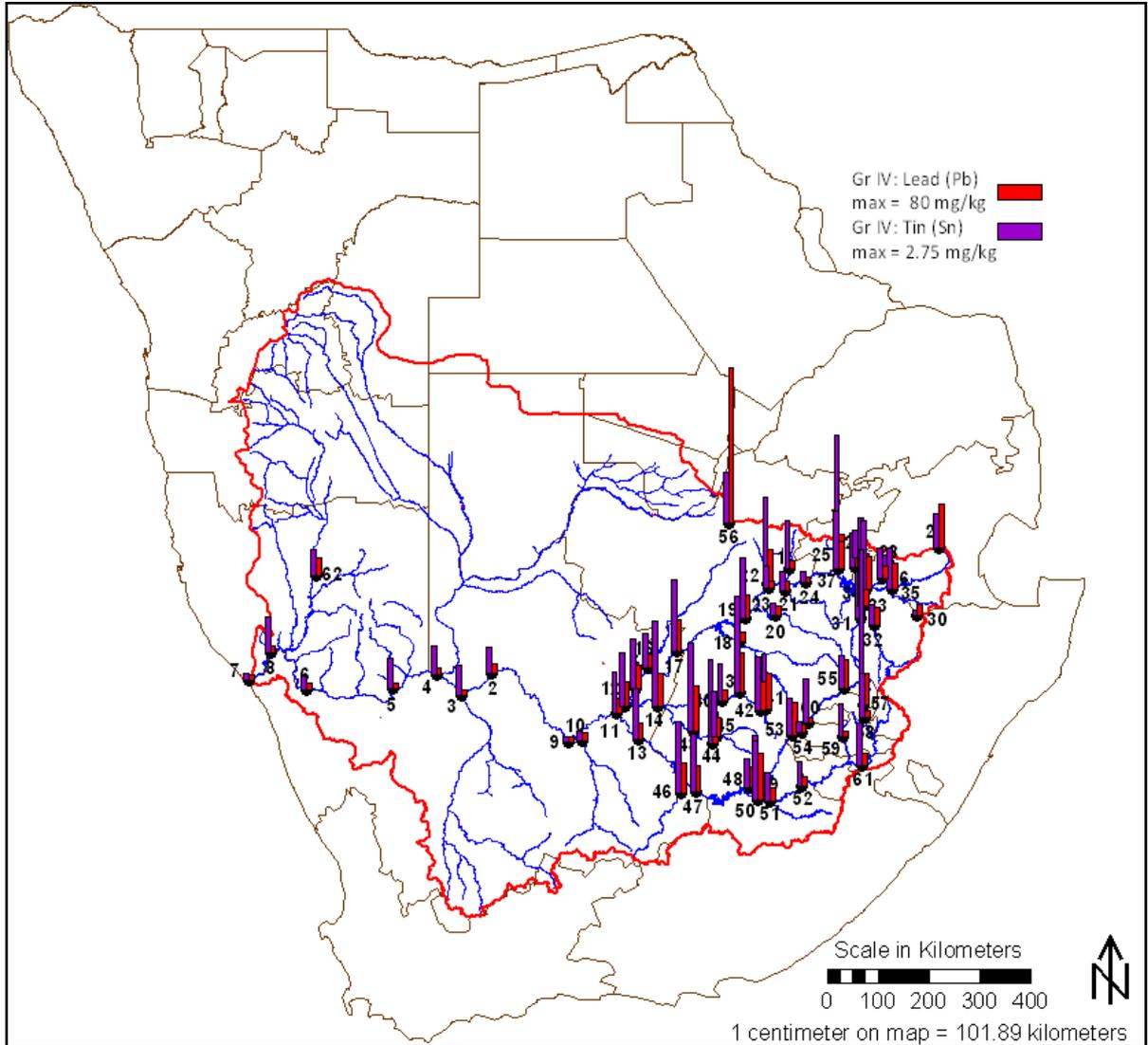
Figure 28: In Group VA, As was the only element analysed. Bar scale is relative.
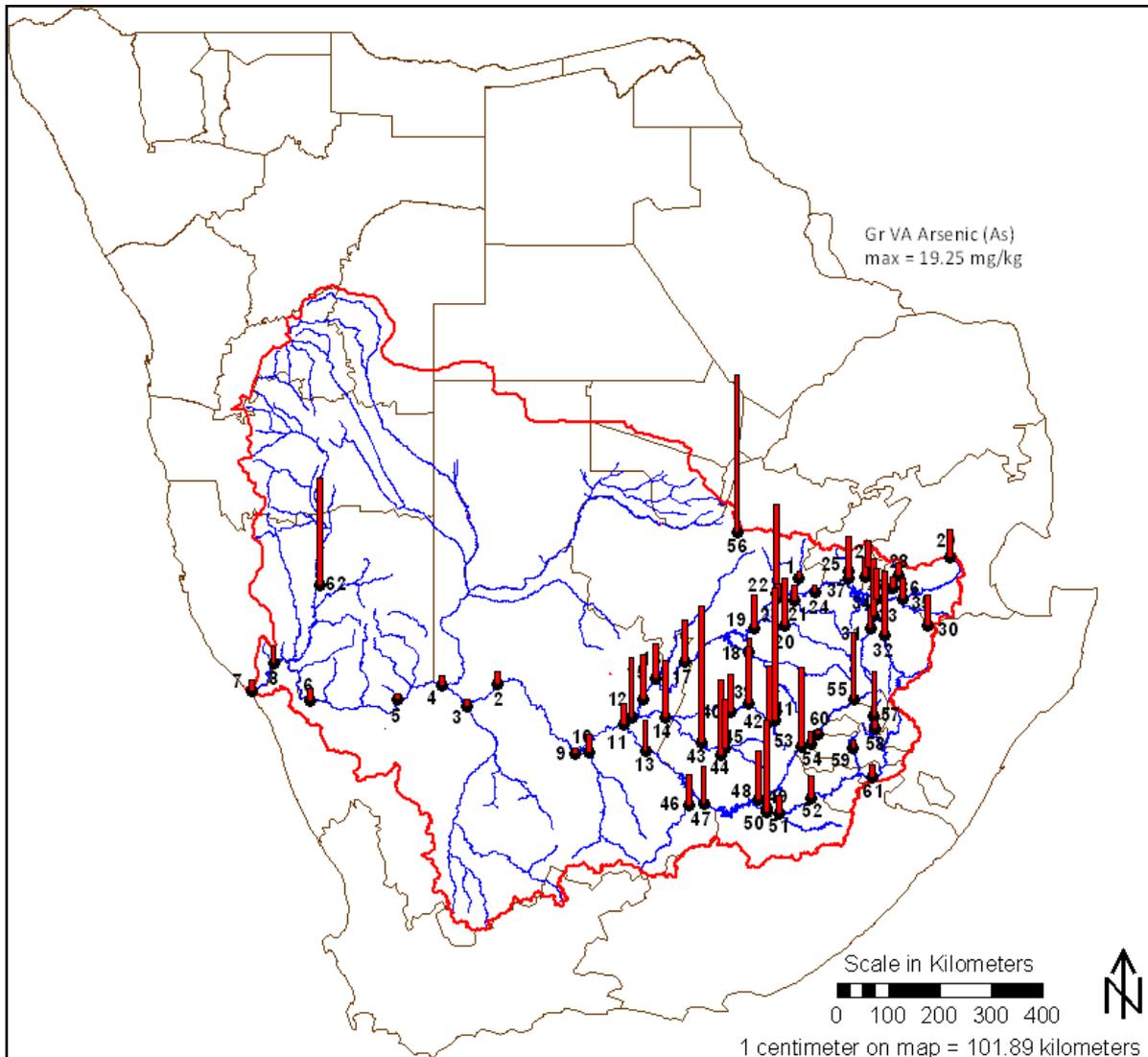
Figure 29: In Group VIA, Se was the only element analysed. Bar scale is relative.
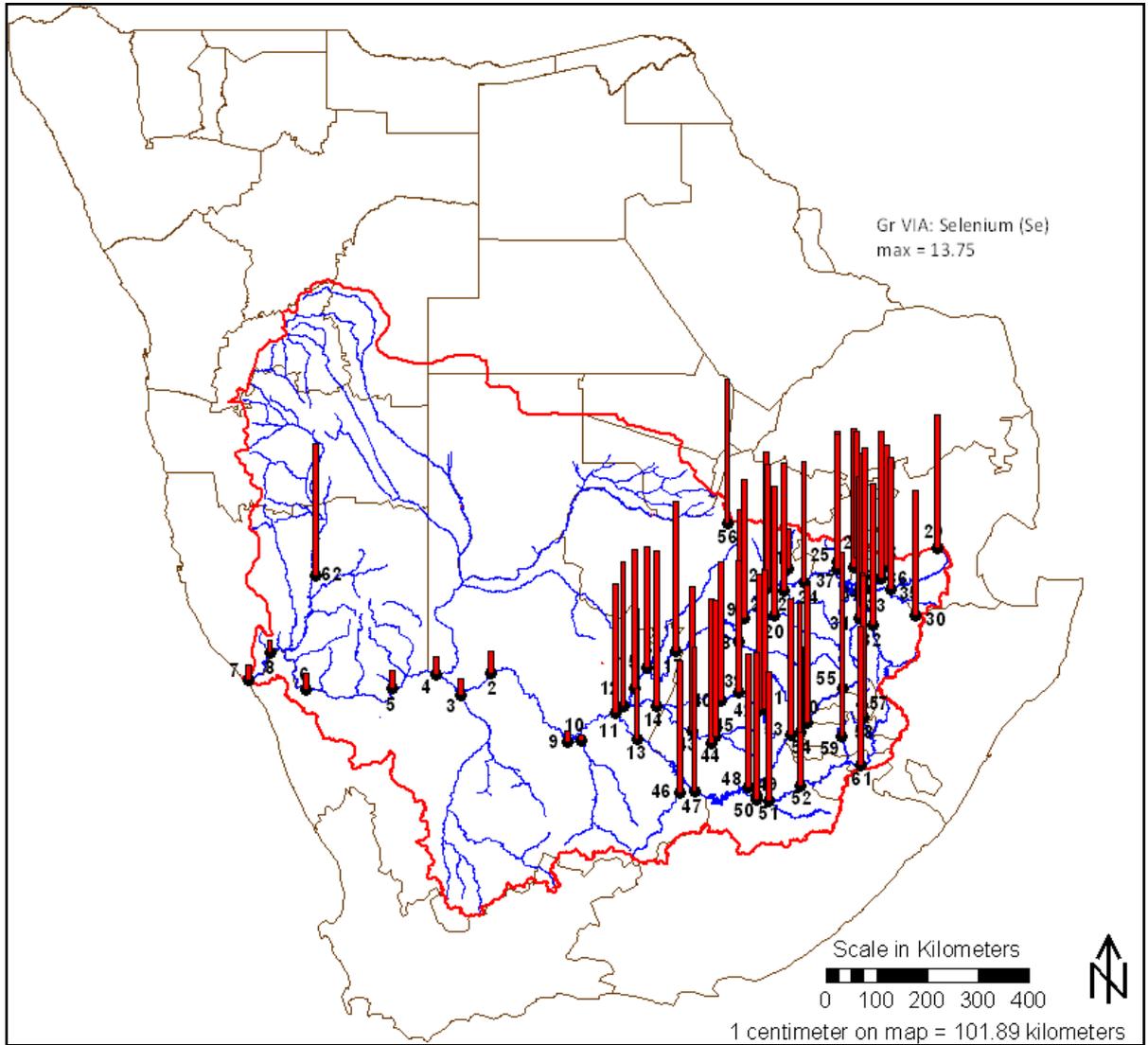
Figure 30: In Group VIIA, only Br and I were analysed. Bar scale is relative.
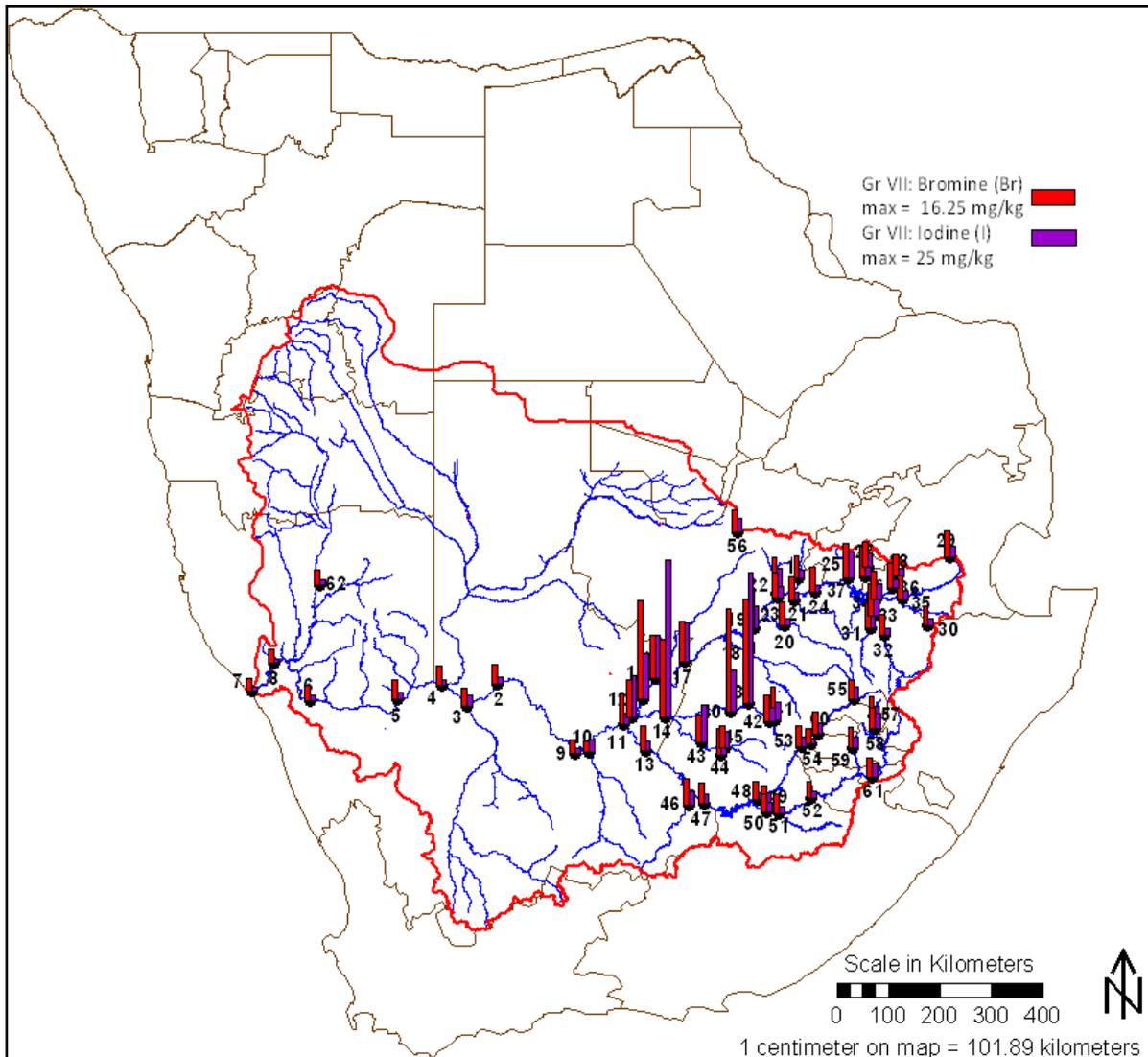
Figure 31: Zn was selected as the representative of all of the transitional metals analysed. Bar scale is relative.
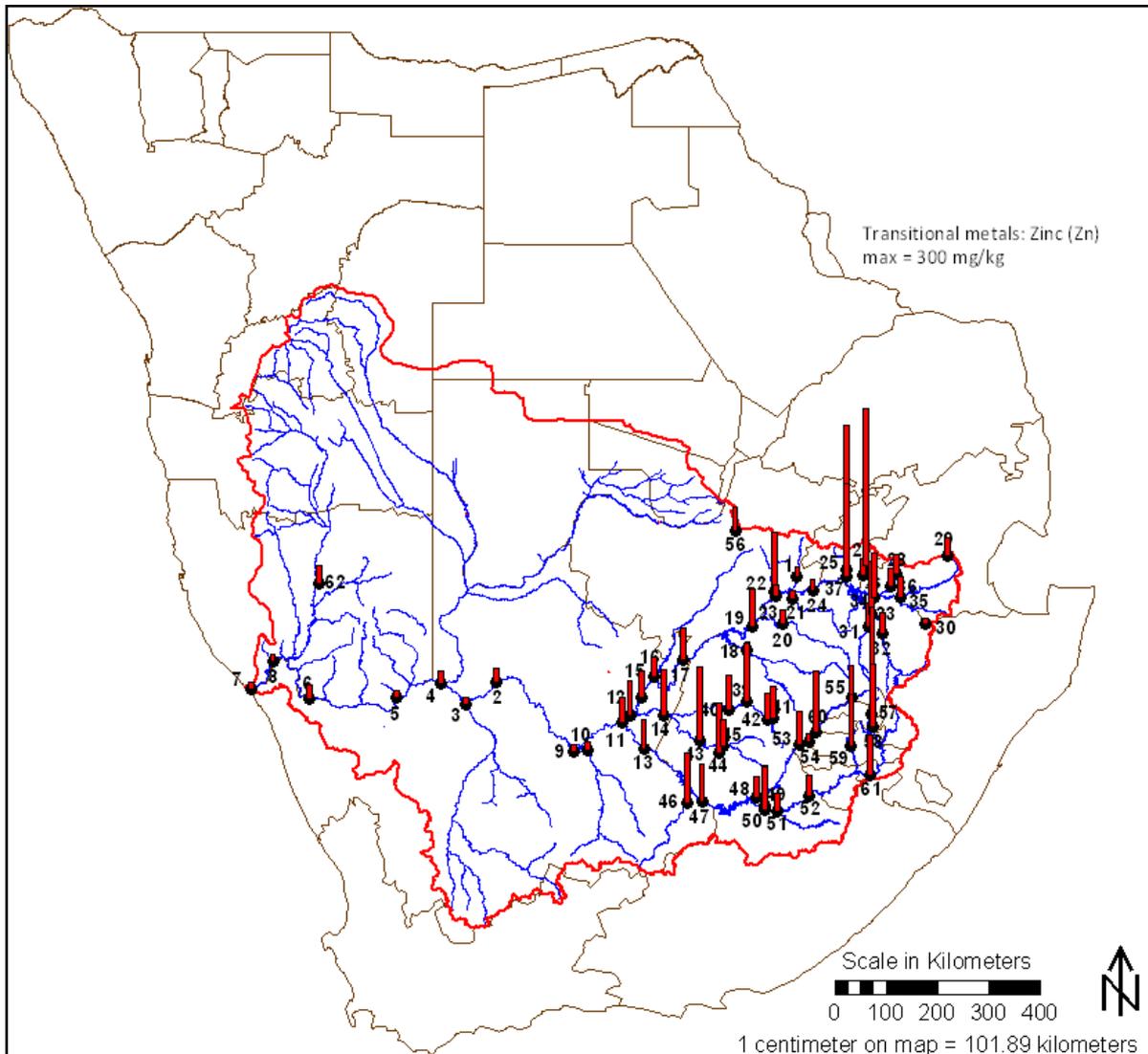
Figure 32: Ce was the only lanthanide analysed. Bar scale is relative.
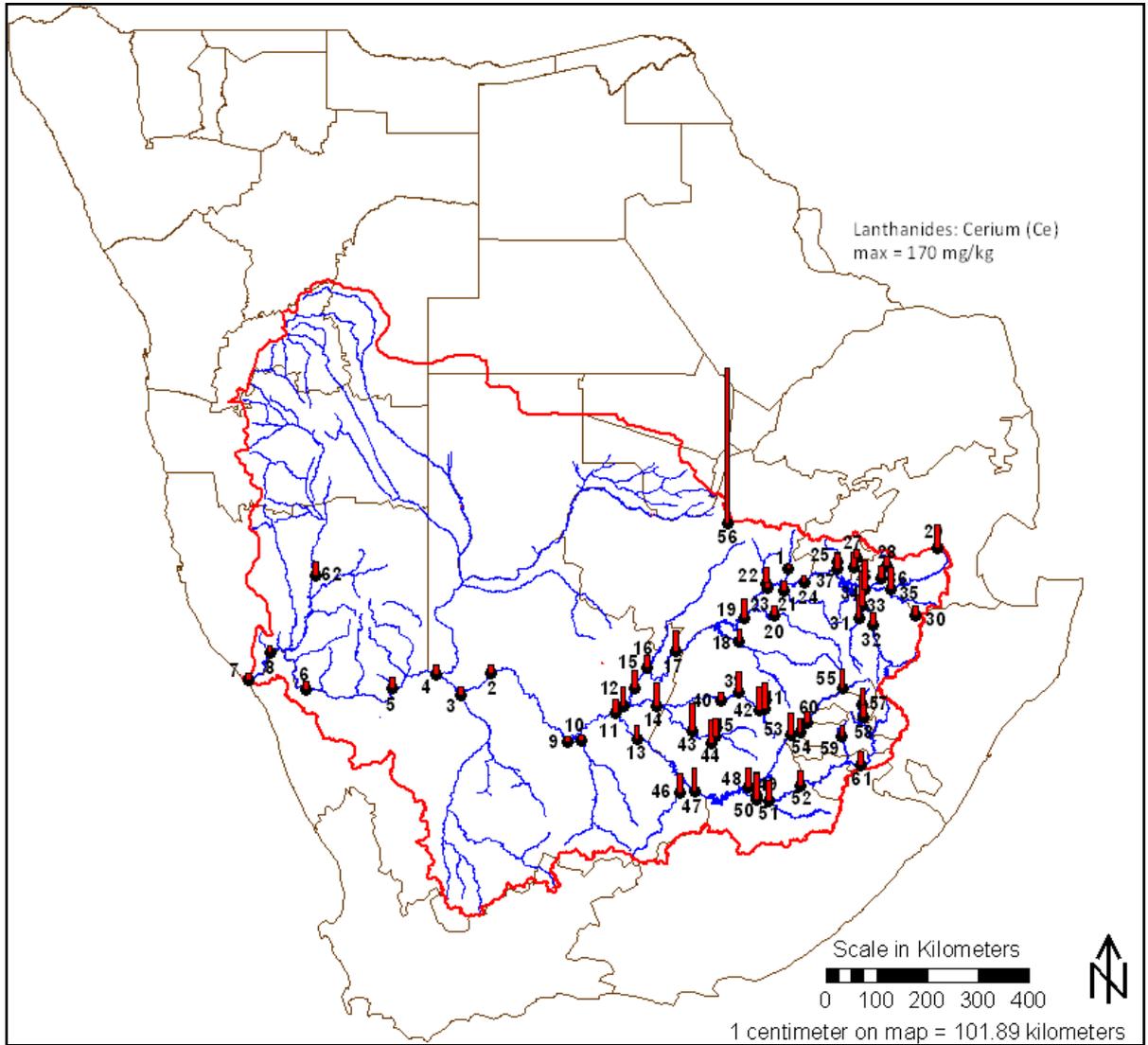
Figure 33: U was the only actinide analysed. Bar scale is relative.
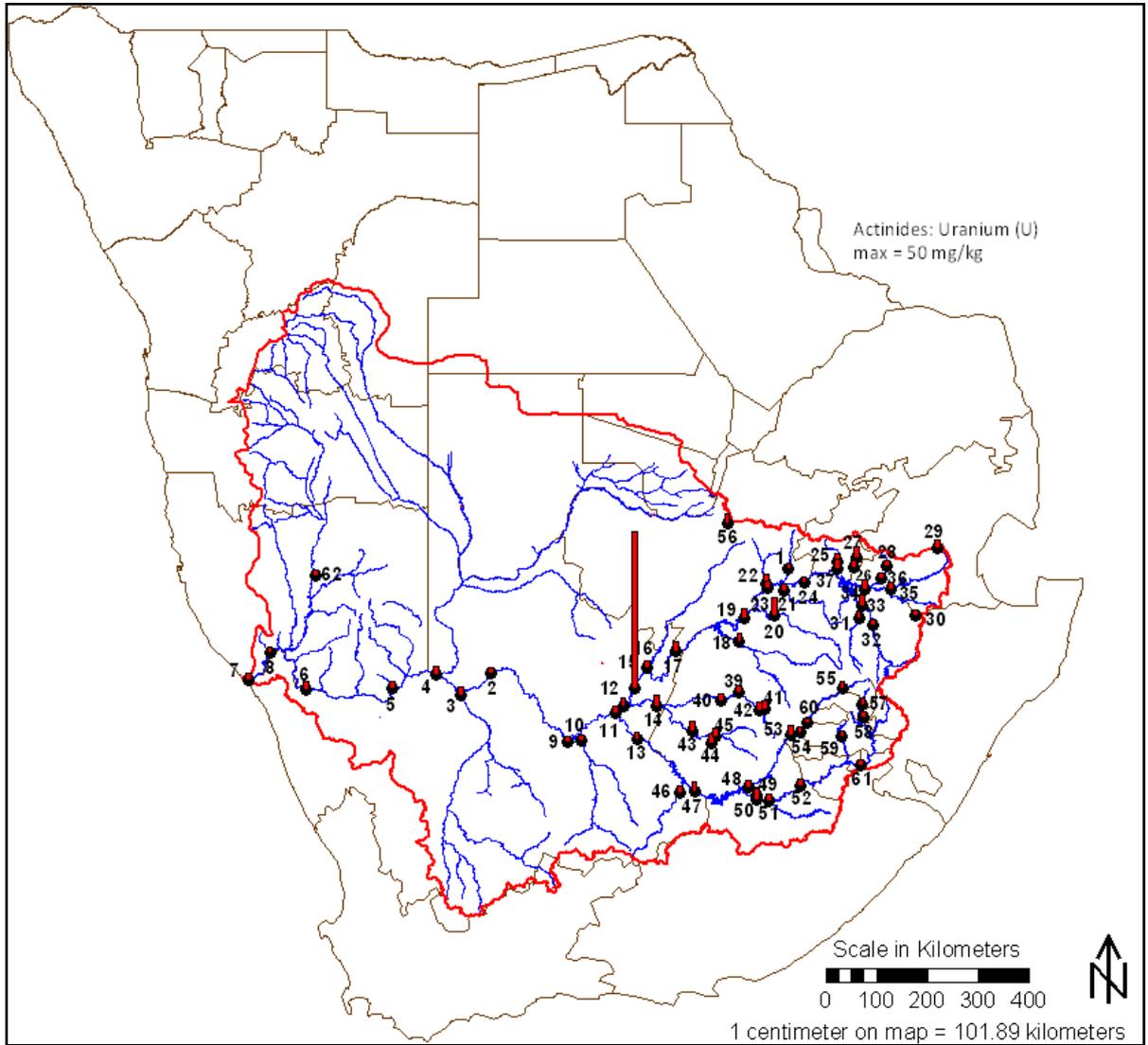
Fish

In this section of the report, the main focus is on 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 wet weight (w.w.) (Wagner & Boman, 2003). This means that the Cu and Cr levels measured for pooled fish fillets in this study is well within the allowable levels (Figure 34).

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 w.w. (Wagner & Boman, 2003). The concentrations were similar between the four sites (Figure 35)

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 (Figure 36). According to the international standards, As may vary between 0.1 to 5 mg/kg w.w. 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 (range: 2.33-5.38 mg/kg d.w.) is higher than that considered to be safe by international standards (0.3 to 2 mg/kg w.w.), especially since standards are reported for wet weight and the results of this study is reported in dry weight (d.w.).

The international standards for Cd are 0.05 to 2 mg/kg w.w. (Wagner & Boman, 2003), for Pb they are 0.5 to 10 mg/kg w.w. (Wagner & Boman, 2003), and for Hg they are 0.5 to 1 mg/kg w.w. (EC, 2006). The levels of Cd, Pb and Hg in the fish analysed in this study (Figure 37) 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 was still below accepted international levels.

Figure 34: Cr and Cu levels in the fillets of the sharptooth catfish. Bar scale is relative for the same element between the sites, but not between the two elements.
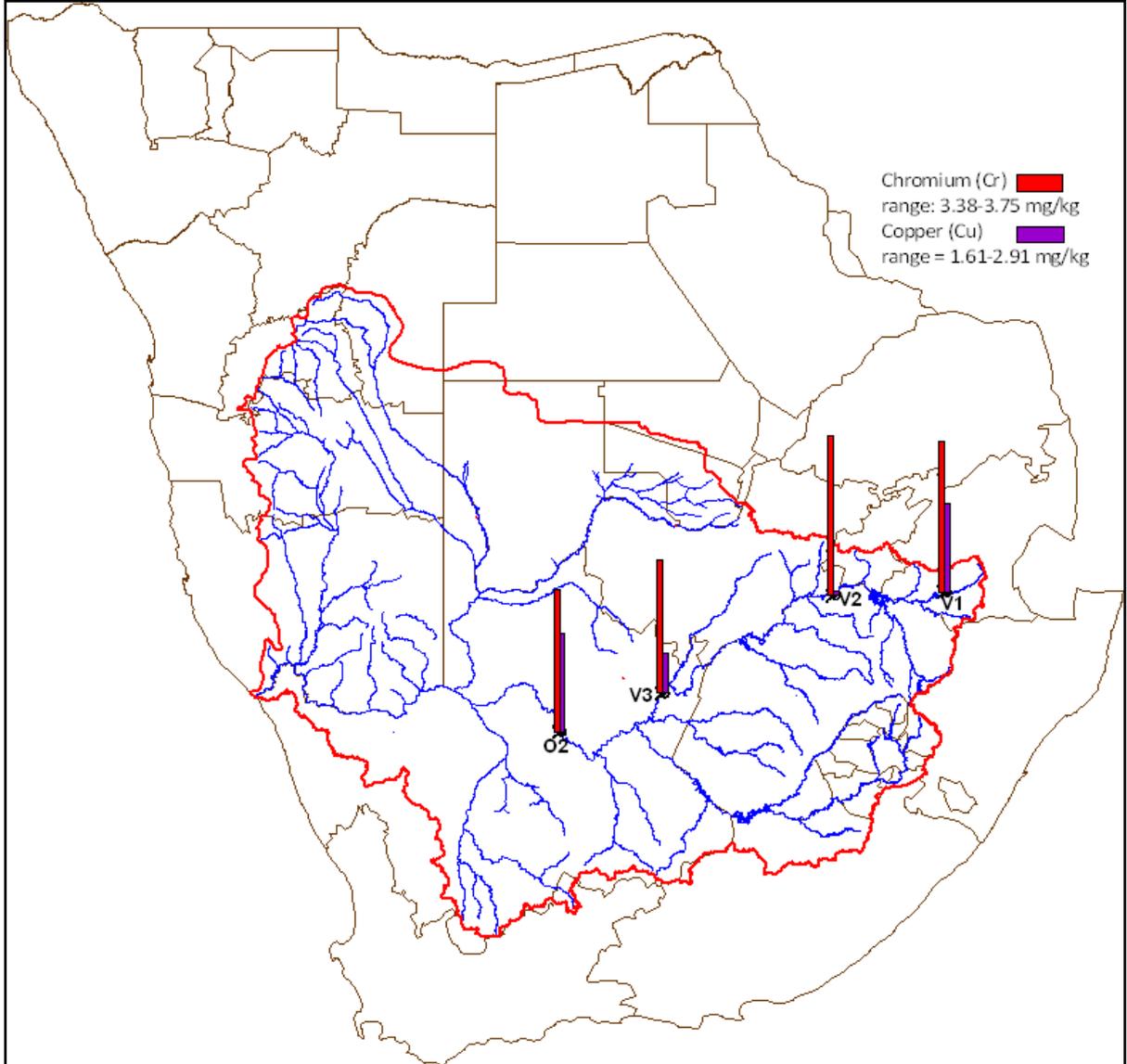
*Figure 35: Zn levels in the fillets of the sharptooth catfish. Bar scale is relative.*
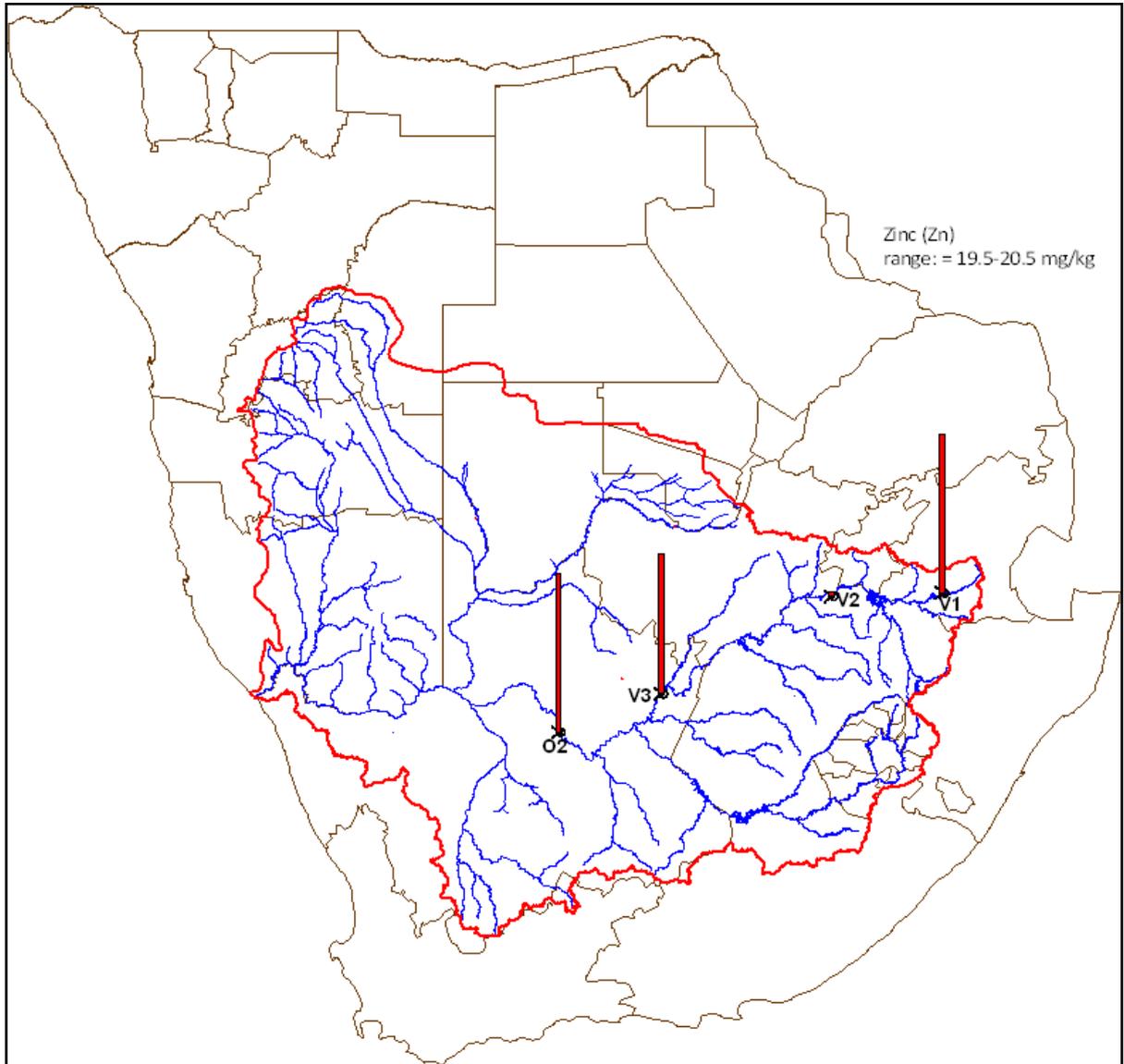
Figure 36: As and Se levels in the fillets of the sharptooth catfish. Bar scale is relative for the same element between the sites, but not between the two elements.
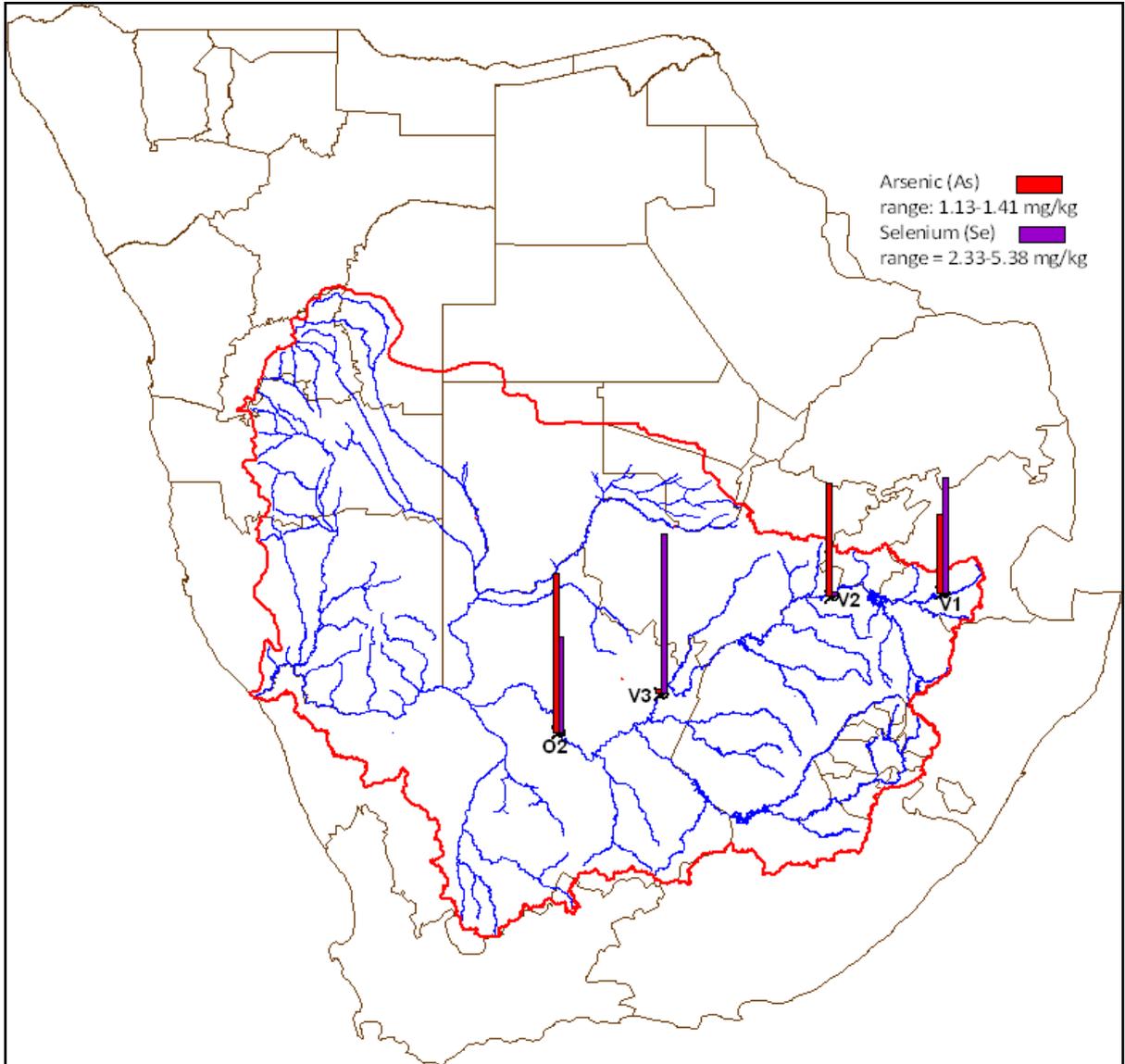
Figure 37: Cd, Pb, and Hg levels in the fillets of the Sharptooth Catfish. Bar scale is relative.
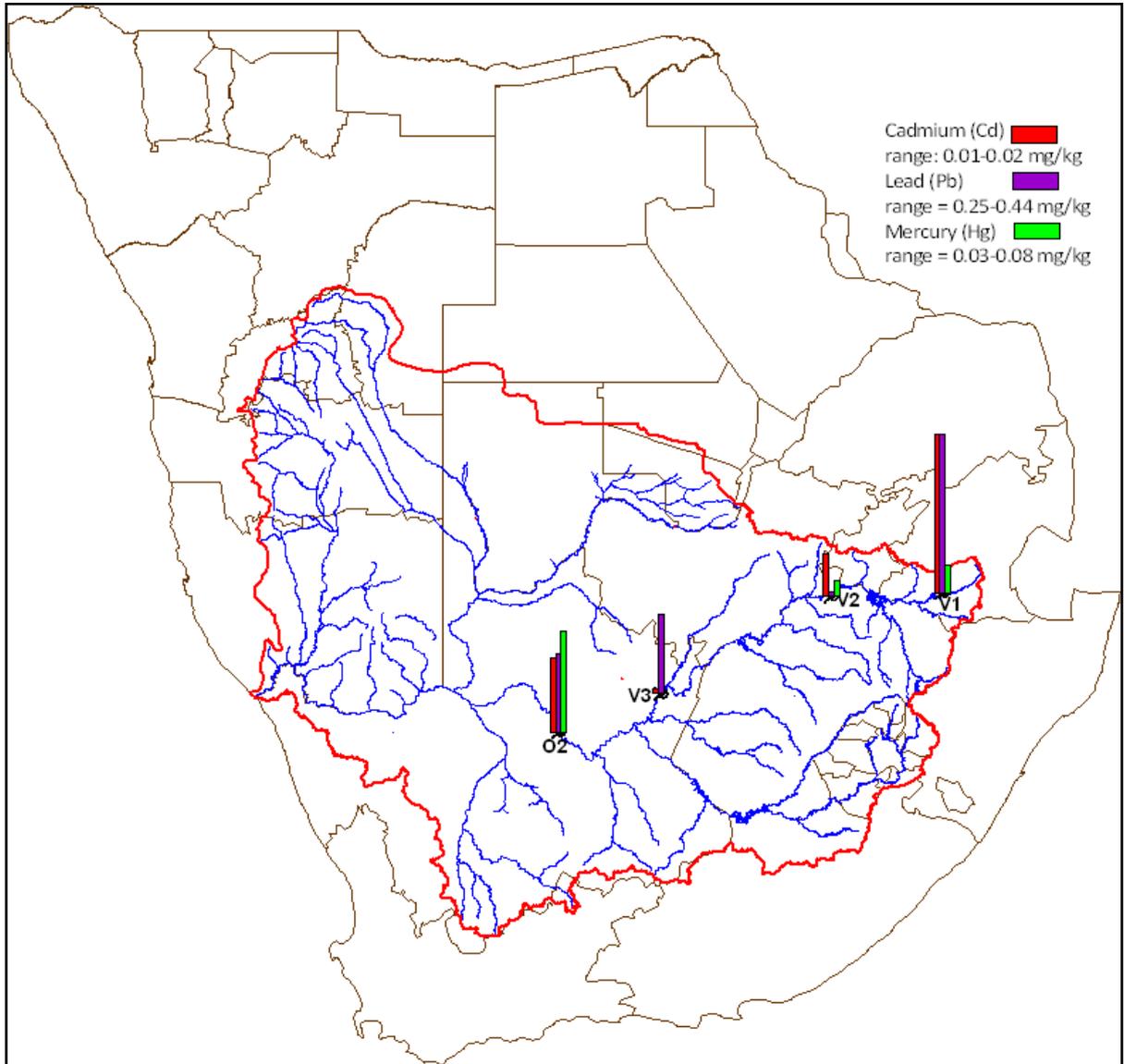
In this section, elemental bioaccumulation factors for fish are reported. A bioaccumulation factor is the ratio of the contaminant concentration in the organism to that of the potential ambient sources (Newman, 2010), which in this case is the sediment. Because this is sediment-related bioaccumulation, the term Biota-Sediment Accumulation Factor (BSAF) is used. The BSAF for the fish samples were calculated using the concentrations at one or two sediment sites closest to where the fish were sampled (Table 11). This was done for each of the fish pools. The mean BSAF for all of the fish were then calculated (Table 11). (Note: It was assumed that all measured levels in the sediment were bio-available to the fish as a precautionary measure, i.e. BSAF may may be much higher than those reported if a smaller fraction of bio-availability was considered). Only BSAF greater than 1 are reported (Table 11; Figure 38).

Table 11: The bioaccumulation factors of those elements that showed bioaccumulation in the fish from the sediment.

Fish pools	Sediment sites	Rb	Rh	Ag	Sn	Pt	Au
V1	35	0.3	2.9	1.2	0.9	5.6	2.3
V2	24	3.7	0.8	1.9	2.3	10.6	1.6
V3	12, 15	1.0	0.4	0.1	0.7	3.5	1.5
O2	2, 9	2.8	0.3	1.5	1.5	3.3	0.2
Mean		*1.9*	*1.1*	*1.2*	*1.3*	*5.8*	*1.4*

The highest BSAF of each element that showed bioaccumulation was at V1 or V2 (Table 11). Platinum showed the strongest bioaccumulation, more than twice as high as the next element, Rb. Platinum was shown to alter the heart rate of zebrafish and decreased egg hatching rate at high concentrations (Osterauer et al., 2009). More studies would be needed to clarify this potential interaction.

Figure 38: The biota sediment bioaccumulation factor (BSAF)for those elements that showed accumulation levels in the fish tissue greater than one.
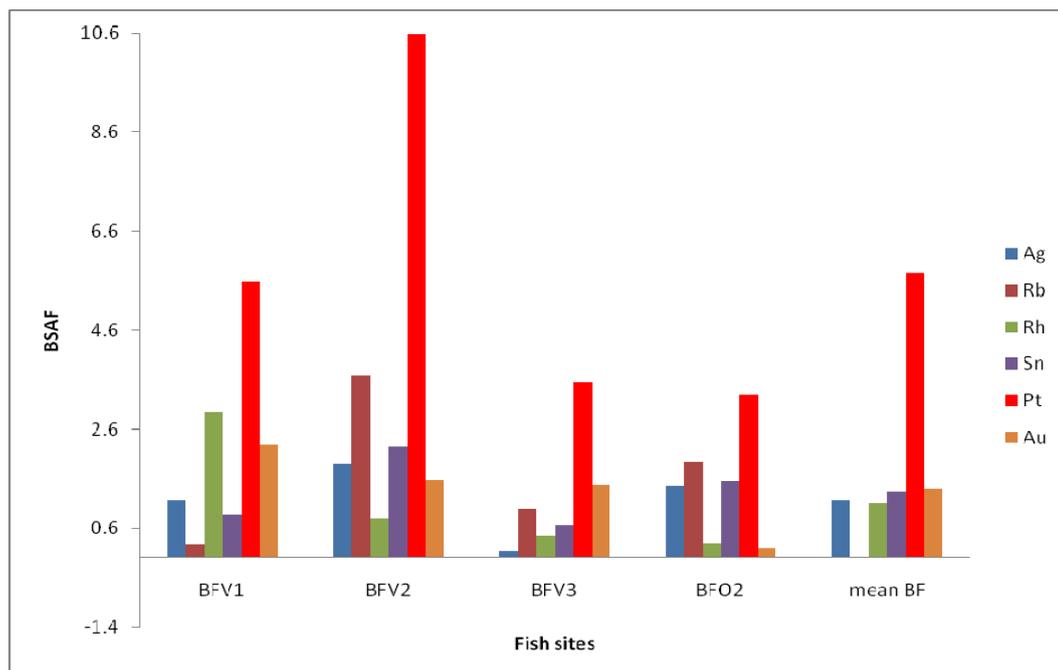
Wild bird eggs

Although eggs of more than one bird species were analysed from all but one site (Table 4), the focus on this section is on the highest concentration of an element measured irrespective of the species in which it was found. The addendum contains all the concentrations for each of the bird sites. Black headed herons were not included in the assessment in this section because they are mainly terrestrial feeders. Sn had the highest level at all of the sites followed by Fe (Table 12). The same four elements, Sn, Fe, B, and Zn were ranked among the top four at each of the egg collection sites

Table 12: The five highest elemental concentrations measured in any of the wild birds' eggs at each of the bird sites. Concentrations are in mg/kg (d.w.) and arranged in decreasing order.

Barberspan			Bloemhof Dam			Eldorado Park			Potchefstroom		
African darter	Sn	235	Great white egret	Sn	280.6	Sacred ibis*	Sn	240	Reed cormorant	Sn	255.4
Grey heron	Fe	230	Little egret	Fe	230	Sacred ibis	Fe	205	Reed cormorant	Fe	204.1
Grey heron	B	115	Great white egret	Zn	75	Sacred ibis	Zn	65	Cattle egret	Zn	75
African darter	Zn	70	Great white egret	B	65	Sacred ibis	B	40	Reed cormorant	B	34.1
Grey heron	Au	70	Great white egret	Au	19.5	Sacred ibis	Al	21	Cattle egret	Ba	17

*Only sacred ibis eggs collected at Eldorado Park were analysed.

In this section, the bioaccumulation of the elements from fish to birds consuming the fish were investigated. This could only be done for elements analysed in both matrices and it is assumed that all of the elements in the fish will be bioavailable to the birds. To form a broad impression of the bioaccumulation across that section of the catchment from which fish and eggs were collected, the bioaccumulation factors were calculated for each bird species relative to each of the fish samples. This approach was followed because the birds would not necessarily feed on the same fish collected for the elemental analysis, nor would the birds' uptake of elements be through food only. It was assumed that all the bird species in this study would consume sharptooth catfish. The mean of these bioaccumulation factors (MBF) were calculated for each element as a broad indicator of what the range of bioaccumulation factors could be, irrespective of the species. A bird species-specific bioaccumulation factor (SSBF) was also calculated for each element to assess if the different species would accumulate the elements differently (Figure 39).

The MBF showed that all the elements bioaccumulated (at levels higher than in fish) in the bird eggs, except Cs. Sn had the highest MBF of 313.6 (Table 13) followed by Au (108.1). The majority of the remaining MBF was less than 10. Six MBFs were between 10 and 20, namely Be, B, Mo, Pd, Tl and U. The grey herons proved to be the bird species which accumulated the greatest percentage of the elements to the highest extent (42%), followed by the cattle egret 26% (Table 13; Figure 39). These results need to be confirmed with closer monitoring of particular bird species

and their known food source. The results of this study only be used as a broad indicator of bioaccumulation in the Orange-Senqu Basin.

Table 13: The mean bioaccumulation factor (MBF) of elements in bird eggs as well as the species specific bioaccumulation factor (SSBF) for the different bird species. MBF and SSBF were calculated assuming the birds consume Clarias gariepinus.

| | MBF | Species specific bioaccumulation factor (SSBF) | | | | | | | |
		Grey heron	African darter	Great white egret	Reed cormorant	Sacred ibis	Little egret	Cattle egret	Glossy ibis
Be	10.7	22.3	9.8	10.9	13.0	12.1	3.7	3.0	4.5
B	10.9	25.5	10.9	18.8	8.5	8.8	5.1	2.1	6.5
Al	2.1	1.9	1.7	1.3	1.4	2.5	1.7	3.5	1.9
Sc	1.8	2.7	1.8	2.1	2.0	1.8	1.3	0.7	1.5
Ti	1.8	0.3	0.2	0.3	0.2	0.2	0.4	10.5	0.3
V	2.1	1.9	2.2	1.5	2.3	2.1	2.4	2.0	2.3
Cr	2.3	1.6	2.3	1.7	2.3	2.2	2.2	3.6	2.2
Mn	3.3	2.8	3.3	2.6	4.0	3.8	3.3	2.2	5.1
Fe	6.8	4.2	3.5	4.1	3.9	3.9	4.2	22.6	3.6
Co	2.8	4.7	1.7	2.3	1.8	3.5	1.6	1.9	4.8
Ni	3.5	4.7	3.5	3.7	3.6	3.9	3.7	1.7	3.2
Cu	3.2	3.5	4.0	3.4	3.2	3.8	2.7	2.2	2.3
Zn	4.5	3.1	3.2	3.7	3.3	3.3	3.7	10.7	3.5
Ga	1.4	1.3	1.4	1.2	1.3	1.6	1.5	1.1	1.8
Ge	1.9	1.8	2.1	1.9	2.1	2.2	2.1	1.3	1.9
As	1.6	1.7	1.7	1.5	1.6	1.6	1.6	1.5	1.7
Se	1.6	2.2	1.8	1.4	1.7	1.4	1.2	1.4	1.9
Rb	1.5	0.2	0.2	0.3	0.4	0.5	0.3	7.9	0.4
Sr	2.7	2.2	2.8	1.8	2.0	4.5	2.1	1.5	5.0
Mo	16.4	16.6	27.4	16.9	23.7	13.0	12.5	8.2	6.0
Pd	14.1	42.3	8.6	23.1	6.6	8.5	3.7	9.5	5.3
Cd	3.4	10.9	2.5	3.7	1.3	3.4	2.5	0.4	0.5
Sn	313.6	324.9	364.2	310.8	345.9	346.1	339.1	166.4	332.0
Cs	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1
Ba	2.3	1.9	2.0	1.6	2.0	2.1	2.1	3.9	2.6
Ce	1.2	1.0	0.6	0.7	0.8	3.3	0.9	0.7	1.1
Pt	3.8	12.9	2.5	4.6	2.1	2.3	1.5	0.6	2.5
Au	108.1	432.7	54.3	206.6	34.4	46.3	18.5	9.6	26.0
Tl	11.3	49.8	4.4	20.1	2.7	4.1	1.4	0.7	1.9
Pb	1.7	3.3	1.3	2.0	1.4	1.9	1.2	1.0	1.5
U	10.9	48.3	3.8	16.6	4.7	3.2	2.1	0.8	2.0
% elements with highest SSBF		41.9	9.7	0.0	0.0	6.5	3.2	25.8	12.9

Shaded area: highest SSBF for each element.

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Figure 39: The proportions to which the different bird species accumulated the elements into their eggs, assuming their only source of exposure through consumption of fish.
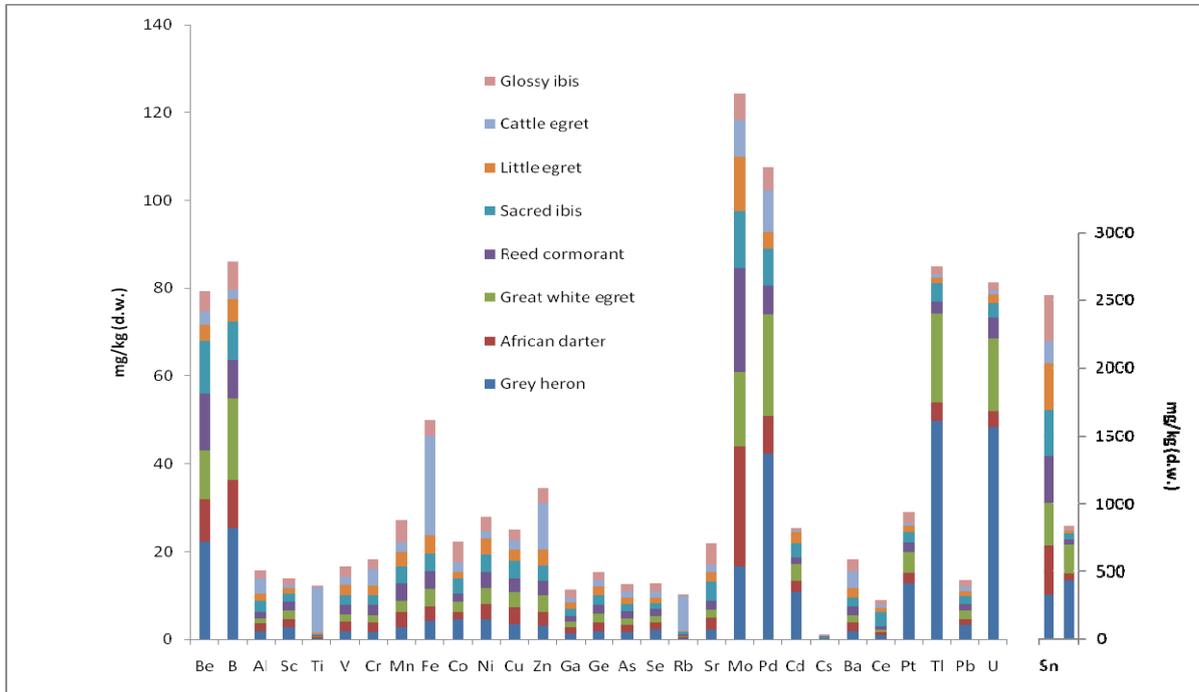
4. Discussion

4.1 Organic pollutants

Dioxin like TEQ

In general, dioxin like TEQ levels was low in all media, but indications of bioaccumulation were seen in from sediment (Figure 6) to fish (Figure 11) and from there to birds (Figure 15). TEQ levels were higher in sediment from the east, becoming 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.

PCBs

PCBS in sediment (Figure 7), as for the dioxin TEQs (Figure 6), were higher towards the eastern than the western parts of the catchment, and then more into Gauteng. In biota, however (Figure 12 and 16), 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.

Organochlorine compounds

In sediments, OCs were higher in Gauteng, and less downstream (Figure 8). The picture in biota, again, differed from the sediment distribution pattern. Although the highest OC levels in fish were from Parys (Figure 13), in birds (Figure 17) the highest levels were from Bloemhof Dam. It would have been very instructive to sample 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 coming from upstream.

PFOS

Although none of the sediments had detectable levels of PFOS, they were quantified in fish (Figure 14) and bird eggs (Figure 18). 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.

PAHs

The three sediment sites with the highest ∑PAH levels were downstream of areas both urban and industrial in South Africa and Lesotho. The source for the PAHs were pyrogenic in nature, often due to the combustion of coal or smelters. The most common PAH was fluoranthene, followed by phenanthrene and benzo(b+k)fluoranthene.

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 in sediment are difficult to measure and more difficult to interpret. However, using pollution distribution patterns on a catchment scale assists in assessing the overall pollution picture and to identify hotspots and areas of interest.

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 Metal Pollution Index (MPI) for sediment site 56, the Molopo Eye, was the highest (Figure 21) and when the Igeo-values were determined, the same site had the most elements with Igeo-values regarded as polluted (Table 9). The same site was also among the 25% sites with the most elements with the highest concentrations (Table 10). A cluster of sites in the Riet and Modder Rivers (Figure 22) also belonged to this 25% sites with the most elements with the highest concentrations. Shared geology between some of the sites could only partially explain this phenomenon, but in depth investigation of the area is deemed necessary to determine the exact cause of this. Two sites in Lesotho (58 and 57; Figure 23) with high levels of elements are also likely to be due to geology rather than mining activities or any other anthropogenic activities. Using the accompanying ARC GIS viewer will further assist in site-specific interpretation.

The levels of the elements in the sediment warrants further investigation, especially in the light of the Igeo values for Se, As, and Hg. However, intensive investigation into the natural background levels for these elements are needed to clarify this observation

When the sediment levels are compared to sediment quality guidelines for The Netherlands (only for As, Ba, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, and Zn (Adriano, 2001) and U and Se (Hamilton, 2004; Sheppard et al., 2005)), 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. The levels for.

The levels of Cu, Cr, Zn, As, Se, Cd, Pb and Ag in the fish fillets were compared to international guidelines deemed safe for human consumption. It was only the Se levels that were higher than the guideline levels and at site V3 it was twice as high as the highest allowable level. Those elements that seemed the most likely to bioaccumulate in the fish, should exposure to sediment be their only exposure pathway, and all of elements were to be bioavailable, were Pt > Rb . > Au > Sn > Ag > Rh (Table 11). None of the other elements had bioaccumulation factors greater than 1. Further assessment is needed on the bio-available fractions of the elements at the sites identified.

Sn had the highest level at all of the bird egg pools followed by Fe (Table 12) and the same four elements, Sn, Fe, B, and Zn had the highest levels at each of the bird egg collection sites (Table 12). All the elements had bioaccumulations factors greater than 1, except for Cs (Table 3), but this is only a broad indication of possible bioaccumulation in the catchment as these calculations were done under a number of assumptions (cf. section 3.2.3). There is also a possibility that the various bird species bioaccumulate different elements differently but the grey heron seemed to bioaccumulate more elements than the other species (Figure 39). The eggs of the grey heron might be a good bio-indicator and the species of choice in situations where only a single bird species may be sampled.

5. Risk assessment

5.1 Background and methods

A human health risk assessment was conducted to determine if the contaminants contained within the sediment, wild bird eggs and fish samples tested may cause adverse health effects to humans if the fish or eggs from these areas are consumed. The methodology, with which this human health risk was assessed, is described by the US-EPA (1988, 1996) and the WHO (2002). Human health risk assessment consists of four steps:

- Hazard Identification. Can exposure lead to toxic or carcinogenic health effects?
- Dose-response assessment. What is the relationship between the agent and incidence of adverse health effect?
- Exposure assessment. What is the sum total of expected exposure to the agent?
- Risk characterization. What is the probability of an adverse effect due to exposure to the agent?

For agents that cause non-cancer toxic effects, a Hazard Quotient (H.Q.) can be calculated, comparing the expected exposure to the agent to an exposure that is assumed not to be associated with toxic effects.

For oral or dermal exposures, the Average Daily Dose (ADD) was compared to a Reference Dose (RfD):

$$HQ = \text{Average Daily Dose / Reference Dose} \qquad \text{Equation 1}$$

Any Hazard Quotient less than 1 is considered safe for a lifetime exposure.

For chemicals that may cause cancer if ingested, risk is calculated as a function of oral Slope Factor and Dose and can be calculated by the following formula:

$$\text{Risk} = 1 - e^{-(\text{Oral Slope Factor} * \text{Lifetime Average Daily Dose})} \qquad \text{Equation 2}$$

In this report the human health risk assessment will be based on the HQ determined for toxic agents and risk calculated for the various carcinogens.

The maximum concentration detected in all sample sites was used as a worst-case scenario to determine what risks (if any) were involved as a screening risk assessment. If a chemical was found to be responsible for risks considered by the US-EPA and WHO to be unacceptably high, a detailed assessment for that contaminant was done, making use of the spread of the data, averages, and identifying which sampling site was responsible for the highest concentrations detected.

Sediment, wild bird eggs and fish samples were tested for various heavy metals, PAHs and POPs. The maximum concentrations measured for each contaminant, for each medium and the corresponding sampling sites were used.

Cross-media transfer equations are used to determine the amount of contaminate that could transfer from the sediment into fish which can be consumed. The formulae used to generate the exposure concentrations based on sediment concentrations was that described by the US-EPA (1990) for sediment to fish concentrations.

$$C(w) = \frac{C(sd)}{(Koc * OC * DN)}$$

Equation 3

$$BCF = (0.79 * \log(Kow)) - 0.40$$

Equation 4

$$C(f) = BCF * \left(\frac{fat}{3}\right) * C(w)$$

Equation 5

Where:

C(f) = Concentration in fish
C(w) = Concentration in water
C(sd) = Concentration in Sediment
DN = Sediment Density (Relative to Water Density of 1.0 kg/l)   (1.90)
OC = Organic Carbon Fraction of Sediment (4.00%)
Koc = Octanol-Carbon Partition Coefficient of the Compound
Kow = Octanol - Water coefficient of the compound
BCF = Bioconcentration factor

These calculations, however, limit the amount of contaminants that can be investigated as there are limited contaminants for which Kow and Koc values are available. To determine the risk posed by contaminants, various exposure parameters are used to assess the average exposure of humans. The exposure parameters used for these evaluations are listed in Table 13.

Table 13: Exposure parameters used to generate exposure estimates.

Exposure parameter	Amount
Events per year	350
Kg per event (fish)	0.054
Kg per event (WBE)	0.060
Body weight	70kg
Exposure duration	30 years

The dose estimates in the following sections in this assessment, as well as the risk estimates derived from them, refer only to the specific exposures that have been described in Table 13.

The average daily dose was calculated taking into account the concentration of the chemicals in sediment, for a 70 kg adult, assuming an intake of 0.054 kg fish and 0.060 kg of wild bird eggs on a daily basis (equivalent to 378 g per week). A range of risks is presented making use of average and 95th percentile concentrations of chemicals detected in the sediment, calculated to represent concentrations expected in fish. The 95th percentile represents the "reasonable maximum" risk.

5.2   Results

The results of the exposure calculations presented as both Average Daily Dose (ADD) and Lifetime Average Daily Dose (LADD) in mg/kg/d for fish, wild bird eggs, and sediment are given in Tables 14 and 15. Based on the exposure assumptions described in the section above, risks of developing cancer and toxic effects were calculated for the contaminant where sufficient data was available and are given in Tables 14 and 15 as well as illustrated in Figures 40 and 41. A Hazard Quotient (HQ) of less than 1 is considered to be safe for a lifetime exposure and not have negative effects (US EPA 1991). A cancer risk of greater than 1 in 100,000 is considered unacceptable (WHO 2002). Most of the chemicals were at concentrations below the "unacceptable" risks level, as defined by both the WHO and US-EPA.

Beryllium, and especially arsenic, in all media investigated, presented high risks of developing cancer (Figure 40). The risk of developing cancer from the consumption of wild bird eggs, is as high as 1 in a 1000. PAHs were only measured in sediment and the following pose between a 2 in 100 000 and 5 in 100 000 risk for the development of cancer; indeno(1,2,3 –cd) pyrene, benz(a)anthracene, benzo(b) fluoranthene and benzo(k) fluoranthene. The other PAHs are still being investigated by the EPA and their slope factors are derived from other isomeric chemicals. Benzo(a) pyrene in sediment poses an "unacceptable" cancer risk of 1 in 10 000. This sediment sample was collected from site 64 which also had significant pyrene, benz(a) anthracene, chrysene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene and pyrene concentrations. Of the persistent organic pollutant, PCBs in wild bird eggs pose a 2 in 10 000 cancer risk. This wild bird egg sample was taken from Bloemhof Dam which also posed a significant arsenic cancer risk.

High toxic health risks (HQ) were again found for arsenic in the wild bird eggs and fish samples. These HQ values exceed 3, which suggest a serious health risk posed. The chromium and selenium HQ value in the wild bird eggs also exceed 1, and pose a possible health risk. These concentrations were measured in pool 15 and pool 1 respectively, and therefore pose individual risks. The only PAH which is an emerging health risk is indeno(1,2,3-cd)pyrene in sediment. The reference dose for this PAH is, however, still under investigation by the EPA, and is only derived from isomeric compounds.

Table 14: The average daily doses (ADD), lifetime average daily doses (LADD), cancer risk and non-cancer risks (hazard quotient) associated with the exposure to the maximum concentrations detected in wild bird eggs and fish.

Contaminant	Wild Bird Eggs				Fish			
POPs	ADD	LADD	HQ[1]	Risk[2]	ADD	LADD	HQ	Risk
	mg/kg*d	mg/kg*d			mg/kg*d	mg/kg*d		
Total PCB	8.72E-05	3.74E-05		2.00E-04	4.89E-06	2.10E-06	0.048	1.61E-05
TetraBDE	1.06E-06	4.56E-07	0.011		1.30E-07	5.55E-08	0.0013	
PentaBDE	3.55E-06	1.52E-06	0.001		7.95E-08	3.41E-08	7.95E-04	
HexaBDE	5.33E-06	2.28E-06	0.027					
HeptaBDE	7.09E-06	3.04E-06						
HexaBB	3.30E-07	1.40E-07	0.0002					
PFOS	0.001997	0.000856						
β-HCH	4.8E-06	2.06E-06		3.70E-06				
HCB	1.00E-06	5.80E-07	0.002	9.00E-07				
Dieldrin	6.00E-06	2.00E-06	0.11	4.00E-05				
Heptachloroepoxide	8.57E-07	3.67E-07						
p,p-DDE	2.47E-04	1.06E-04		4.00E-05				
p,p-DDD	5.00E-06	2.00E-06		5.00E-07	6.94E-07	2.98E-07		1.24E-06
p,p-DDT	7.00E-06	3.00E-06	0.02	1.00E-06				
Heavy metals								
Aluminium	1.43E-02	6.12E-03	0.002		1.79E-05	7.69E-06	2.56E-06	
Arsenic	1.58E-03	6.77E-04	5.26		1.10E-03	4.71E-04	3.66	3.14E-04
Boron	5.24E-02	2.24E-02	0.26		2.89E-03	1.24E-03	0.01	
Barium	1.46E-02	6.24E-03	0.07		5.40E-03	2.31E-03	0.027	
Beryllium	8.14E-05	3.49E-05	0.04	1.50E-04	5.79E-06	2.48E-06	0.003	5.77E-07
Cadmium	9.10E-05	3.90E-05	0.18		1.54E-05	6.61E-06	0.015	
Cobalt	3.00E-04	1.29E-04			6.36E-05	2.73E-05		
Chromium	5.86E-03	2.51E-03	1.17		2.89E-03	1.24E-03	0.96	
Copper	8.57E-03	3.67E-03			2.70E-03	1.16E-03		
Iron	1.97E-01	8.45E-02			5.98E-02	2.56E-02		
Mercury	8.14E-03	3.49E-03						
Manganese	4.29E-03	1.84E-03	0.031		9.45E-04	4.05E-04	0.007	
Nickel	1.76E-03	7.53E-04	0.088		1.27E-03	5.46E-04	0.06	
Lead	1.37E-03	5.88E-04			3.66E-04	1.57E-04		
Antimony	1.16E-05	4.96E-06	0.029		4.44E-03	1.90E-03	0.89	
Selenium	6.16E-03	2.64E-03	1.23					
Titanium	6.43E-03	2.76E-03			2.12E-02	9.09E-03		
Uranium	4.11E-05	1.76E-05			9.06E-05	3.88E-05		
Vanadium	2.53E-03	1.08E-03	0.28		9.64E-04	4.13E-04	0.11	
Zinc	4.62E-02	1.98E-02	0.15		1.83E-02	7.85E-03	0.06	

Table 15: The average daily doses (ADD), lifetime average daily doses (LADD), cancer risk and non-cancer toxic effects (hazard quotient) associated with the exposure to the maximum concentrations detected in sediment.

Contaminant	Sediment			
POPs	ADD	LADD	HQ	Risk
	mg/kg/d	mg/kg/d		
Total PCB	9.57E-08	4.10E-08	9.57E-04	3.16E-07
TetraBDE	1.99E-08	8.52E-09	1.99E-04	
PentaBDE	5.92E-08	2.54E-08	5.92E-04	
HexaBDE	1.80E-07	7.72E-08	9.01E-04	
Lindane	7.00E-06	3.00E-06	2.27E-02	
p,p-DDE	8.24E-08	3.53E-08		1.20E-08
o,p'-DDD	4.79E-08	2.05E-08		4.93E-09
p,p-DDT	9.45E-08	4.05E-08	1.89E-04	1.38E-08
Heavy metals				
Arsenic	1.35E-04	5.79E-05	0.45	8.68E-05
Beryllium	7.88E-06	3.38E-06	3.94E-03	1.45E-05
Lead	7.24E-04	3.10E-04	3.62E-03	
PAH				
Acenaphthene	2.18E-03	9.34E-04	3.63E-02	
Acenaphthylene	3.28E-06	1.41E-06		
Anthracene	1.10E-05	5.00E-06	3.60E-05	
Benz(a)anthracene	8.03E-05	3.44E-05		2.51E-05
Benz(a)pyrene	3.80E-05	1.60E-05		1.00E-04
Benzo(b)fluoranthene	1.54E-04	6.58E-05	1.75	4.81E-05
Benzo(ghi)perylene	1.02E-04	4.39E-05	3.41E-03	
Benzo(k)fluoranthene	1.54E-04	6.58E-05		4.81E-05
Chrysene	9.26E-05	3.97E-05		2.90E-07
Dibenz(ah+ac)anthracene	1.51E-05	6.46E-06	1.71E-02	
Fluoranthene	2.47E-04	1.06E-04	6.19E-03	
Fluorene	3.10E-05	1.30E-05	7.75E-04	
Indeno(1,2,3-cd)pyrene	7.65E-05	3.28E-05	0.869	2.39E-05
Naphthalene	2.64E-05	1.13E-05	1.32E-03	
Phenanthrene	8.81E-05	3.78E-05	2.94E-03	
Pyrene	8.60E-05	3.70E-05	2.87E-03	

Figure 40: The risk of developing cancer determined from the maximum concentrations detected in wild bird eggs, fish and sediment.
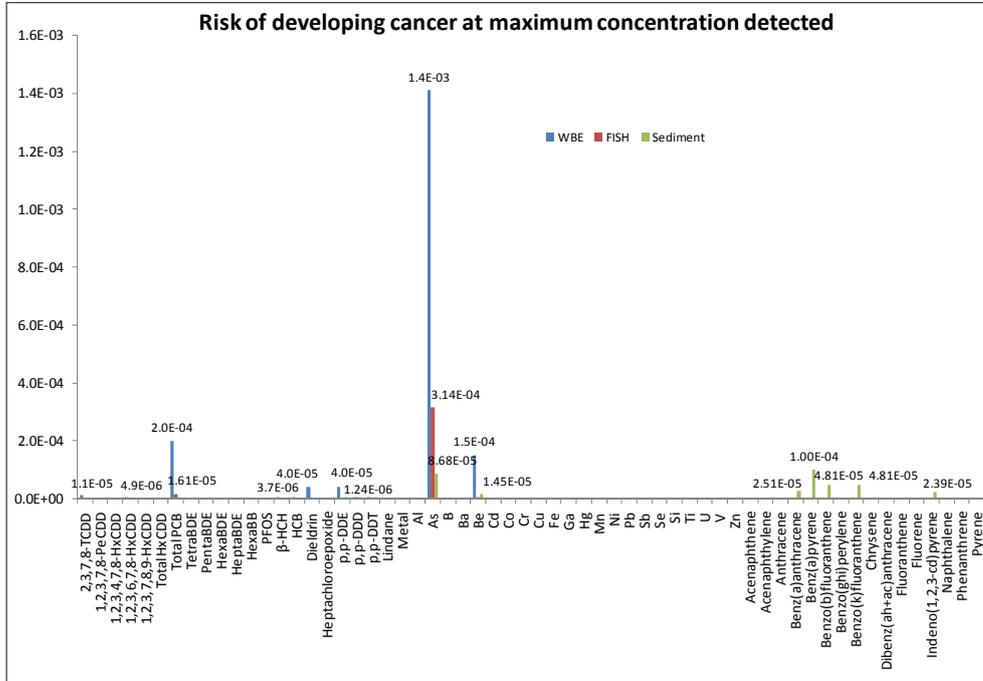

Figure 41: The hazard quotient determined from the maximum concentrations detected in wild bird eggs, fish and sediment.
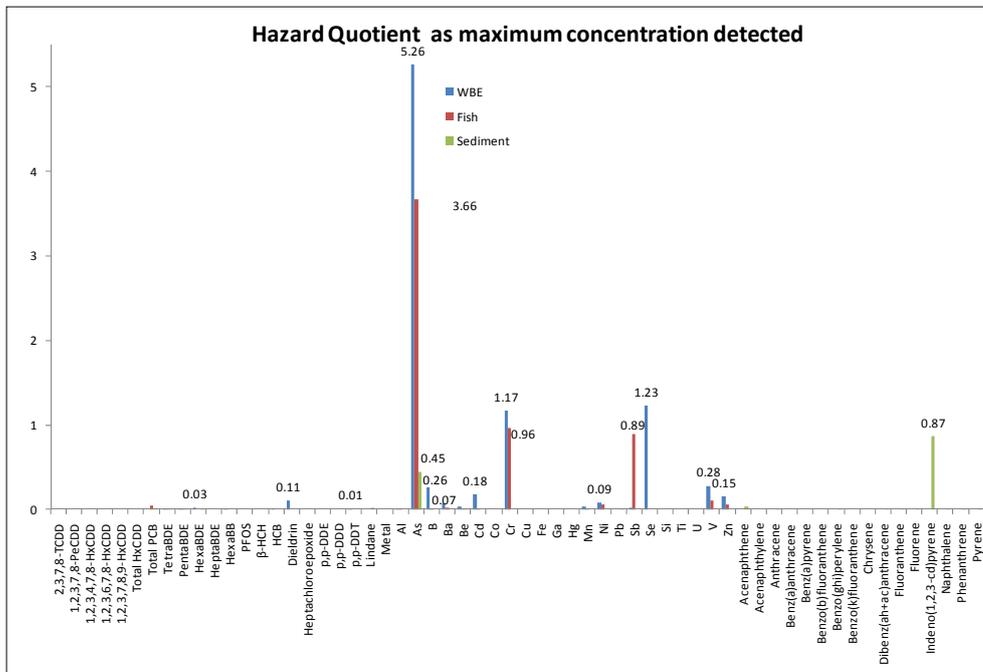
The driver of the human health risk was identified through this exercise. The chemicals responsible for the risks include arsenic, benzo(a)pyrene, PCBs and to a lesser extent chromium and selenium.

Arsenic (ATSDR, 2007). The EPA classifies arsenic a human carcinogen and likely to cause skin, liver, bladder and lung cancer. Exposure to higher than average levels of arsenic occur mostly in the workplace, near hazardous waste sites, or in areas with high natural levels in water. Ingesting very high levels of arsenic can result in death. Exposure to lower levels can cause nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, and a sensation of "pins and needles" in hands and feet. Studies in animals show that large doses of arsenic that cause illness in pregnant females, can also cause low birth weight, foetal malformations, and even foetal death.

Benzo(a)pyrene (BaP) is considered the most potent of PAHs. For the public, the main route of exposure to PAHs is from inhalation of air or ingestion of food. Following chronic exposure in an occupational setting a decrease in lung function was reported, as well as chest pain, respiratory irritation, cough, dermatitis and depressed immune system, although in most cases it was not possible to evaluate the contribution of BaP to such effects. In animals, few adverse effects were observed in rats or hamsters exposed to BaP via inhalation. Following ingestion, myelotoxicity and hepatotoxicity was observed. In mice, BaP has been shown to cross the placenta and cause adverse developmental and reproductive effects. Dietary administration during gestation reduced fertility and foetal abnormalities whereas administration by gavage caused an increase in foetal death and decreased fertility (U.S.EPA, 2007).

Polychlorinated biphenyls (PCBs) are mixtures of over 200 individual chlorinated compounds (known as congeners). There are no known natural sources of PCBs. Health effects that have been associated with exposure to PCBs include neurobehavioral and immunological changes in children. PCBs are known to cause cancer in animals. Developmental delays were seen at all ages and were greater in children smaller in size (ATSDR, 2001). Both the EPA and the International Agency for Research on Cancer (IARC) and WHO have classified PCBs are probable human carcinogenic.

Chromium (ATSDR, 2008) is known to be a human carcinogen. People are exposed to chromium by ingesting contaminated food or drinking water or breathing contaminated workplace air. Chromium(VI) at high levels can damage the nose and cause cancer. Ingesting high levels of chromium(VI) may result in anaemia or damage to the stomach or intestines.

Selenium (ATSDR, 2003). Inorganic selenium is not classified as a human carcinogen. Low doses of selenium are needed to maintain good health. However, exposure to high levels can cause adverse health effects. Short-term oral exposure to high concentrations of selenium may cause nausea, vomiting, and diarrhoea. Chronic oral exposure to high concentrations of selenium compounds can produce a disease called selenosis. The major signs of selenosis are hair loss, nail brittleness, and neurological abnormalities (such as numbness and other odd sensations in the extremities).

5.3   Discussion

This section of the report examined whether possible human health effects might be anticipated based on chemical contaminants detected in sediment, wild bird egg and fish samples. In order to determine whether this is possible, a human health risk assessment was conducted modelling the chemical contaminant concentrations expected in fish based on levels detected in sediments. Trans-media calculations (sediment to fish) were conducted based on individual chemical parameters described in the earlier sections.

The screening risk assessment identified the chemicals that could be responsible for adverse health effects if fish were to be eaten, over a 30-year period. The contaminants over the risk threshold were identified as arsenic, benzo(a)pyrene, PCBs, chromium and selenium. The type of adverse effect that might result was also identified as predominantly carcinogenic associated with arsenic, benzo(a)pyrene and PCBs exposure, with other toxic effects being anticipated from heavy metal exposure to chromium, arsenic and selenium.

This screening risk assessment has highlighted that possible health risks can be anticipated resulting from ingestion of fish or eggs on a regular basis.

There are many uncertainties in any health risk assessment, and this study presents a screening or rapid human health risk assessment. This was used to provide an indication of potential health risks and should be investigated in more detail. In addition to sample variation, dose calculations also represent uncertainty, based on the assumption of the number of times a year that people eat fish and the amount of fish eaten. The identified human health hazard will have to be evaluated in more detail.

6. Concerns and recommendations

6.1 Areas of concern

Elements in sediment

The elemental composition of sediments was difficult to associate with sediment source geology due to the very complex geology of the system, the huge drainage area covered, and the numerous tributaries and flood events. It must be noted that this assessment is based on complete digestion of the sediment and does not imply that these elements will be in water or bio-available. It has however, found areas of concern where more in-depth assessments should be done to determine whether the levels are higher than other areas because natural background or due to disturbance, agricultural run-off, industry, urbanisation, mining, or a combination. The health risk assessment found concerns for arsenic, chromium, and selenium. Based on elemental analyses and risk assessment of sediments from 61 sites, the areas in the Orange-Senqu basin that were deemed to be of concern are:

- Molopo Eye (56) due to Ga, Cr, Mn, Ni, Ag, and Se,
- Vaal River at Schmidtsdrift (15) due to uranium,
- The areas associated with the Riet River and Koranna Spruit (12, 14, 39, 41, and 44) due to a combination of higher than average levels of several elements,
- The Caledon and Makbomatso rivers draining into the Senqu and Orange rivers (49, 50, 55, 57, 58, and 60) due to a combination of higher than average levels of several elements,
- Skoon Spruit (22) due to higher than average levels of Fe, Ni, and other elements,
- Fish River, due to higher than average levels of As.

Elements in biota

The major activity of this survey was on sediment levels of compounds. Bio-availability can be ascertained by looking at elemental levels in biota. The elements in biota are derived from the environment and are therefore taken up by fish and birds as they are bio-available. Fish and bird eggs were collected from four sites each. Arsenic and beryllium was found to pose significant cancer hazard in bird eggs and fish. This aspect needs further investigation as the sites with higher levels in eggs and fish were mostly far away from industry and it was not possible to determine the sources. The levels in bird eggs in particular needs closer scrutiny, as very little data is available on the impacts of these elements on biota and the humans and other organisms that consume them.

Organic compounds in sediments

In general, the levels of all compounds except PAHs were fairly low, but with strong indications that industrial activities and combustion (pyrogenic) processes contribute. The levels of higher benzo(a)pyrene were deemed to pose unacceptable high cancer risks. The highest concentrations (and therefore the higher risks) were found at sites 16, 17, 22, 54, 60 and 64. The sources of the PAHs at all these sites were pyrogenic in nature, but the exact type of activity needs further on-site investigation.

Dioxin TEQ and indicator PCBs were associated with industrial activities in Gauteng and possibly mining or residential combustion in the North-West Province. The relatively high levels in and close to Lesotho cannot be explained as we have very little knowledge of any activities or conditions that could explain such quantities.

The generally low levels of organochlorine pesticides found in sediments at the sites sampled is a positive finding. However, detectable levels found at Blesbokspruit, Suikerbosrand, Potchefstroom, and Klerksdorp needs careful monitoring.

Organic compounds in biota

Our results show that the levels of organic compounds do not reflect the levels in sediments. Care should be taken with interpretation as the biota were not collected at sites that were sampled for sediments. The low number of available sites for fish and bird eggs sampling hinders interpretation. However, the patterns do not quite agree with what is seen in sediment. Except for organochlorine pesticides, the highest levels of dioxin TEQ, PCBs and PFOS were from isolated sites, far removed from industrial areas. The high levels of PFOS in fish at Boegoeberg and Rooipoort, and in bird eggs from Bloemhofdam and Barberspan suggests sources other than industry. It might be linked to unknown releases from agriculture (although it should then be similar to OC distribution), or unknown uses in mining in the drier, central parts of the country. There are no indications from literature on this. The high levels of PFOS in bird eggs from a dam and a pan suggest that impoundments be act as a trap for PFOS. The levels of PFOS are quite high compared to European levels. Although a health risk could not be assessed due to lack of supporting data, PFOS sources and environmental distribution needs much closer scrutiny. Consumption of PFOS via fish by humans should be seen as a serious concern.

6.2 Recommendations

Elements

Now that specific areas of concern have been identified, more attention should be targeted on these areas on determining sources and processes, as well as the bio-availability of these elements in water and sediment.

Attention should be given to identify communities that may be exposed to higher than recommended levels of elements in water and water-associated food. Water used for irrigation for instance, may contaminate produce.

Historic background levels seemingly have never been collected on this scale before, and the data collected should be curated such that future comparisons and trend monitoring can be made.

Organic compounds

Communities potentially exposed to hazardous levels of PAHs should be identified and investigated as to sources of pyrogenic composition. Interventions can then be proposed to reduce PAHs emissions. Such interventions would also reduce releases of dioxins and PCBs.

The probability exist that there are more sites and communities that may experience hazardous exposures from PAHs than was covered by this system-wide survey. This project has identified both pyrogenic and petrogenic sources, and additional areas can now be identified from activities alone. Concentrations of industry, mining and residential areas seem to characterise areas with high PAHs levels in sediment.

The dynamics and sources that resulted in the higher than expected levels of certain organic compounds (especially PFOS) in biota in isolated areas need to be better understood. The risks these compounds pose to biota needs to be better understood as the number of samples that could be analysed were restricted.

A monitoring programme should be instituted to track changes.

Historic samples should be stored, as more compounds are likely to be added to the Stockholm Convention. Collections then need not be repeated, as samples will be available.

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