



ORASECOM Report: ORASECOM/004/2015



# ORANGE-SENQU WATER RESOURCES QUALITY JOINT BASIN SURVEY 2 (JBS 2) – *FINAL REPORT*

## *PERSISTENT ORGANIC POLLUTANTS AND METALS SURVEY IN 2015*



November 2015

# ORASECOM

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# 1 INTRODUCTION

## 1.1 *Project Background*

The Orange-Senqu River originates in the highlands of Lesotho from where it flows westwards to its mouth at Alexander Bay/Oranjemund on the Atlantic West Coast. At Douglas, the Orange-Senqu River joins the Vaal River (also flowing from the east). The river basin is the third largest in southern Africa, after the Zambezi and the Congo, covering an area of 1 000 000 km<sup>2</sup>. Four countries – Botswana, Lesotho, Namibia, and South Africa - share the basin.

Lesotho is located entirely within the basin, covers only 5% of the total Basin area, but contributes over 40% of the stream flow from only 5% of the total basin area. Lesotho is one of the smaller users of water, but South Africa, with some 60% of the basin area is by far the biggest user of water. This water supports the economic heartland of South Africa, which encompasses the industrial Vaal Triangle and the gold- and platinum mining regions. Botswana is part of the basin although this part is entirely covered by the Kalahari Desert with very little surface runoff, but groundwater contributes to its water demands. In the Lower Orange-Senqu, the water requirements are primarily for irrigation from Namibia and South Africa and to maintain environmental flows to the estuary at Alexander Bay/Oranjemund. However, water quality and periodic floods remain a concern.

It follows from the above that the effective management of the Orange-Senqu River Basin is particularly complex, but also its sustainable management is vital to the economy and people of the region. Consequently, the riparian States prioritised this basin for the establishment of a Shared Watercourse Institution under the revised Southern African Development Community (SADC) Protocol for Shared Watercourses. The Orange-Senqu River Commission (ORASECOM) was established in 2000 as one of the first joint-basin commissions to be established under the Protocol. The ORASECOM Programme included six thematic areas: Institutional and organisational 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. During the Project Development Facility Bloc B, UNDP prepared a preliminary Trans-boundary Diagnostic Analysis (TDA) of the Basin, adopted by ORASECOM in April 2008. As part of the TDA, a survey was done over the entire Basin of POPs, PAHs, heavy metals and other elements in sediments, fish, and eggs of aquatic birds. All initiatives facilitated or led by the ORASECOM, including the UNDP-GEF project (2008 -2015), supported activities under one of those six thematic areas.

During the project preparatory phase of the UNDP-GEF project, a preliminary Trans-boundary Diagnostic Analysis (TDA) of the Basin was developed and adopted by ORASECOM in April 2008. A preliminary TDA identified a knowledge gap on the POPs and heavy metals in the basin and the collection of such data was prioritized.

The four southern African countries that share the Orange–Senqu River basin (Botswana, Lesotho, Namibia and South Africa) are parties to the Stockholm Convention on Persistent Organic Pollutants (POPs), which currently targets 22 chemicals and classes of chemicals. Previously, research on POPs in the Orange–Senqu River basin concentrated on pesticides

such as DDT. Only recently has more attention been given to POPs such as dioxins and polybrominated diphenyl ethers (PBDEs). Little is known about polycyclic aromatic hydrocarbons (PAHs) in the catchment, and there are very few studies available on concentrations of elements, including heavy metals, in sediments and biota. Five years ago, the first complete survey for POPs, PAHs and heavy metals was undertaken for the basin under the umbrella of ORASECOM's 2010 Joint Basin Survey and as a contribution to the transboundary diagnostic analysis (TDA) of the Orange–Senqu River basin. Sediments were sampled in September 2010 at 61 sites, 33 of which were in the Vaal River catchment. The remaining 28 sites were along the Orange–Senqu River and its other tributaries, with one site in Namibia and five in Lesotho. Fish and wild bird eggs were sampled at four sites each to investigate the concentrations of the compounds and elements in the biota of the Orange–Senqu River basin.

The final report of this portion of the TDA was published in 2013 (ORASECOM, 2013). Its executive summary is reproduced below as background to this project.

### **Executive summary of the 2013 report on POPs, PAHs, and elemental levels in sediment, fish and wild bird eggs of the Orange-Senqu River Basin**

#### **INTRODUCTION AND METHODOLOGY**

The four southern African countries that share the basin of the Orange–Senqu River – Botswana, Lesotho, Namibia and South Africa – are all parties to the Stockholm Convention on Persistent Organic Pollutants (POPs), which currently targets 22 chemicals and classes of chemicals. Previously, research on POPs in the Orange–Senqu River basin concentrated on pesticides such as DDT. Only recently has more attention been given to POPs such as dioxins and polybrominated diphenyl ethers (PBDEs). Little is known about polycyclic aromatic hydrocarbons (PAHs) in the catchment, and there are very few studies available on levels of elements, including heavy metals, in sediments and biota. The original scope of this study was to undertake a survey and assessment of POPs and heavy metals in water bodies and riverine sediments, under the umbrella of ORASECOM's 2010 Joint Basin Survey and as a contribution to the transboundary diagnostic analysis (TDA) of the Orange–Senqu River basin. During the study, PAHs were added as an additional research topic because of their detrimental effects to humans and wildlife. Sediments were sampled in September 2010 at 61 sites, 33 of which were in the Vaal River catchment. The remaining 28 sites were along the Orange–Senqu River and its other tributaries, with one site in Namibia and five in Lesotho. These sites largely conform to the sites used by other components of the Joint Basin Survey. Fish and wild bird eggs were sampled at four sites each to investigate the levels of the compounds and elements in the biota of the Orange–Senqu River basin. Samples for POPs and PAHs were sent to an accredited laboratory in Germany for analyses on high-resolution gas chromatography and mass spectrometry (HRGC-MS), while samples for elemental composition were analysed at North-West University in Potchefstroom, using inductively coupled plasma mass spectrometry (ICP-MS).

#### **RESULTS AND DISCUSSION**

Organic pollutants



Levels of dioxin-like toxic equivalents (TEQ) were low in all media. In sediments, TEQ levels were higher in the east, and mostly undetectable towards the mouth. The relatively higher TEQ level in fish from Rooipoort in the Vaal River, downstream of Delportshoop requires further investigation, and a species-specific analysis is needed for birds.

As for TEQ levels, polychlorinated biphenyls (PCBs) in sediment were higher towards the eastern than the western parts of the catchment, and were relatively high in fish from Rooipoort. Similarities in distribution of TEQs and PCBs can be expected, given that the former includes dioxin-like PCBs. Appreciable levels were found in bird eggs, especially at Bloemhof Dam.

Levels of organochlorine compounds (OCPs) in sediments were higher in Gauteng, and mostly undetectable in the rest of the basin. In fish the highest OCP levels were from Parys, but in bird eggs the highest levels were from Bloemhof Dam, which may act as a retainer of some compounds originating upstream. Unfortunately, sediments and fish were not sampled at this site.

None of the sediments had detectable levels of perfluorooctane sulfonate (PFOS), but fish from the two sampling sites in the central parts of the basin contained PFOS, while bird eggs from Barbers Pan and especially Bloemhof Dam had surprisingly high levels. A more in-depth species-specific assessment needs to be done, but water samples along the length of the river would also be useful in indicating PFOS distribution, and will be considered in a new sampling event.

The three sediment sites with the highest levels of total PAHs were downstream of urban and industrial areas in South Africa and Lesotho. The PAH distribution pattern could be linked to pyrogenic sources, typically either coal or smelter operations. The most common PAH was fluoranthene, followed by phenanthrene and benzo(b+k) fluoranthene.

#### Heavy metals and trace elements

The metal pollution index (MPI) – the geometric mean of all of the elements analysed – was highest for sediment site 56, the Molopo Eye, and when the geoaccumulation index (Igeo) values were determined the same site had the most elements with Igeo values regarded as polluted. This site, together with a cluster of sites in the Riet and Modder rivers, also belonged to the 25% of sites with the most elements with the highest concentrations. Shared geology between some of the sites could partially explain this, but in-depth investigation of the area is deemed necessary to determine the exact cause. High levels of elements at two sites in Lesotho are also likely to be due to geology rather than mining or any other anthropogenic activities.

The generally high Igeo values for selenium, arsenic and mercury in sediments throughout the basin warrant further investigation, with clarification on the natural background levels of these elements. However, levels of elements at all sediment sites except the Molopo Eye compared favourably with sediment quality guidelines for the Netherlands, and were considered to be of low concern.

In fish, levels of elements for which international guidelines and food safety standards are available were found to be within acceptable limits. Platinum was the element most likely to bioaccumulate, assuming that 100% of the measured concentrations in sediment would be

bioavailable to fish. In bird eggs, tin had the highest level and also the highest bioaccumulation factor, but this is not necessarily an indication of toxicity.

The grey heron seemed to bioaccumulate more elements than the other bird species. However, the bioaccumulation results for both fish and birds should be treated with caution, as a number of assumptions had to be made in the calculations.

#### Health risk assessment

A human health risk assessment was conducted to determine whether chemical contaminants in sediment posed a risk to humans consuming fish and wild bird eggs. The method uses cross-media transfer equations to model the amount of contaminant that could be expected in fish based on levels detected in sediments. Contaminants that could potentially be responsible for adverse health effects if fish or eggs were eaten regularly over a 30-year period were then identified.

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 predominantly carcinogenic in the case of exposure to arsenic, benzo(a)pyrene and PCBs, while other toxic effects could be anticipated with arsenic, chromium and selenium exposure.

However, this exercise was based on a number of assumptions and should be viewed as a rapid risk assessment for screening purposes. It aimed to provide an indication of potential health risks resulting from ingestion of fish or eggs on a regular basis, but the true human health hazard will have to be evaluated in more detail before interventions are considered.

#### AREAS OF CONCERN

##### Organic pollutants

In sediments, the levels of all compounds except PAHs were fairly low, but the distribution patterns suggest that industrial activities and combustion (pyrogenic) processes contribute to pollution in the basin. At high levels, benzo(a)pyrene was deemed to pose an unacceptably high cancer risk. Dioxin-like TEQ and indicator PCBs were associated with industrial activities in Gauteng and possibly mining or residential combustion in North West Province. The relatively high levels in and close to Lesotho cannot be explained. Organochlorine pesticides were generally at low levels at the sediment sites sampled, but detectable levels at Blesbok Spruit, Suikerbosrand, Potchefstroom and Klerksdorp highlight the need for further monitoring.

The levels of organic compounds in biota did not reflect the levels in sediments. However, the results should be interpreted with caution, as fish and bird eggs were collected from only a few sites that were not sampled for sediments. The highest levels of dioxin-like TEQ, PCBs and PFOS were from isolated sites, far removed from industrial areas. The high levels of PFOS in fish at Boegoeberg (upstream of Upington on the Orange River) and Rooipoort, and in bird eggs from Bloemhof Dam and Barbers Pan, suggest sources other than industry. These may be linked to agriculture (although PFOS distribution should then be similar to that of OCPs), or unknown uses in mining in the drier, central parts of South Africa. The levels are high compared to European levels, so PFOS sources and distribution patterns demand closer scrutiny. Human consumption of PFOS via fish could potentially be a serious concern.

## Heavy metals and trace elements

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. Furthermore, this assessment is based on complete digestion of the sediment, which aims to release the elements into solution so that they can be analysed. In reality, the elements in sediment will not necessarily be present in the surrounding water or bioavailable.

Nevertheless, the study has identified areas of concern where more in-depth assessments should be done to determine whether high levels of elements are due to natural factors or to disturbance, agricultural runoff, industry, urbanisation, mining, or a combination of these factors. The health risk assessment indicated that arsenic, chromium and selenium levels are potentially hazardous to human health. Based on elemental analyses and risk assessment of sediments from 61 sites, the areas in the Orange–Senqu River basin that were deemed to be of concern are:

- Molopo Eye due to gallium, chromium, manganese, nickel, silver and selenium.
- Vaal River at Schmidtsdrift due to uranium.
- The areas associated with the Riet River and Koranna Spruit due to a combination of higher than average levels of several elements.
- The Caledon and Malibamatso rivers draining into the Senqu and Orange–Senqu rivers due to a combination of higher than average levels of several elements.
- Skoon Spruit due to higher than average levels of iron, nickel and other elements.
- Fish River due to higher than average levels of arsenic.

The elements in biota are derived from the environment and are taken up by fish and birds as they are bioavailable. The health risk assessment indicated that arsenic and beryllium could potentially pose significant cancer hazards to humans consuming bird eggs and fish. This aspect needs further investigation as the sites with high levels in eggs and fish were mostly far away from industry and it was not possible to determine the pollution sources. The levels in bird eggs, in particular, need closer scrutiny, as very little data is available on rates of consumption by humans and other organisms, or on the impacts of these elements on biota.

## RECOMMENDATIONS

### Organic pollutants

- Communities potentially exposed to hazardous levels of PAHs should be identified and the contributing pyrogenic sources investigated, so that interventions to reduce emissions of PAHs can be proposed. Such interventions would also reduce releases of dioxins and PCBs.
- There are likely more sites and communities potentially experiencing hazardous exposure to PAHs than revealed by this basin-wide survey. The study has identified both pyrogenic and petrogenic sources, and additional areas can now be identified by focusing on industrial hubs, mining sites and residential areas where these sources are known to occur.
- The dynamics and sources of certain organic compounds (especially PFOS) in biota in isolated areas need further investigation to better understand the reasons for unexpectedly high concentrations, and to establish the associated risk to biota.

- A monitoring programme should be instituted to track changes, and a selection of samples stored so that retrospective analyses can be conducted as new compounds are added to the Stockholm Convention.

#### Heavy metals and trace elements

- Now that specific areas of concern have been identified, these should be investigated further to determine the sources and processes contributing to high levels of these elements in water and sediment, as well as their bioavailability.
- Communities that may be exposed to higher than recommended levels of elements in water and water-associated food should be identified. Water used for irrigation, for instance, may contaminate produce.
- Background levels of elements have not been collected on this scale previously, so the data collected should be curated to allow for future comparisons and trend monitoring.

#### CONCLUSION

The 2010 study, published in 2013, has shown that sediment analysis alone will not provide sufficient information to assess contaminant levels in biota and the threat to human health. Sediment levels of elements, in particular, need to be interpreted against local geology, soil structure and industrial activities. Furthermore, elements contained in sediment will not necessarily be present in the surrounding water and bioavailable to fish, or occur in a toxic form. Conversely, POPs can be transported far from their place of origin, so high levels in biota convey little information about their sources. Nevertheless, determining pollutant distribution patterns on a basin scale assists in assessing the overall pollution picture and in identifying hotspots for more detailed investigation.

## 1.2 Project Aim

The survey of POPs, heavy metals, PFCs, PAHs, and other compounds of concern for the Orange-Senqu River basin is now included in the 5-yearly Joint Basin Survey – an exercise institutionalized by ORASECOM. The UNDP-GEF ORASECOM project has now provided support to the POPs survey and the results will be included in the Joint Basin Survey of 2015.

Based on recommendations to ORASECOM in the 2013 report, the present survey of POPs, heavy metals, PFCs, PAHs, and other compounds of concern for the Orange-Senqu River basin is now included in a five-yearly institutionalised Joint Basin Survey by ORASECOM. The previous sampling was in 2010.

An assessment of the previous results facilitated a contraction of the number of POPs to be analysed, as well as adding new POPs that have been added to the Stockholm Convention since the start of the previous report, as well as adding candidate POPs. The following organic micro-pollutants were measured:

- 1) DDTs (all six isomers),
- 2) PCBs (indicator),
- 3) Chlordanes,
- 4) Heptachlor,
- 5) HCHs,
- 6) Chlordecone
- 7) Endosulfanes,
- 8) Dicofol,
- 9) All Stockholm Convention brominated flame retardants, including DecaBDE,
- 10) Dechloranes,
- 11) Chlorinated naphthalenes,
- 12) Hexachlorobutadiene,
- 13) HCB,
- 14) PeCB,
- 15) PFOS and PFBA,
- 16) Short-chained chlorinated paraffins, and
- 17) PAHs (priority PAHs).

The following elements were measured:

- 1) Hg and methyl mercury,
- 2) Mn,
- 3) V,
- 4) Cr,
- 5) Co,
- 6) Ni,
- 7) Cu,
- 8) Ag,
- 9) Cd,
- 10) Sn,
- 11) Sn,
- 12) Se,
- 13) U,
- 14) As,
- 15) Pb,
- 16) Ce,
- 17) Sr,
- 18) Ba, and
- 19) Fe.

Because the Minamata Convention on Mercury has been negotiated and finalised, mercury and methyl mercury will receive additional attention. As of 27 June 2015, 128 countries have signed the convention, and 12 have ratified it. Lesotho and South Africa has signed the convention, and Lesotho has ratified it.

## 2 PERSISTENT ORGANIC POLLUTANTS AND PAHs

### 2.1 *Materials and Methods*

Due to budget constraints, this survey covered sediments from 16 selected sites, and fish and wild bird eggs from three sites. For orientation and background, a map of the original sites and their numbers are provided in Appendix A. The 16 sediment sampling sites were identified from the 2013 report (ORASECOM 2013), based on either high concern or presumed background sites with low levels of contamination. One site was in Namibia, and one in Lesotho. Based on previous experience, three sites (Lenasia, Bloemhof Dam, and Upington) contributed sediment, fish and bird egg samples. Sediment, fish and bird egg samples were collected, treated and shipped to the same laboratories as described in the 2013 report. The same accredited laboratories and analytical methods were used as for the analyses of the samples collected in 2010. Based on the previous report, some chlorinated dioxin and furans were not analysed because they occurred in very low concentrations and were not deemed to be of concern on a Basin scale. The analyses for these compounds are also very costly.

#### *Sediment sampling*

All sampling equipment was made of stainless steel or glass. Sample contamination or cross-contamination was prevented by rinsing every utensil before a sampling event with acetone and hexane. Acetone removes polar organic contaminants and hexane non-polar organic contaminants.

Sediment samples were prepared at each site by collecting the top five centimetres of under-water sediment 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. Samples were collected as close as possible to the 2010 collection points. The sediment was air-dried, ground, and sieved (mesh size 0.5 mm).

Riverine sediment is a variable matrix whose organic and inorganic composition depends on many factors such as underlying geology, upstream geology, hydrology, organic material input etc. Due to the large Basin that was sampled, many tributaries, and large differences in geology, it was not possible to collect sediment that is the same throughout. Although there are ways of standardising, most sediment quality guidelines report on whole sediment. In the case of this project, overall geographic distribution and changes with time are the main concerns.

The dried samples were shipped to an accredited laboratory in Germany (Oekometric GmbH in Beyreuth) for POPs analysis. The analysis was done for all the POPs listed above, as well as mercury and methyl mercury. The sediment and biota was also analysed for the 16 polycyclic aromatic hydrocarbons (PAH's) deemed of concern by the USEPA.

Sediment samples were analysed for the elements listed above, using inductively coupled plasma mass spectrometry (ICP-MS). The samples were completely digested with concentrated HNO<sub>3</sub> at 50-60 °C and allowed to evaporate to 5 ml. The samples were further treated with H<sub>2</sub>O<sub>2</sub> and allowed to cool before 3 M mol/L 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. To determine the basic elemental composition of each site, complete digestion was done and the elemental levels compared with the geology of the area.

### *Fish sampling*

After obtaining the necessary provincial permits, Sharptooth Catfish (*Clarias gariepinus*) was collected at each of the three sites. A 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). As they are omnivorous and often feed close to the bottom they are ideal to sample for determining the levels of pollutants in fish: 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 to reveal any bio-accumulation. They also have a large distribution and occur throughout 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 and killed and the fillet sampled. Fillet for POPs analysis were wrapped in pre-cleaned aluminium foil. (Pre-cleaning includes rinsing 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. Fillets 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. Approximately the same mass of flesh 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.

### *Aquatic bird egg sampling*

Bird eggs were collected at the three breeding colonies listed above. The breeding colony at Upington was also sampled. This colony could not previously be sampled as it was flooded in 2010 (ORASECOM, 2013). 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 then thawed. Eggs from the same species from different localities were pooled to obtain a sample large enough for determination of the analytes (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.

## **2.2 Results and Discussion**

The summarised results of the POPs analyses are presented in Table 1. Fish in all cases were sharptooth catfish. Due to differences in timing of breeding and distribution of birds, different species bred at different sites, and as for the previous report, no species were breeding concurrently at all three sites. However, the same species as in 2010 were sampled at Lenasia (the colony relocated five kilometres to the west and we found it with aerial reconnaissance) and at Bloemhof Dam.

## **2.3 Organic Compounds including POPS**

*POPs that were not present in measurable quantities.*

This project included POPs that were not included in the 2010 survey as they were only added to the Stockholm Convention after 2010.

- Endosulfan: (insecticide) No measurable quantities of this compound were detected in either sediment or biota.
- Chlordecone: (insecticide) No measurable quantities of this pesticide were detected in either sediment or biota.
- Dicofol: (insecticide) No measurable quantities of this pesticide were detected in either sediment or biota.
- Hexachlorobutadiene: (industrial chemical) No measurable quantities of this compound were detected in either sediment or biota.
- Dechlorane plus: (industrial chemical) No measurable quantities of this compound were detected in either sediment or biota.
- Heptachlorobenzene: (industrial chemical) No measurable quantities of this compound were detected in either sediment or biota.
- Chlorinated naphthalenes: (industrial chemical) No measurable quantities of this compound were detected in either sediment or biota.

The absence of measurable quantities of these compounds indicates that these compounds are not of concern in the Basin. However, there may be sources and hotspots outside the region that should be tested before it can be concluded that these banned Stockholm Convention compounds or candidate compounds are of little concern for the larger region.

*Sediments and biota: New POPs*

For some of the compounds below, this will be the first record for the region.

Hexabromobiphenyl (HBB): As far as we are aware, this report presents the first data from Southern Africa for this compound. It was used as a fire retardant in three main commercial products: acrylonitrile-butadienestyrene (ABS) thermoplastics for constructing business machine housings, and in industrial (e.g. motor housing), and electrical (e. g. radio and TV parts) products: as a fire retardant in coatings and lacquers, and in polyurethane foam for auto upholstery. It has also been used as a flame retardant in cable housings and insulators. There is no known current production in the world. It has a half-life of six months once released and is transported over long ranges by water, dust and biota. It is immunotoxic, hepatotoxic, genotoxic, and endocrine disruptive (amongst a number of negative effects). The sources for the residues detected here is unknown, but may likely be waste products slowly releasing to the environment.

**Table 1** : Results of the analysis of sediments, fish, and wild bird egg analyses for persistent organic pollutants and candidate POPs. Where available, the comparable 2010 data are provided. Endosulfan, dicofol, chlordecone, hexachlorobutadiene, dechlorane plus, and chlorinated naphthalenes were not detected in measurable quantities and are not presented in Table 1. Shaded cells indicate increases since 2010.

Site	Sediments ng/kg dw	PCBs 2015	PCBs 2010	PCB TEQ 2015	PCB TEQ 2010	Sum BFR 2015	Sum BFR 2010	HBB	Sum PFAS 2015	Sum PFAS 2010	Sum OCPs 2015	Sum OCPs 2010	PeCB	SCCP
2		688	0	0.03	0.00	0.0868	0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
11		100	0	0.01	0.00	<LOQ	3540	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
12		3551	0	0.92	0.00	3360	14746	<LOQ	<LOQ	<LOQ	1700	<LOQ	0.3	90
15		977	0	0.23	0.00	790	<LOQ	<LOQ	<LOQ	<LOQ	300	<LOQ	<LOQ	<LOQ
22		7873	2040	0.56	0.48	6435	514	<LOQ	<LOQ	<LOQ	7900	1700	0.3	88
23		4172	3881	0.16	0.10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
25		6394	2142	0.99	0.16	0.0067	340	<LOQ	<LOQ	<LOQ	1500	700	<LOQ	30
27		806	1502	0.12	0.20	1000	<LOQ	<LOQ	<LOQ	<LOQ	1300	8500	<LOQ	<LOQ
30		712	0	0.04	0.00	380	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
39		159	970	0.02	0.14	480	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	500	<LOQ	<LOQ
51		151	0	0.02	0.00	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
55		176	0	0.02	0.00	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
56		955	2317	0.04	0.34	0.0006	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
60		676	1224	0.04	0.07	410	543	<LOQ	<LOQ	<LOQ	<LOQ	700	<LOQ	<LOQ
62		1168	0	0.04	0.00	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Bloemhof Dam</b>		125		0.02		<LOQ		<LOQ		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Biota ng/kg ww</b>														
<b>Lenasia Fish</b>		25447		1.39		3546		36	28000		19000		<LOQ	11700
<b>Bloemhof Dam Fish</b>		88444		1.89		17		<LOQ	21000		940		<LOQ	7800
<b>Upington Fish</b>		624		0.07		71		<LOQ	58000		1210		<LOQ	3200
<b>Lenasia Glossy Ibis</b>		41523	35310	3.89	2.14	8097	20073	150	32000	69000	42000	155000	<LOQ	28400
<b>Bloemhof Dam Grey Heron</b>		33509	10189	3.40	1.56	1021	447	16	79000	725000	95000	95000	<LOQ	20300
<b>Upington Reed Cormorant</b>		6887		1.22		944		15	65000		55000		<LOQ	7200

<LOQ = Below limits of quantification

No quantifiable HBB was found in sediments. However, low concentrations were found in biota. Because they have been found in biota together with its known chemical and physical properties, it can be assumed that HBB is also present in sediments at concentrations below the limits of quantification (LOQ).

Short-chained chlorinated paraffins (SCCPs): As far as we are aware, this is the first report from Southern Africa on SCCPs in biota. The major uses of SCCPs are in metalworking. It is also used in paints, adhesives, sealants, leather fat liquors, plastics and rubber. It is still in production worldwide and large amounts are being used, with a concomitant release to the environment, mainly from metalworking. They can persist for up to one year in sediments, and has been found in high concentrations in Arctic animals. It is possibly carcinogenic, and toxic to aquatic organisms.

A previous WRC report (Roos *et al*, 2012) included a small dataset on SCCPs in sediments – very low concentrations were measured. Here, we found no quantifiable residues of SCCPs in sediments, but appreciable concentrations in biota. The implications of the concentrations in fish and bird eggs are not clear, but it raises a concern that should be addressed in the future. It also indicates that SCCPs should be monitored in biota and not only in abiotic media.

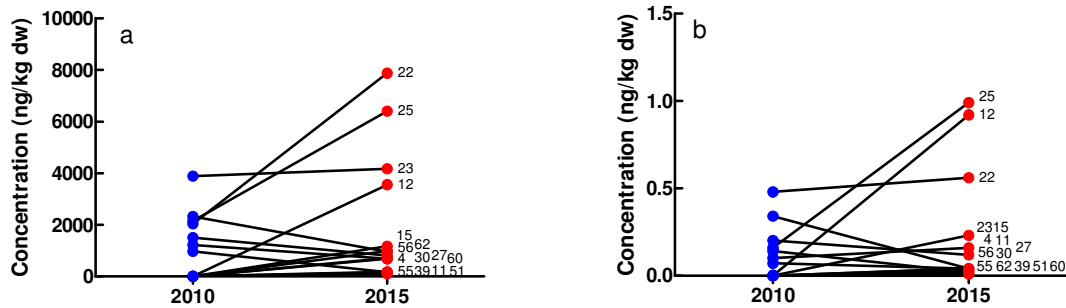
Pentachlorobenzene (PeCB): PeCB has a half-life of 45-7300 days and is transported over long distances via air, water, and biota. It causes hypertrophy of liver cells, increased kidney weight, and is fetotoxic (amongst a range of effects). In humans it causes a depression of the nervous system and is possibly carcinogenic. PeCB is produced during incomplete combustion, is or has been used in many industrial processes, occurs in dyestuffs, and occurs as impurities in many pesticide formulations.

There is no known production. Only sparse data is available from Southern Africa. Here we report low concentrations in sediments from only two sites (Table 1), but no quantifiable residues were found in biota. Pending more data, we may conclude that PeCB is probably of little concern in the Basin, but further surveys are suggested.

#### *Sediments and biota: Existing POPs and PAHs*

Table 1 lists the data of the existing POPs, in some cases together with their 2010 data for comparisons.

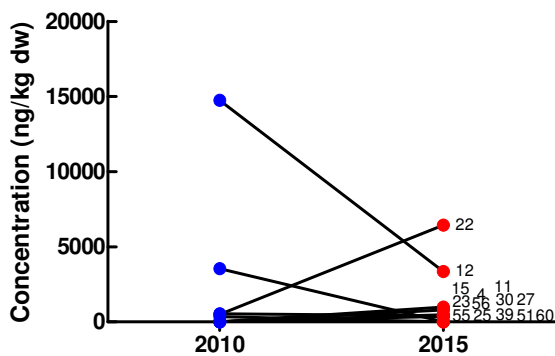
Total PCBs: At 11 sites, the concentrations increased compared with 2010, and four sites showed decreases (Table 1; Figure 1a). The PCB toxic equivalents - TEQs - (the sum of their toxicities based on congeners) also increased at the same 11 sites (Table 1; Figure 1b), and decreased at the other four. In biota, it increased both in concentrations and TEQ at the two sites for which there are comparable data.



**Figure 1 :** Changes in PCB concentrations (a) and PCB Toxic Equivalents (b).

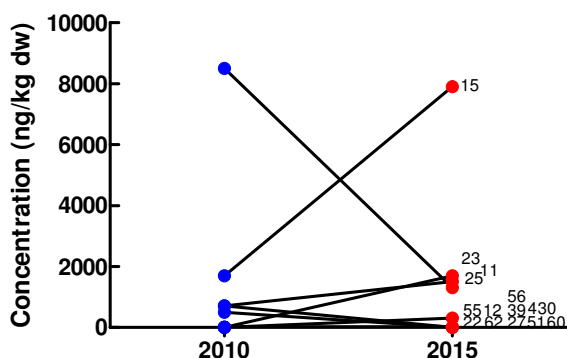
Based on this data, we can conclude that PCBs at some sites and in biota seem to become a bigger problem. PCBs were already identified as a substance of concern and priority action in the Basin.

Brominated flame retardants (BFRs): BFR concentrations in sediments (Table 1), increased at seven sites, decreased at three sites, and remained below LOQ at four sites (Figure 2). Again, it seems as if this compound is also increasing its environmental presence. In biota, it was found in fish from all three sites, and occurred in relatively higher concentrations per site than the fish from the same sites. The reason for this is the inclusion of Deca BDE, a compound that was not measured in 2010, but now added as it is now part of the Stockholm Convention. Where it occurred in quantifiable concentrations, it made up the bulk of the BFRs. Therefore, we now raise a concern about this class of compound, and specifically for DecaBDE. More research is needed on this compound specifically.



**Figure 2 :** Changes in brominated flame retardants

Sum organochlorine pesticides (OCPs): Consideration of Table 1 and Figure 3 shows that OCPs in sediment increased at four sites, and decreased at three. The bulk of the OCPs is made up of *p,p'*-DDE, as before in 2010. It decreased by an order of magnitude in Ibis from Lenasia and remained the same in Grey Heron from Bloemhof Dam. OCPs remain a concern, but since all production and use has been terminated, except in the case of DDT for malaria control, the concentrations are expected to reduce even further with time. DDT is not used in Basin for malaria control. Whenever monitoring is carried out in the future, it is recommended to include the current suite of pesticides.



**Figure 3 :** Changes in the sum of organochlorine pesticides

Perfluorinated substances (PFAS): The Stockholm Convention has listed PFOS and PFOA as POPs. In the 2010 survey, we only included PFOS. For this survey, based on interim work, we also included PFOA. As in 2010, now quantifiable residues were found in sediments of PFOS, nor of PFOA. However, in 2010, large quantities of residues were found in bird eggs, especially in Grey Heron eggs from Bloemhof Dam (Table 1). In this survey, large amounts were still present, but lower than in 2010. The differences are most likely due to natural variations rather than a decrease in background concentrations, as an interim study specifically dealing with PFOS in the Basin (Swiegelaar & Bouwman, 2014) has found even higher concentrations in some eggs than the 2010 reported concentrations. PFOA, now also measured, was not found in fish, but was present in bird eggs. In bird eggs, it made up about 1-5%. For the first time, eggs from Upington were collected and showed lower but still quantifiable concentrations when compared with the upstream Lenasia and Bloemhof Dam bird eggs. Bird eggs could not be collected from Upington in 2010 due to flooding.

We conclude that PFOS remains a big problem in the Basin. However, the sources are unknown. Mitigation measures are therefore difficult to formulate. Continued monitoring of concentrations in biota, and continued searching for sources are urgently required. PFOS remains a compound of concern for the Basin.

Polycyclic Aromatic Hydrocarbons PAHs: The 16 US EPA PAHs were at quantifiable concentrations in the sediment samples (Table 2), but the parent compounds could not be found in the fish or egg samples as they are metabolised. Nine of the 15 sites that were sampled had fold increases (e.g. a fold increase of 2 means a two-fold increase ) for the sum of PAHs and three had fold increases for most of its congeners, of sites 25 (Klip River West), 30 (Klip River East) and 62 (Fish River) (Figure 4). Phenanthrene had the highest fold increase (>1000) at site 62, but it was fluorene that showed the biggest fold increases for most of the sites (Table 2). Sites 12 (Douglas) and 22 (Skoonspruit) had the highest concentration increases (Figure 4). Site 22 is located in a gold mining region and the increase may be related to industrial activity. Site 12 is isolated but downstream of site 22 and may reflect additional loadings coming from upstream.

**Table 2:** Concentrations ( $\mu\text{g}/\text{kg dm}$ ) of PAHs in sediment from 2010 to compare to the concentrations of sediment from the same sites in 2015. The fold effect (FE) is determined by dividing 2015 concentrations with 2010 concentrations. The shaded cells indicate a fold increase of more than 1.

	Bloemhof Dam				2				11				12				15			
	2015	2010	2015	FE	2010	2015	FE	2010	2015	FE	2010	2015	FE	2010	2015	FE	2010	2015	FE	
Naphthalene	0.3	19	0.3	0.0	4	0.3	0.1	10.7	67.5	6.3	8	7.2	0.9							
Acenaphthylene	11.3	0.3	0.3	1.0	0.3	0.7	2.3	0.6	10.2	17	0.7	15	21.4							
Acenaphthene	43.5	6.7	33.6	5.0	4.7	24.7	5.3	4	34.5	8.6	1.3	59	45.4							
Fluorene	126.7	2.8	58.1	20.8	1.6	48.5	30.3	2.7	59.3	22	3.6	236.8	65.8							
Phenanthrene	0.3	11.6	0.3	0.0	5.7	0.3	0.1	9.8	426.4	43.5	11.6	1.3	0.1							
Anthracene	0.3	1.1	0.3	0.3	0.6	0.3	0.5	0.9	117.2	130.2	1.3	0.3	0.2							
Fluoranthene	0.3	0.9	0.3	0.3	0.8	0.3	0.4	3.1	453.3	146.2	4.6	0.3	0.1							
Pyrene	0.3	0.6	0.3	0.5	0.3	0.3	1.0	2.4	379.4	158.1	3.6	0.3	0.1							
Benz(a)anthracene	0.3	0.5	0.3	0.6	0.3	0.3	1.0	1	112.1	112.1	1.4	0.3	0.2							
Chrysene	0.3	0.7	0.3	0.4	0.6	0.3	0.5	1.7	102.9	60.5	2	0.3	0.2							
Benzo(b+k)fluoranthene	0.3	0.7	0.3	0.4	0.3	0.3	1.0	2.6	342.7	131.8	4	2.4	0.6							
Benz(a)pyrene	0.3	0.3	0.3	1.0	0.3	0.3	1.0	1	175.4	175.4	1	1	1.0							
Indeno(1,2,3-cd)pyrene	0.3	0.3	0.3	1.0	0.3	0.3	1.0	1.2	141.6	118	1.6	0.3	0.2							
Benzo(ghi)perylene	0.3	0.3	0.3	1.0	0.3	0.3	1.0	1.1	89.4	81.3	1.6	0.3	0.2							
Dibenz(ah+ac)anthracene	0.3	0.3	0.3	1.0	0.3	0.3	1.0	0.3	30	100	0.3	0.3	1.0							
Totals	185.1	46.1	95.6	2.1	20.4	77.5	3.8	43.1	2541.9	59	46.6	325.1	7.0							

**Table 2 (continued):** Concentrations ( $\mu\text{g}/\text{kg dm}$ ) of PAHs in sediment from 2010 to compare to the concentrations of sediment from the same sites in 2015. The fold effect (FE) is determined by dividing 2015 concentrations with 2010 concentrations. The shaded cells indicate a fold increase of more than 1.

	22			23			25			27		
	2010	2015	FE	2010	2015	FE	2010	2015	FE	2010	2015	FE
Naphthalene	34.5	65	1.9	2.9	0.3	0.1	18.5	73.3	4.0	16.4	1.2	0.1
Acenaphthylene	4.8	57.1	11.9	0.3	0.3	1	2.6	15.8	6.1	2.9	18.5	6.4
Acenaphthene	9.5	43	4.5	16.6	48.9	2.9	7.1	8.7	1.2	5.1	33.9	6.6
Fluorene	13.8	55.3	4	1.2	219.3	182.8	8.8	38.6	4.4	6.4	175.6	27.4
Phenanthrene	99.8	511.9	5.1	7.2	0.3	0	24.5	141.3	5.8	43.5	19.4	0.4
Anthracene	15.6	192	12.3	1	0.3	0.3	5.7	32.1	5.6	6.9	2.8	0.4
Fluoranthene	153.3	1106.5	7.2	5.1	1.5	0.3	26.9	190	7.1	60.6	28.7	0.5
Pyrene	116.4	911	7.8	3.8	0.3	0.1	30.2	143.7	4.8	45.9	20.5	0.4
Benz(a)anthracene	46.9	276.5	5.9	2	0.3	0.2	12	30.4	2.5	21.5	6.9	0.3
Chrysene	65	336.3	5.2	2.2	1.5	0.7	13.2	36.8	2.8	25.2	8.3	0.3
Benzo(b+k)fluoranthene	119.2	891.8	7.5	4	1.8	0.5	23.7	87.9	3.7	44.5	22.8	0.5
Benzo(a)pyrene	58.3	476.5	8.2	2	0.8	0.4	11.3	49.3	4.4	22.6	12.1	0.5
Indeno(1,2,3-cd)pyrene	53.6	507.9	9.5	2	0.7	0.4	10.2	29.5	2.9	19.3	9.4	0.5
Benzo(ghi)perylene	67	348.7	5.2	1.3	0.3	0.2	10	2.6	0.3	20.5	1.4	0.1
Dibenz(ah+ac)anthracene	9.5	86.8	9.1	0.3	0.2	0.7	1.8	6.7	3.7	3.6	1.9	0.5
Totals	867.2	5866.3	6.8	51.9	276.8	5.3	206.5	886.7	4.3	344.9	363.4	1.1

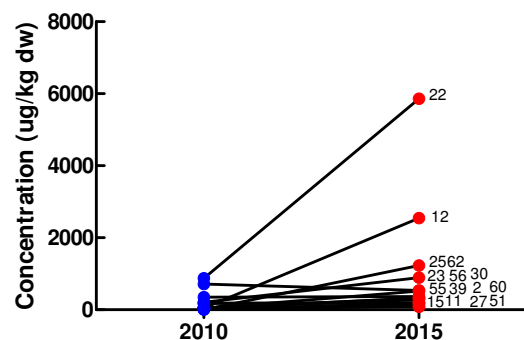


**Table 2 (continued):** Concentrations ( $\mu\text{g}/\text{kg dm}$ ) of PAHs in sediment from 2010 to compare to the concentrations of sediment from the same sites in 2015. The fold effect (FE) is determined by dividing 2015 concentrations with 2010 concentrations. The shaded cells indicate a fold increase of more than 1.

	30			39			51			55		
	2010	2015	FE	2010	2015	FE	2010	2015	FE	2010	2015	FE
Naphthalene	0.7	46.3	66.1	47.10	0.30	0.0	0.30	24.40	81.3	11.5	0.3	0.0
Acenaphthylene	0.3	15.9	53.0	1.10	0.30	0.3	0.30	39.60	132.0	0.8	37.9	47.4
Acenaphthene	25.6	34	1.3	3.50	38.00	10.9	9.10	37.00	4.1	4.5	48.3	10.7
Fluorene	0.6	343.7	572.8	3.40	145.60	42.8	0.30	70.80	236.0	1.9	223	117.4
Phenanthrene	5.1	28.3	5.5	13.70	0.30	0.0	0.30	0.30	1.0	5.2	0.3	0.1
Anthracene	0.3	2.4	8.0	2.50	0.30	0.1	0.30	0.30	1.0	0.6	0.3	0.5
Fluoranthene	0.3	11.3	37.7	16.30	0.30	0.0	0.30	0.30	1.0	2.6	0.3	0.1
Pyrene	0.3	7.3	24.3	13.40	0.30	0.0	0.30	0.30	1.0	1.6	0.3	0.2
Benz(a)anthracene	0.3	2.5	8.3	7.40	0.30	0.0	0.30	0.30	1.0	1.2	0.3	0.3
Chrysene	0.3	4	13.3	9.20	0.30	0.0	0.30	0.30	1.0	2.4	0.3	0.1
Benzo(b+k)fluoranthene	0.3	10.6	35.3	20.90	0.60	0.0	0.30	0.50	1.7	2.5	0.3	0.1
Benz(a)pyrene	0.3	4.1	13.7	8.40	0.80	0.1	0.30	0.30	1.0	0.9	0.3	0.3
Indeno(1,2,3-cd)pyrene	0.3	4	13.3	11.10	0.30	0.0	0.30	0.30	1.0	1.2	0.8	0.7
Benzo(ghi)perylene	0.3	2.1	7.0	13.80	0.30	0.0	0.30	0.60	2.0	1.4	0.8	0.6
Dibenz(ah+ac)anthracene	0.3	0.9	3.0	1.90	0.30	0.2	0.30	0.30	1.0	0.3	0.3	1.0
Totals	35.3	517.4	14.7	173.70	188.30	1.1	13.30	175.60	13.2	38.6	313.8	8.1

**Table 2 (continued):** Concentrations ( $\mu\text{g}/\text{kg dm}$ ) of PAHs in sediment from 2010 to compare to the concentrations of sediment from the same sites in 2015. The fold effect (FE) is determined by dividing 2015 concentrations with 2010 concentrations. The shaded cells indicate a fold increase of more than 1.

	56			60			62		
	2010	2015	FE	2010	2015	FE	2010	2015	FE
Naphthalene	50.5	0.3	0.0	30.8	42.2	1.4	0.30	14.60	48.7
Acenaphthylene	1.2	0.3	0.3	9	3.9	0.4	0.30	1.00	3.3
Acenaphthene	1.5	46	30.7	4.2	33	7.9	1.70	30.90	18.2
Fluorene	2.8	96.3	34.4	17.3	68.9	4.0	0.30	245.80	819.3
Phenanthrene	14.6	27.6	1.9	102.1	304.9	3.0	0.70	746.00	1065.7
Anthracene	2.6	5.5	2.1	12.5	35	2.8	0.30	167.50	558.3
Fluoranthene	14.1	1.3	0.1	176.4	9.2	0.1	0.30	3.70	12.3
Pyrene	18.4	0.3	0.0	121.6	4.6	0.0	0.30	2.40	8.0
Benz(a)anthracene	10.2	1.2	0.1	34.1	1.5	0.0	0.30	0.30	1.0
Chrysene	9.2	1.1	0.1	42.8	5.5	0.1	0.30	1.70	5.7
Benzo(b+k)fluoranthene	27.7	2.2	0.1	59.4	14	0.2	0.30	7.40	24.7
Benz(a)pyrene	7	1.1	0.2	25.5	1.2	0.0	0.30	0.50	1.7
Indeno(1,2,3-cd)pyrene	9.6	0.3	0.0	34.1	2.8	0.1	0.30	1.50	5.0
Benzo(ghi)perylene	7.6	0.3	0.0	37.6	3.1	0.1	0.30	0.30	1.0
Dibenz(ah+ac)anthracene	1.6	0.3	0.2	3.8	0.8	0.2	0.30	0.60	2.0
Totals	178.6	184.1	1.0	711.2	530.6	0.7	6.30	1224.2	194.3



**Figure 4 :** Changes in the sum of PAHs in sediments

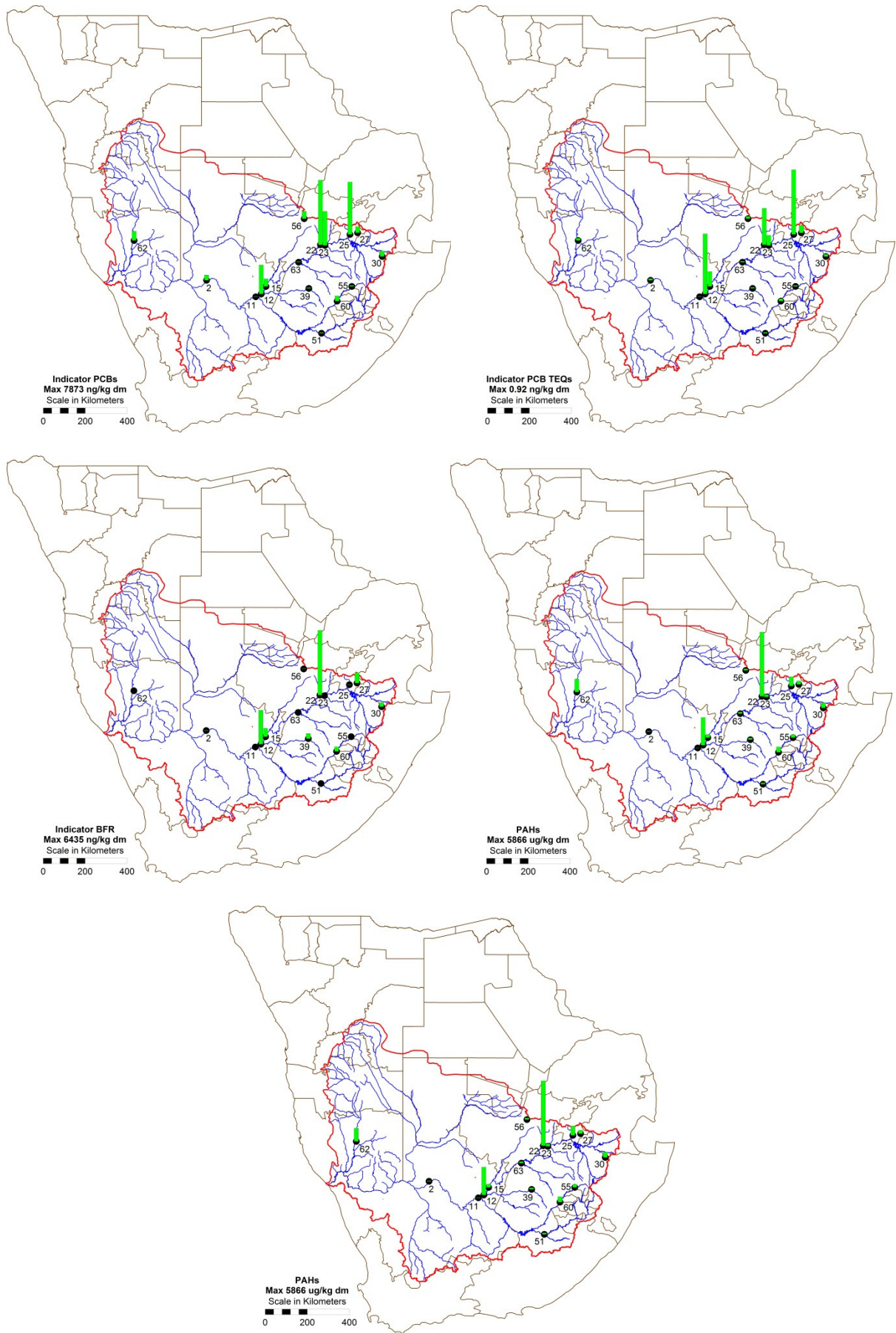


Figure 5 : Geographical representation of the distribution of organic pollutants

Figure 5 represents the geographical distribution of the organic pollutants in sediments. The pattern of distribution reflects that of the 2010 survey, but with lower concentrations in and near Lesotho. PAHs, PCBs, and BFRs are higher towards the east of the basin, and then mainly in the north in the Gauteng and gold mining regions.

## 2.4 Conclusions

Of the new and candidate POPs, endosulfan, chlordecone, dicofol, hexachlorobutadiene, dechlorane plus, heptachlorobenzene, and the chlorinated naphthalenes were not detected at quantifiable concentrations in sediment, fish or bird eggs. Although they were not detected in quantifiable amounts, this does not directly imply that they are not an issue. There may be hotspots that have been missed.

Only pentachlorobenzene (PeCB), the short-chained chlorinated paraffins (SCCPs), and hexabromobiphenyl (HBB) of the new and candidate POPs have been quantified. This data represents very scarce information for Southern Africa and Africa. PeCB was found at very low concentrations in two sediment samples, but SCCPs although only quantified at three sites, had appreciable concentrations in fish and bird eggs. Not much is known about the toxic effects of SCCPs in fish and birds, and even less is known of SCCPs in biota in warmer climates. However, the concentrations indicate that concern is warranted and should be investigated further. The HBB data represents a completely unique dataset for the region. It was not found in quantifiable quantities in sediments, but low concentrations in two bird egg samples were found. Again, before HBB is considered as of no consequence, further studies are needed.

PCBs and BFRs increased at more sites than decreased. While this class of POPs was not judged as of concern in the 2013 report, due to the increases in sediments and persistent presence in biota, we now suggest that enough data is available to raise a concern.

PFAS (Perfluorinated alkyl substances) has decreased in biota (it was not quantified in sediment in 2010 or 2015), but remains very high and of concern. PFOA, not measured in 2010, only occurs at <5% in biota when present. From this perspective PFOA is therefore of less concern. However, serious concerns remain about PFOS.

The sum of the organochlorine pesticides (OCPs) declined in more sediment sites than increased. This is to be expected as none of the OCPs except DDT is being manufactured anymore, and DDT is not used in the catchment for any purpose. However, it remains in appreciable quantities in biota and needs to be monitored, especially *p,p'*-DDE.

PAHs increased at all but two sites. Fluorene was the compound with the greatest overall composition, indicating pyrogenic origins. The largest concentration increases occurred at sites 12 and 22 (Table 2; Figure 4). The increase at site 62 in Namibia was unexpected as it is an isolated site. This may be due to a temporary local source such as waste burning close to the sampling site, or an indication of a new source upstream. This increase at site 22 (Skoon Spruit) is probably related to industrial activities in this gold mining region, while the increase at site 12 (Douglas), downstream of site 22, is probably a reflection of this. The Skoon Spruit region is now also an area of concern regarding PAHs, as this is one of the sites with the highest PAH concentrations known in the Basin. In conclusion, PAHs remains a problem and concern for the Basin.

## 3 HEAVY METALS AND ELEMENTS

### 3.1 Materials and Methods

The results of the elemental analysis for 2015 were compared to that of 2010 for sediment, fish and bird eggs. Limits of detection were treated by replacing the value with half the limit of detection. The decrease or increase in concentrations is presented as a fraction of fold effect (FE; an FE of 2 means a two-fold increase). Fractions greater than 1 indicates the fold increase of a pollutant in 2015 compared to its concentration in 2010. The fold decrease is smaller than 1 when pollutant concentration is less than the 2010 concentrations. A new site, Bloemhof Dam that was not sampled in 2010 for its sediment, was sampled this round. Because both fish and wild bird eggs were sampled at all the sites, biomagnification can be determined. Sediment samples could be compared directly between 2010 and 2015 as 15 of the original 61 sites were sampled again, and Bloemhof Dam was added. However, fish and wild bird eggs could not be collected at the exact same sites as in 2010 and although the same fish species was collected (*Clarias gariepinus*—sharp-toothed catfish) the variety of bird species collected was smaller in 2015 than in 2010. The mean of the pollutant concentrations in the fish from the four sites that were sampled in 2010 was calculated to be compared to that of the concentrations in the fish of the 2015 sites. Of the four fish sampling places in the 2010 sampling event, there was only one site in 2010 that could be resampled in 2015, i.e. the Bloemhof Dam. In 2010 bird eggs were also collected from four sites of which only the Bloemhof Dam was resampled in 2015. The closest we could find wild bird eggs to Lenasia (2010) was at Eldorado (2015) 20 km south west. Birds move their breeding sites and therefore in this report the concentrations in Grey Heron eggs from Bloemhof Dam, Reed Cormorant from Upington and Glossy Ibis from Lenasia were compared to the same species of 2010, but not necessarily from the same sites as no eggs of that particular species could be found at those particular sites during 2015.

#### *Heavy metals and trace elements in sediment:*

The concentrations of 2010 were also listed together with the 2015 concentrations for the sediment sites (Table 3). The Bloemhof Dam site was a new site for 2015 and was included because fish as well as bird eggs were collected at this site. Concentrations in abiotic as well as biotic matrices can indicate biomagnification. To facilitate comparisons with the 2010 report, a map with corresponding site numbers is provided in Appendix A.

The element with the highest concentration in all 16 sites of 2015 was Fe followed by aluminium with the second highest concentration at 15 sites. The elements which followed include Ca>Mg>K>P>Na.

There was only one site (30; Klip River East) that showed a 1.5 fold increase in total elemental concentration from 2010 to 2015 with 19 of the 31 (61.3%) elements showing fold increases greater than 1 (Table 3). The element at this site with the greatest fold increase (of 5) was rubidium (Rb). Other sites that had five or more elements with fold increases greater than 1 (i.e.16%) include sites 10 (Brak River) and 27 (Blesbok Spruit; 32%), 11 (Orange River at Douglas; 22.5%), 2 (Orange River at Upington; 16%), 12 (Vaal River at Douglas; 16%), 22 (Skoon Spruit at Klerksdorp; 16%), and 23 (Klip River West; 16%). The element that showed

the biggest fold increase across all of the sites was Au with a FI of 7 at site 10. It was also the element that had fold increase at 50% of the 16 sites. Molybdenum (Mo) had fold increases at 43.8% of the sites followed by Ti and Rb with 37.5% (Table 3).

**Table 3:** Comparison between 2010 and 2015 elemental concentrations (mg/kg dry mass) of sediment with the fold effect (FE), i.e. either fold increase (> 1) or decrease (< 1). The fold effect (FE) is determined by dividing 2015 concentrations with 2010 concentrations with shaded cells indicating a fold increase of more than 1.

	Bloemhof Dam				2				10				11			
	2015	2010	2015	FE	2010	2015	FE	2010	2015	FE	2010	2015	FE			
Be	0.10	0.35	0.26	0.7	0.35	0.28	0.8	0.58	0.28	0.5						
B	1.77	32.50	1.59	0.1	4.50	2.39	0.5	20.25	1.97	0.1						
Na	231.70	1050.00	720.75	0.7	275.00	369.00	1.3	1550.00	706.25	0.5						
Mg	223.58	7000.00	3605.00	0.5	6750.00	2572.50	0.4	12500.00	3637.50	0.3						
Al	1390.50	14000.00	8917.50	0.6	7750.00	6145.00	0.8	23250.00	8827.50	0.4						
K	209.28	775.00	624.25	0.8	1600.00	821.75	0.5	1575.00	620.00	0.4						
Ca	221.50	9500.00	5927.50	0.6	6250.00	4117.50	0.7	10000.00	5892.50	0.6						
Ti	43.38	800.00	913.25	1.1	172.50	182.60	1.1	925.00	974.00	1.1						
V	6.21	40.00	38.98	1.0	19.75	17.29	0.9	62.50	49.90	0.8						
Cr	19.36	22.75	24.72	1.1	25.00	28.48	1.1	50.00	28.65	0.6						
Mn	8.42	237.50	153.10	0.6	192.50	136.75	0.7	325.00	175.80	0.5						
Fe	1842.75	15750.00	16365.00	1.0	8250.00	8510.00	1.0	24000.00	16620.00	0.7						
Co	1.08	12.50	10.39	0.8	4.50	4.88	1.1	19.50	10.64	0.6						
Ni	2.37	42.50	14.22	0.3	21.25	11.09	0.5	70.00	13.94	0.2						
Cu	2.19	24.50	16.74	0.7	11.50	8.35	0.7	42.50	18.16	0.4						
Zn	2.46	37.50	22.22	0.6	27.50	19.60	0.7	57.50	71.88	1.3						
As	0.39	3.25	1.48	0.5	3.75	1.25	0.3	4.25	1.50	0.4						
Se	0.35	2.08	0.67	0.3	0.65	0.59	0.9	11.50	0.70	0.1						
Rb	2.81	2.75	5.39	2.0	4.50	8.75	1.9	6.75	5.13	0.8						
Sr	1.27	27.50	35.00	1.3	19.00	18.01	1.0	27.50	28.68	1.0						
Mo	0.36	0.73	0.41	0.6	0.11	0.33	3.1	0.33	0.45	1.4						
Pd	0.14	0.85	0.33	0.4	0.17	0.25	1.5	0.48	0.33	0.7						
Ag	0.21	4.00	0.38	0.1	1.00	0.21	0.2	4.75	0.25	0.1						
Cd	0.03	0.09	0.06	0.6	0.04	0.05	1.4	0.11	0.47	4.4						
Ba	9.27	90.00	55.23	0.6	45.00	33.45	0.7	117.50	48.73	0.4						
Pt	0.00	0.17	0.01	0.0	0.01	0.01	0.7	0.01	0.01	0.4						
Au	0.29	0.68	0.29	0.4	0.04	0.29	7.2	0.10	0.29	3.0						
Hg	0.03	1.53	0.05	0.0	0.21	0.03	0.1	0.58	0.03	0.0						
Tl	0.02	0.50	0.05	0.1	0.10	0.06	0.6	0.23	0.05	0.2						
Pb	1.31	5.75	4.76	0.8	5.00	3.29	0.7	8.50	11.02	1.3						

U	0.27	0.48	0.30	0.6	0.40	0.31	0.8	0.83	0.33	0.4
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**Table 3 (continued):** Comparison between 2010 and 2015 elemental concentrations (mg/kg dry mass) of sediment with the fold effect (FE), i.e. either fold increase (> 1) or decrease (< 1).

	12			15			22			23		
	2010	2015	FE	2010	2015	FE	2010	2015	FE	2010	2015	FE
Be	1.23	0.43	0.4	1.13	0.22	0.2	0.80	0.49	0.6	0.28	0.21	0.8
B	21.50	2.39	0.1	17.00	1.47	0.1	13.75	1.80	0.1	11.50	1.74	0.2
Na	850.00	242.83	0.3	2250.00	293.75	0.1	725.00	318.50	0.4	500.00	324.50	0.7
Mg	15250.00	966.50	0.1	17000.00	1469.50	0.1	12000.00	1811.50	0.2	2175.00	879.75	0.4
Al	27500.00	4652.50	0.2	20750.00	4180.00	0.2	16250.00	7582.50	0.5	5250.00	3930.00	0.8
K	3750.00	213.90	0.1	3000.00	639.25	0.2	1525.00	686.00	0.5	675.00	418.50	0.6
Ca	16000.00	2907.50	0.2	24500.00	3487.50	0.1	9250.00	3547.50	0.4	3250.00	1636.50	0.5
Ti	425.00	170.33	0.4	300.00	194.05	0.7	227.50	144.65	0.6	120.00	134.40	1.1
V	67.50	38.73	0.6	55.00	12.32	0.2	65.00	36.20	0.6	24.25	13.00	0.5
Cr	95.00	154.28	1.6	85.00	23.44	0.3	152.50	119.83	0.8	45.00	31.13	0.7
Mn	1000.00	1333.50	1.3	725.00	104.40	0.1	925.00	377.50	0.4	400.00	78.18	0.2
Fe	30000.00	20000.00	0.7	23250.00	7787.50	0.3	40000.00	18147.50	0.5	7250.00	5802.50	0.8
Co	25.00	13.38	0.5	22.00	5.82	0.3	32.50	14.07	0.4	15.00	5.97	0.4
Ni	112.50	23.13	0.2	97.50	7.90	0.1	172.50	22.87	0.1	55.00	11.32	0.2
Cu	42.50	38.88	0.9	42.50	8.47	0.2	47.50	29.38	0.6	23.00	8.39	0.4
Zn	75.00	72.65	1.0	60.00	12.92	0.2	122.50	88.15	0.7	35.00	10.36	0.3
As	8.50	3.94	0.5	6.75	0.97	0.1	11.75	5.31	0.5	3.50	1.01	0.3
Se	12.75	0.59	0.1	12.25	0.49	0.0	11.75	0.86	0.1	11.00	0.64	0.1
Rb	16.75	3.34	0.2	13.50	6.25	0.5	11.00	11.25	1.0	4.25	6.51	1.5
Sr	30.00	21.71	0.7	40.00	13.14	0.3	16.25	14.80	0.9	7.75	9.24	1.2
Mo	0.45	0.86	1.9	0.55	0.35	0.6	0.83	1.17	1.4	0.38	0.55	1.5
Pd	0.53	0.21	0.4	0.48	0.24	0.5	0.33	0.28	0.9	0.25	0.21	0.9
Ag	5.00	0.44	0.1	14.75	0.16	0.0	10.25	0.68	0.1	3.00	0.39	0.1
Cd	0.17	0.14	0.8	0.12	0.04	0.4	0.85	0.15	0.2	0.06	0.05	0.7
Ba	157.50	127.08	0.8	155.00	30.25	0.2	147.50	99.08	0.7	57.50	28.75	0.5
Pt	0.01	0.01	0.5	0.03	0.00	0.1	0.01	0.02	1.5	0.02	0.01	0.9
Au	0.13	0.29	2.3	0.09	0.29	3.2	0.50	0.29	0.6	0.11	0.32	3.1
Hg	0.58	0.03	0.1	0.53	0.03	0.1	0.98	0.26	0.3	0.38	0.03	0.1
Tl	0.35	0.11	0.3	0.28	0.05	0.2	0.21	0.11	0.6	0.13	0.05	0.4
Pb	13.50	49.45	3.7	12.50	3.04	0.2	18.25	36.63	2.0	4.75	3.24	0.7
U	1.50	1.10	0.7	50.00	0.34	0.0	1.68	2.19	1.3	0.98	0.68	0.7



**Table 3 (continued):** Comparison between 2010 and 2015 elemental concentrations (mg/kg dry mass) of sediment with the fold effect (FE), i.e. either fold increase (> 1) or decrease (< 1).

	27			30			39		
	2010	2015	FE	2010	2015	FE	2010	2015	FE
Be	0.53	0.43	0.8	0.50	0.61	1.2	1.58	0.49	0.3
B	9.25	2.27	0.2	8.00	1.35	0.2	16.75	2.34	0.1
Na	425.00	328.25	0.8	400.00	358.25	0.9	2750.00	524.75	0.2
Mg	1375.00	1162.50	0.8	1125.00	1411.75	1.3	16250.00	3090.00	0.2
Al	8000.00	9142.50	1.1	3750.00	10610.00	2.8	27500.00	10760.00	0.4
K	475.00	411.50	0.9	450.00	851.50	1.9	6500.00	1350.25	0.2
Ca	4250.00	2148.75	0.5	1650.00	1899.50	1.2	13000.00	6800.00	0.5
Ti	50.00	60.90	1.2	90.00	196.65	2.2	350.00	316.50	0.9
V	25.00	26.58	1.1	25.00	33.15	1.3	55.00	28.63	0.5
Cr	57.50	65.68	1.1	25.00	41.33	1.7	90.00	44.63	0.5
Mn	1075.00	603.75	0.6	775.00	480.25	0.6	1700.00	320.00	0.2
Fe	11250.00	13450.00	1.2	12000.00	14737.50	1.2	27500.00	12800.00	0.5
Co	40.00	18.27	0.5	12.00	10.45	0.9	21.50	9.79	0.5
Ni	160.00	28.60	0.2	16.75	9.49	0.6	95.00	15.79	0.2
Cu	32.50	17.67	0.5	17.00	16.74	1.0	50.00	15.95	0.3
Zn	300.00	65.75	0.2	22.00	21.60	1.0	120.00	20.89	0.2
As	4.75	1.56	0.3	5.25	2.23	0.4	8.25	2.17	0.3
Se	11.25	0.61	0.1	11.00	0.99	0.1	11.75	0.81	0.1
Rb	3.50	8.20	2.3	3.25	17.66	5.4	19.00	15.72	0.8
Sr	6.75	11.13	1.6	5.50	18.98	3.5	52.50	33.40	0.6
Mo	0.20	0.45	2.3	0.33	0.69	2.1	0.48	0.47	1.0
Pd	0.24	0.25	1.1	0.14	0.41	3.0	0.50	0.41	0.8
Ag	5.25	0.18	0.0	2.75	0.30	0.1	8.75	0.39	0.0
Cd	0.40	0.09	0.2	0.04	0.08	2.3	0.14	0.07	0.5
Ba	60.00	45.73	0.8	97.50	123.40	1.3	300.00	86.83	0.3
Pt	0.16	0.00	0.0	0.01	0.00	0.6	0.01	0.00	0.4
Au	0.10	0.29	2.9	0.15	0.30	2.0	0.07	0.29	4.3
Hg	0.33	0.03	0.1	0.30	0.04	0.1	0.40	0.03	0.1
Tl	0.12	0.06	0.5	0.12	0.13	1.1	0.30	0.12	0.4
Pb	10.00	5.86	0.6	6.00	10.51	1.8	21.50	7.36	0.3
U	2.30	0.71	0.3	0.38	0.91	2.4	1.15	0.76	0.7

**Table 3 (continued):** Comparison between 2010 and 2015 elemental concentrations (mg/kg dry mass) of sediment with the fold effect (FE), i.e. either fold increase (> 1) or decrease (< 1).

	51			55			56			60		
	2010	2015	FE	2010	2015	FE	2010	2015	FE	2010	2015	FE
Be	0.55	0.4255	0.8	1.175	0.3305	0.3	3	0.322	0.1	0.525	1.4055	2.7
B	13	2	0.2	7	1.31425	0.2	8.75	2.03275	0.2	5.5	3.715	0.7
Na	3000	1026	0.3	1975	526.25	0.3	350	771.75	2.2	2500	547	0.2
Mg	10500	6380	0.6	17750	3192.5	0.2	50000	5662.5	0.1	30000	3895	0.1
Al	21750	16330	0.8	42500	10725	0.3	13500	9970	0.7	62500	13875	0.2
K	1975	1054.5	0.5	1500	852.25	0.6	800	739.75	0.9	1425	1752.5	1.2
Ca	8750	7845	0.9	16750	3107.5	0.2	110000	11060	0.1	27500	9390	0.3
Ti	875	702.25	0.8	1600	524.5	0.3	350	1010	2.9	4000	212	0.1
V	60	36.775	0.6	135	33.75	0.3	207.5	53.425	0.3	175	35.975	0.2
Cr	37.5	34.5	0.9	140	31.775	0.2	450	28.825	0.1	70	40.025	0.6
Mn	275	242.475	0.9	2400	171.975	0.1	60000	265	0.0	1125	1680.25	1.5
Fe	22500	20195	0.9	52500	14345	0.3	45000	20797.5	0.5	62500	33325	0.5
Co	14	13.1925	0.9	47.5	8.51	0.2	117.5	11.82	0.1	37.5	26.5	0.7
Ni	57.5	21.61	0.4	135	13.77	0.1	250	17.3925	0.1	175	26.675	0.2
Cu	37.5	32.975	0.9	75	18.3075	0.2	80	21.5275	0.3	137.5	448.75	3.3
Zn	47.5	26.05	0.5	70	17.87	0.3	55	25.5	0.5	125	457.75	3.7
As	4	1.384	0.3	9.25	1.01875	0.1	19.25	1.70025	0.1	2.5	13.805	5.5
Se	11.5	0.793	0.1	12	0.88875	0.1	12.75	0.7635	0.1	12.25	1.43525	0.1
Rb	8.25	10.9075	1.3	6	9.42	1.6	4	6.295	1.6	4	17.0825	4.3
Sr	27.5	39.275	1.4	57.5	16.75	0.3	80	40.4	0.5	92.5	53.3	0.6
Mo	0.2275	0.39275	1.7	0.55	0.35875	0.7	4	0.5155	0.1	0.45	2.5175	5.6
Pd	0.25	0.389	1.6	0.425	0.3635	0.9	0.475	0.36775	0.8	0.525	0.64625	1.2
Ag	3.5	0.33975	0.1	4.25	0.247925	0.1	23	0.44975	0.0	5.25	0.36875	0.1
Cd	0.07	0.0805	1.2	0.12	0.056675	0.5	0.1875	0.07195	0.4	0.145	0.199925	1.4
Ba	97.5	77.175	0.8	325	61.45	0.2	8500	65	0.0	127.5	220.025	1.7
Pt	0.0525	0.005345	0.1	0.00675	0.0547	8.1	0.175	0.0069425	0.0	0.02025	0.005925	0.3
Au	0.03	0.29425	9.8	0.0275	0.29275	10.6	0.03	0.2895	9.7	0.0275	0.2865	10.4
Hg	0.155	0.027	0.2	0.2075	0.025425	0.1	0.185	0.028275	0.2	0.165	0.027225	0.2
Tl	0.1375	0.073475	0.5	0.1675	0.066675	0.4	3.25	0.051775	0.0	0.0825	0.169475	2.1
Pb	7.75	5.925	0.8	15.5	4.7875	0.3	80	5.56	0.1	4.25	27	6.4
U	0.95	0.49475	0.5	0.9	0.984	1.1	1.575	0.3805	0.2	0.35	1.506	0.95

**Table 3 (continued):** Comparison between 2010 and 2015 elemental concentrations (mg/kg dry mass) of sediment with the fold effect (FE), i.e. either fold increase (> 1) or decrease (< 1).

	62		
	2010	2015	FE
Be	0.525	1.47225	2.8
B	7	9.4	1.3
Na	1275	762.5	0.6
Mg	7500	10437.5	1.4
Al	8750	24482.5	2.8
K	1375	4370	3.2
Ca	13500	17090	1.3
Ti	250	58.125	0.2
V	32.5	39.375	1.2
Cr	18.25	43.4	2.4
Mn	425	602.75	1.4
Fe	18500	34100	1.8
Co	9	17.525	1.9
Ni	32.5	28.425	0.9
Cu	42.5	35.15	0.8
Zn	47.5	80.8	1.7
As	13.75	8.7875	0.6
Se	11.75	2.00525	0.2
Rb	5.25	38.8	7.4
Sr	24	92	3.8
Mo	1.15	1.123	1.0
Pd	0.3	0.697	2.3
Ag	1.875	0.34775	0.2
Cd	0.115	0.207	1.8
Ba	125	251.25	2.0
Pt	0.002875	0.0044725	1.6
Au	0.02325	0.29475	12.7
Hg	0.135	0.044325	0.3
Tl	0.11	0.33775	3.1
Pb	10.25	22.0175	2.1
U	0.775	1.28275	1.7

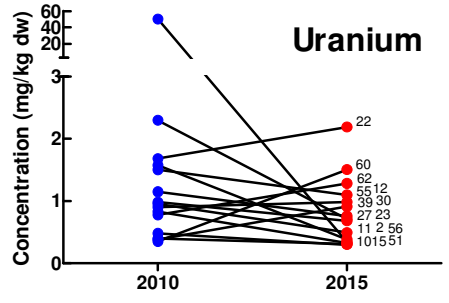
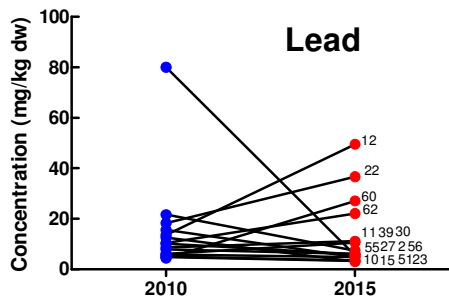
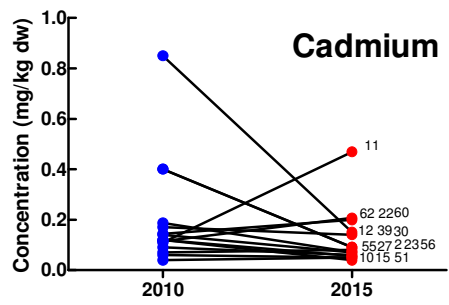
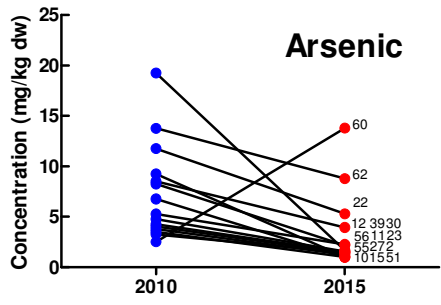
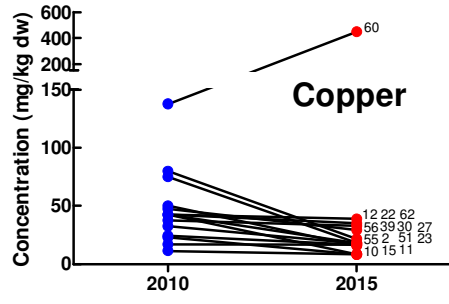
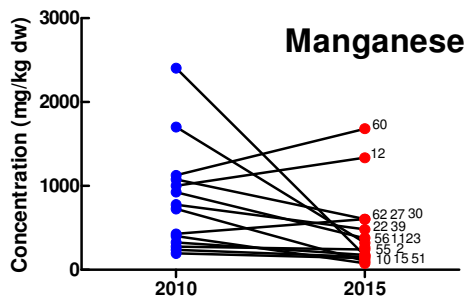
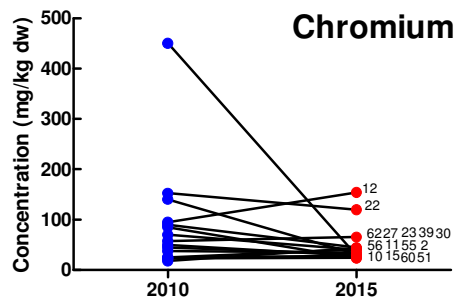
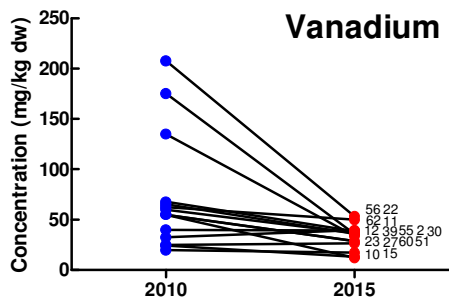
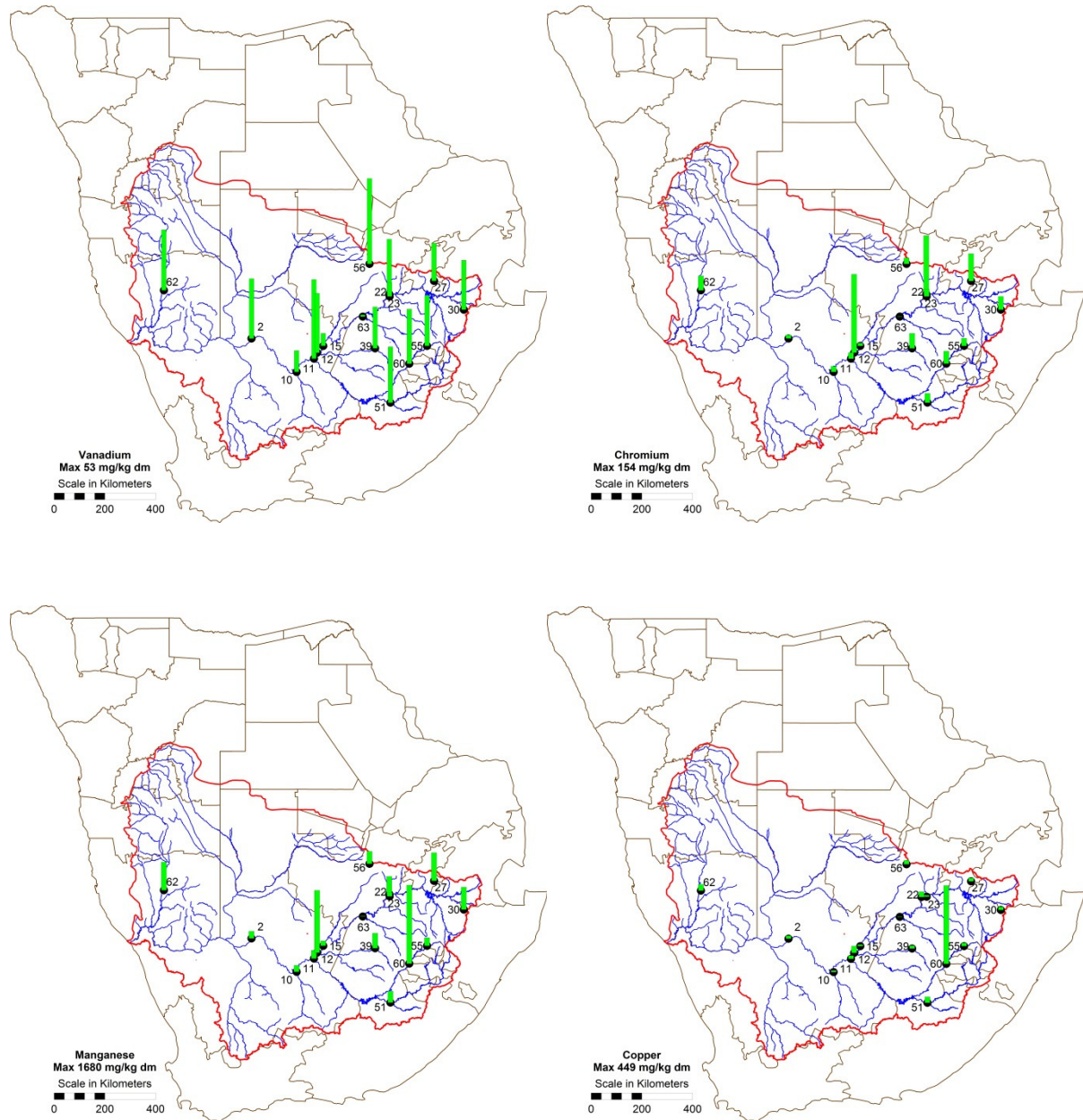


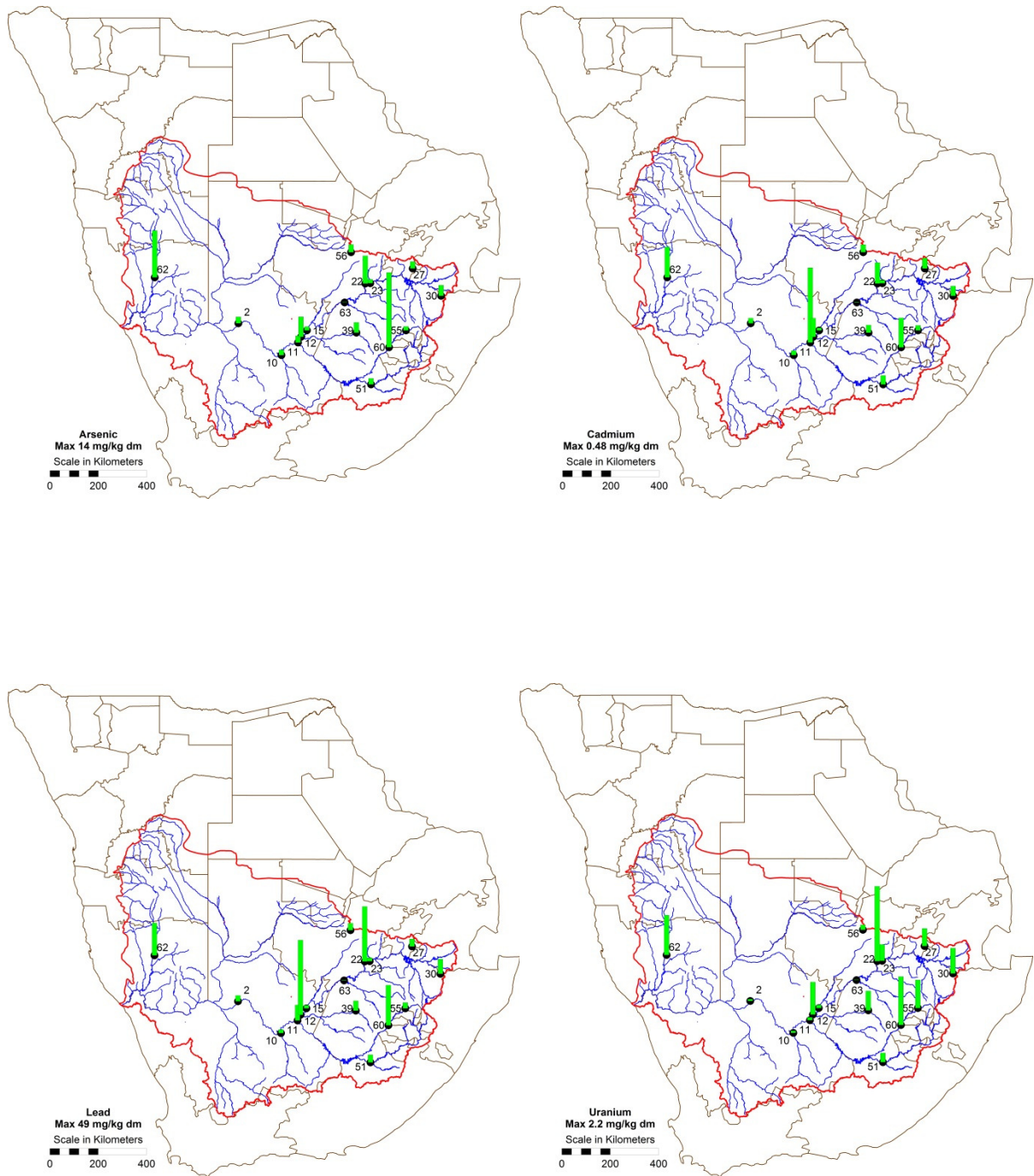
Figure 6 : Changes in the sum of selected elements in sediments

Figure 6 graphically represents the changes in elemental concentrations in sediments. Sites such as 56 (Molopo Eye) and 15 (Schmidtsdrift) that had high concentrations in 2010, showed strong decreases in 2015 for lead, vanadium, manganese, and copper. Copper and arsenic increased at site 60 (Kelekequ River). Especially copper is of concern here. Overall, most of the sites had decreased concentrations and some remained about the same.

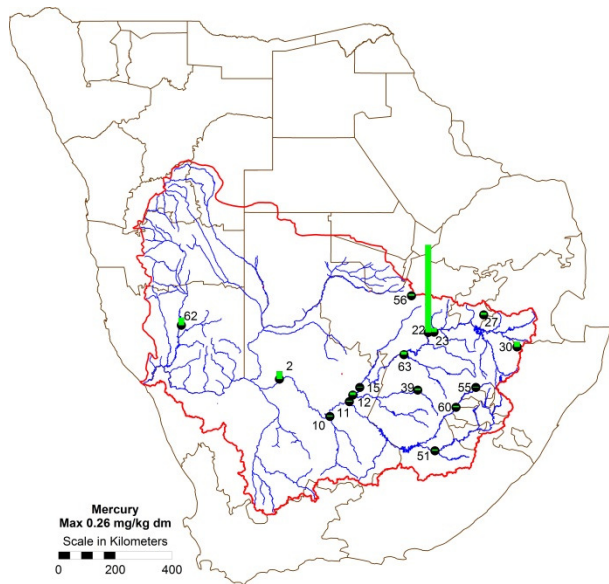
Figure 7 represents the 2015 data geographically.



**Figure 7 : Geographical distribution of elements in sediments across the Basin**



**Figure 7 continued:** Geographical distribution of elements in sediments across the Basin



**Figure 7 continued:** Geographical distribution of elements in sediments across the Basin

The geographical representation of the 2015 data shows patterns similar to the 2010 survey and the organic pollutants in Figure 6. Here however, there are some compounds that have relatively higher concentrations near Lesotho. Site 22 (Skoon Spruit), as for the elements, also show stands out and would probably need more attention.

*Fish and wild bird eggs:*

The 2010 results for the elements in the fish were averaged to create a single value per element. This was needed to compare 2010 results to 2015 results as there were no similar sites between 2015 and 2010. The averaged 2010 concentrations were compared to each of the new sites of 2015 and fold effects calculated.

When the sum of the elemental concentrations were compared there was an approximate two fold increase in the concentrations of elements at all three the sites from which fish was collected in 2015 (Table 4). For Bloemhof Dam and the Upington sites there were fold increases of 62.5% of the measured concentrations and 59% for Lenasia. Bismuth (Bi) seemed to have the biggest fold increase of greater than 60 for all three sites (Table 4), followed by antimony (Sb) with a fold increase of almost 30.

Direct comparison between the concentrations in the wild bird eggs between 2010 and 2015 could not done as eggs were collected from different sites. The approach was explained in the materials and methods section.

As for the fish samples, bismuth and antimony showed the biggest fold increase across all the bird egg samples (Table 5). In the Glossy Ibis eggs bismuth's fold increase was almost 1 500 times greater. The sum of the element concentrations between the various sites indicated no real fold increase despite the large fold increases of Bi and Sb. There were a selection of other elements that had a minor fold increase and the patterns of fold increase is very similar between Grey Heron and Reed Cormorant, however the Glossy Ibis fold increase pattern seems different (Table 5).

**Table 4** : Concentrations (mg/kg dm) of elements in fish tissue from 2010 to compare to the concentrations of fish from three sites in 2015. The fold effect (FE) is determined by dividing 2015 concentrations with 2010 concentrations. The shaded cells indicate a fold increase of more than 1.

	Bloemhof Dam			Lenasia		Upington	
	2010	2015	FE	2015	FE	2015	FE
<b>Be</b>	0.01	0.03	4.7	0.03	4.6	0.02	4.5
<b>B</b>	3.47	1.11	0.3	0.79	0.2	1.13	0.3
<b>Na</b>	912.50	2567.50	2.8	2935.00	3.2	3702.50	4.1
<b>Mg</b>	1006.25	1732.25	1.7	1887.75	1.9	1712.75	1.7
<b>Al</b>	9.06	26.93	3.0	13.99	1.5	26.28	2.9
<b>K</b>	10 656.25	16 922.50	1.6	19 577.50	1.8	20 057.50	1.9
<b>Ca</b>	390.63	1782.25	4.6	1007.50	2.6	3602.50	9.2
<b>Ti</b>	23.81	16.18	0.7	17.44	0.7	18.91	0.8
<b>V</b>	1.17	0.59	0.5	0.60	0.5	0.62	0.5
<b>Cr</b>	3.56	11.02	3.1	13.34	3.7	12.34	3.5
<b>Mn</b>	0.99	1.73	1.7	1.93	1.9	2.54	2.6
<b>Fe</b>	54.69	185.40	3.4	49.93	0.9	62.98	1.2
<b>Co</b>	0.05	0.13	2.6	0.22	4.2	0.12	2.3
<b>Ni</b>	0.47	0.19	0.4	0.12	0.3	0.22	0.5
<b>Cu</b>	2.35	2.14	0.9	2.49	1.1	2.85	1.2
<b>Zn</b>	20.22	27.63	1.4	26.33	1.3	26.63	1.3
<b>As</b>	1.28	0.09	0.1	0.18	0.1	0.09	0.1
<b>Se</b>	4.08	2.87	0.7	3.10	0.8	7.60	1.9
<b>Rb</b>	9.38	13.04	1.4	42.50	4.5	8.77	0.9
<b>Sr</b>	0.73	2.02	2.7	0.78	1.1	3.77	5.1
<b>Mo</b>	0.09	0.21	2.2	0.19	2.0	0.17	1.8
<b>Pd</b>	0.10	0.13	1.3	0.15	1.5	0.12	1.3
<b>Ag</b>	3.66	0.11	0.0	0.35	0.1	0.13	0.0
<b>Cd</b>	0.01	0.04	3.3	0.03	2.7	0.03	3.1
<b>Sb</b>	0.01	0.21	32.0	0.18	27.0	0.19	28.9
<b>Ba</b>	6.22	0.88	0.1	0.59	0.1	0.95	0.2
<b>Pt</b>	0.17	0.01	0.1	0.02	0.1	0.01	0.1
<b>Au</b>	0.10	0.42	4.1	0.41	4.0	0.32	3.1
<b>Tl</b>	0.10	0.00	0.0	0.01	0.1	0.01	0.1
<b>Pb</b>	0.34	0.42	1.2	0.25	0.7	0.22	0.7
<b>Bi</b>	0.01	0.37	66.6	0.34	61.3	0.34	61.0
<b>U</b>	0.05	0.03	0.6	0.03	0.6	0.03	0.6
<b>Total</b>	13 111.80	23 298.40	1.8	25 584.05	2.0	29 252.65	2.2



**Table 5 : Concentrations (mg/kg dm) of elements in wild bird eggs from 2010 to compare to the concentrations of eggs in 2015. The fold effect (FE) is determined by dividing 2015 concentrations with 2010 concentrations. The shaded cells indicate a fold increase of more than 1. Comparisons were run between the same bird species.**

	Grey Heron					Reed Cormorant				Glossy Ibis			
	Barbers Pan		Bloemhof Dam		2015	Potchefstroom		Bloemhof Dam		Upington	Potchefstroom		Lenasia
	2010	FE	2010	FE		2010	FE	2010	FE		2010	FE	
<b>Be</b>	0.15	0.2	0.08	0.3	0.03	0.10	0.3	0.04	0.6	0.03	0.02	1.1	0.03
<b>B</b>	115.00	0.0	61.11	0.0	0.68	34.05	0.0	25.00	0.0	0.70	22.50	0.0	0.96
<b>Na</b>	9000.00	1.4	11 110.00	1.2	12 875.00	13 052.50	1.0	13 018.75	1.0	13 455.00	11 500.00	0.7	8352.50
<b>Mg</b>	1050.00	0.8	999.90	0.8	834.00	1135.00	1.0	1093.58	1.0	1093.00	1150.00	0.5	529.75
<b>Al</b>	16.00	2.1	12.22	2.7	33.35	10.22	6.7	10.42	6.6	68.88	14.00	2.6	36.45
<b>K</b>	6000.00	1.1	7221.50	0.9	6477.50	7945.00	0.7	8332.00	0.7	5705.00	8000.00	0.8	6495.00
<b>Ca</b>	2900.00	0.9	3055.25	0.8	2498.50	2667.25	0.9	2759.98	0.9	2486.75	2650.00	0.8	2087.00
<b>Ti</b>	7.50	1.4	6.11	1.7	10.30	5.28	2.5	5.21	2.5	13.03	6.00	1.7	10.35
<b>V</b>	2.35	0.2	2.17	0.2	0.51	2.67	0.2	2.66	0.2	0.61	2.65	0.2	0.55
<b>Cr</b>	5.00	2.4	6.67	1.8	12.03	8.51	1.6	7.81	1.8	13.73	8.00	1.5	12.14
<b>Mn</b>	3.15	0.6	2.44	0.7	1.81	4.94	1.1	2.92	1.9	5.57	5.00	0.4	2.14
<b>Fe</b>	230.00	1.6	222.20	1.6	361.25	204.30	1.8	223.92	1.6	359.50	195.00	0.5	95.60
<b>Co</b>	0.35	0.8	0.10	2.6	0.26	0.09	5.7	0.09	5.5	0.48	0.23	0.4	0.09
<b>Ni</b>	2.05	0.4	1.28	0.7	0.90	1.14	2.7	1.46	2.1	3.11	1.15	0.1	0.16
<b>Cu</b>	7.00	4.1	8.33	3.5	28.75	5.39	1.0	8.85	0.6	5.43	5.00	0.8	3.89
<b>Zn</b>	65.00	0.9	61.11	1.0	58.88	62.43	0.5	72.91	0.4	32.35	70.00	0.6	38.63
<b>As</b>	2.25	0.0	2.06	0.0	0.05	1.99	0.0	2.14	0.0	0.03	2.15	0.0	0.05
<b>Se</b>	10.00	0.5	6.11	0.8	5.01	6.24	0.9	6.25	0.9	5.46	7.00	0.4	2.71
<b>Rb</b>	1.10	3.0	2.39	1.4	3.28	3.86	0.7	2.60	1.0	2.54	2.65	3.0	7.85
<b>Sr</b>	1.85	5.5	1.28	8.0	10.25	1.48	2.0	1.46	2.0	2.92	3.60	1.1	4.09
<b>Mo</b>	1.45	0.6	1.61	0.5	0.84	1.76	0.4	2.60	0.3	0.69	0.55	0.9	0.50
<b>Pd</b>	6.50	0.0	1.56	0.1	0.13	0.74	0.2	0.52	0.3	0.16	0.50	0.4	0.21
<b>Cd</b>	0.15	0.2	0.07	0.4	0.03	0.01	5.8	0.02	1.4	0.03	0.01	31.0	0.16
<b>Sb</b>	0.01	27.6	0.01	21.3	0.17	0.01	25.3	0.01	27.6	0.14	0.01	9.3	0.13
<b>Ba</b>	12.50	0.1	11.11	0.1	1.11	13.05	0.2	11.46	0.2	2.34	16.00	0.1	2.06
<b>Pt</b>	2.95	0.00	0.39	0.0	0.01	0.25	0.0	0.29	0.0	0.01	0.33	0.0	0.01
<b>Au</b>	70.00	0.0	11.67	0.0	0.32	3.63	0.1	2.86	0.1	0.32	2.45	0.2	0.45
<b>Hg</b>	7.00	0.0	3.56	0.0	0.07	3.23	0.0	2.19	0.0	0.11	1.60	0.1	0.11
<b>TI</b>	8.50	0.0	1.17	0.0	0.00	0.31	0.0	0.21	0.0	0.01	0.18	0.1	0.02
<b>Pb</b>	1.60	0.3	0.56	0.9	0.51	0.41	0.4	0.52	0.3	0.18	0.48	1.4	0.67
<b>Bi</b>	0.00	264.3	0.00	144.4	0.34	0.00	186.4	0.00	77.6	0.34	0.00	1455.7	0.42
<b>U</b>	2.90	0.0	0.31	0.1	0.04	0.09	0.5	0.22	0.2	0.05	0.07	0.5	0.03

<b>Total</b>	19 532.31	1.2	22 814.30	1.0	23 215.90	25 175.90	0.9	25 598.93	0.9	23 258.48	23 667.12	0.7	17 684.68
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## 3.2 Discussion

### *Sediment:*

Reflecting on which sediment sites showed fold increases for both PAHs and elements, the following four were identified: 12 (Vaal River at Douglas), 22 (Skoon Spruit), 30 (Klip River East) and 62 (Fish River). The increase in pollutant concentrations at both sites 12 and 22 can be explained by their downstream positions in the hardest working river in South Africa, the Vaal River. In fact, site 12 is the farthest downstream site in the Vaal River at the point of its confluence with the Orange River and should therefore have the highest pollutant load of the entire stretch of the Vaal River. The Skoon Spruit is a tributary receiving run-off from an active gold mining region in South Africa, which might explain the increased elemental concentrations. The increase in PAHs might not necessarily be due to localised releases in the direct vicinity of the site as these pollutants are easily transported by air and could have been carried to that area from the more industrially active Gauteng province and Vaal Triangle region.

Site 30 is situated in the Klip River East which is in the proximity of the coal mining region of South Africa as well as most of the country's coal fire power stations generating electricity. The power generation might explain the increase in PAHs as these are known to be created by combustion processes (Culotta et al., 2006) and the coal mining might have contributed to the increase in elemental concentrations, and although this was a slight fold increase of 1.5 calculated on the sum of the elements (Table 3), it is based on a slight increase of 19 of 31 elements (61%).

### *Biota:*

The fact that there was a general increase in fold effect across of elements at all three sites from which fish were sampled—although they were not from the exact same place as in 2010—indicates towards a catchment wide increase in the elemental concentration (Table 4). It was on average only a two times increase.

There does not seem to have been a real increase in elemental concentrations in the wild bird eggs between 2010 and 2015 (Table 5). However, the two elements that should be flagged are bismuth and antimony as their concentrations seems to have soared compared to the 2010 results. These same two elements also had relatively high fold increases in the fish tissue with bismuth's between 61 and 66 and that of antimony between 27 and 32 (Table 4).

Antimony enters the environment during mining and processing of ores and in the production of antimony combinations such as alloys and oxides. Small amounts of antimony are released by incinerators and coal-burning power plants (ATSDR, 1992). Antimony trioxide is used as a flame retardant in the plastics industry in canvas, paints and tenting material (Davis et al. 1986). There is some evidence in literature that antimony can be harmful to mammals when inhaled and ingested (ATSDR, 1992) but no evidence thereof in birds. Recently antimony has been listed as a priority pollutant of interest in both the USA and EU. It is regarded a toxic trace element and a suspected human carcinogen (Fu et al 2010). Bismuth is the by-product of the processing of metal ores such lead, silver, tin, copper, and zinc. Bismuth has been replacing lead in many applications as it shares many characteristics of lead, but is much less toxic to living organisms (Yang & Sun 2012). There are many applications for bismuth in

medicine and health care because of its effectiveness in treating diseases caused by microbial infections and its potential activity against viruses and tumours (Yang & Sun 2012). Toxicity problems with Bi and its compounds occur mainly when used as a therapeutic agent during prolonged application, leading to kidney failure or mental disorders (Michalke et al., 2008). No evidence of harmful effects of Bi towards bird health could be discovered in the literature.

Comparison of 2015 elemental concentrations between sediment, fish and Grey Heron eggs: The concentrations of the same metals and trace elements were compared between the abiotic sediment and the biotic matrices, i.e. fish tissue and wild bird eggs, specifically the Grey Heron, from the same site, Bloemhof Dam (Table 6). There were an increase of sodium (Na), magnesium (Mg), potassium (K) and calcium (Ca) from sediment to fish to bird egg content. Zinc (Zn) also had a two fold increase from sediment to fish and another two fold increase to bird eggs, while selenium (Se) first increased 8 times from sediment to fish and then a 1.7 times increase to bird eggs. There was a slight increase in gold concentrations as well between sediment and the biota. Aluminium (Al), cobalt (Co) and iron (Fe) seem to decline in concentration from sediment to biota. Although these results are from single sample analysis, and no statistical significant difference could be calculated, there seem to be evidence of bio-magnification of Na, Mg, K, Ca, Zn, and Se between the sediment and biota.

Methyl mercury (MeHg) was included in the 2015 analysis as it is one of the organic forms of mercury and the form that most easily bio-accumulates in organisms higher up in the food web and is more toxic than the inorganic form. However, there seems little evidence of this in the data of Bloemhof Dam (Table 6). The concentrations of methyl mercury was also lower than the Codex Alimentarius maximum residue concentration (MRL) for human consumption, set at 0.5 mg/kg, indicating no direct risk, but the situation should be monitored.

**Table 6** : Metal and trace element concentrations in sediment, fish and wild bird eggs sampled at Bloemhof Dam during 2015.

	<b>Sediment (mg/kg dm)</b>	<b>Sharptooth catfish (mg/kg wm)</b>	<b>Grey Heron (mg/kg wm)</b>
Be	0.10	0.03	0.03
B	1.77	1.11	0.68
Na	231.70	2567.50	12875.00
Mg	223.58	1732.25	834.00
Al	1390.50	26.93	33.35
K	209.28	16922.50	6477.50
Ca	221.50	1782.25	2498.50
Ti	43.38	16.18	10.30
V	6.21	0.59	0.51
Cr	19.36	11.02	12.03
Mn	8.42	1.73	1.81
Fe	1842.75	185.40	361.25
Co	1.08	0.13	0.26
Ni	2.37	0.19	0.90
Cu	2.19	2.14	28.75
Zn	2.46	27.63	58.88
As	0.39	0.09	0.05
Se	0.35	2.87	5.01
Rb	2.81	13.04	3.28
Sr	1.27	2.02	10.25
Mo	0.36	0.21	0.84
Pd	0.14	0.13	0.13
Cd	0.03	0.04	0.03
Ba	9.27	0.88	1.11
Pt	0.00	0.01	0.01
Au	0.29	0.42	0.32
Hg	0.03	0.00	0.07
methyl-Hg	0.10	0.11	0.07
Tl	0.02	0.42	0.00
Pb	1.31	0.37	0.51
U	0.27	0.03	0.04

## 4 SUMMARY AND CONCLUSIONS

This project is an assessment of the first five-yearly follow-up of the extensive sampling and analyses of POPs, PAHs, and elements in sediments, fish and bird eggs from the Orange-Senqu River Basin, previously sampled in 2010 (ORASECOM, 2013). Restrictions allowed only a limited number of samples to be comprehensively analysed. Based on the 2013 report, some compounds were left out as they were not deemed of concern at the Basin scale. In their place, new POPs and candidate POPs were included that have been added to the Stockholm Convention since the 2010 sampling campaign. Sampling, sample treatment, sample shipment and analyses was done in the same way and by the same laboratories using the same methods as for the 2010 campaign. The 2010 and 2015 data is therefore considered comparable, providing a good basis for time trend and hotspot detection.

For both the organic and inorganic matrixes, large and small differences in changes in concentrations occurred in sediments at some sites, less at others. The causes of these are not known, but likely reflect differences in sedimentation, releases, and movement of biota, between 2010 and 2015. For many elements, concentrations increased in biota and are of concern. Methyl mercury has been measured for the first time in the Basin. Although not present in quantifiable amounts in sediment samples, bot mercury and methyl mercury was present in appreciable amounts in fish and bird eggs. However, the concentrations did not exceed the Codex Alimentarius maximum residue concentrations (MRLs of 0.5 mg/kg). Although this means that for this single pooled sample that human consumption may be considered safe, it is not enough to pronounce equivocally so. More studies are needed for the entire Basin as there are sources of mercury (especially illegal gold mining) that may cause elevated concentrations of mercury in fish. A risk assessment was not part of this study, but the results of the present study broadly conformed to the previous results (ORASECOM, 2013), and should be the same.

The pollutant situation at most sites deteriorated (higher concentrations of pollutants) with some showing decreases. Some sites showed improvements. Organic compounds of concern remain PAHs, PCBs, and PFOS, but now also BFRs, and OCPs. The organic compound that should be monitored before deciding on whether it is of lesser concern is SCCPs. Elements of concern are Al, Cr, Cu, Bi, Sr, Sb, Au, Hg, Pb, and U. Because mercury and methyl mercury data is only available on a small scale from these reports, more should be done on this pollutants (especially in biota) to obtain clarity on whether it is a problem, where it is a problem, and how large a problem and priority it is. The impetus of the Minamata Convention that is attracting more Parties should be considered an important motivation.

Although this study was restricted to a sub-sample of the previous sites (only 16 vs. 61), the patterns of pollution, as far as can be discerned, remained similar and therefore the areas of concern as well. The rivers draining Gauteng and the gold mining areas remain an area of concern, as well as the areas downstream of the Drakensberg Mountains. The Vaal – Orange confluence has increased in prominence and should be closely monitored. It is recommended that these three areas be subjected to a much denser sampling effort to delineate the areas of concern and better understand the possible sources before targeted interventions can be planned. The current scale of the sampling effort is not fine enough to attempt any detailed planning. Because we now know the compounds of concern (PAHs, PCBs, BFR, etc.)

analyses could be targeted to these compounds only, thereby reducing costs and expanding the coverage. The next five-year survey should again sample all the previous sites, add sites that have come to attention from other studies, and include more biota.

This assessment indicates that a selection of the initial sample may provide enough information to track broad changes in a large system such as the Orange-Senqu River Basin over time. The data collected during 2010 and 2015 is now a valuable resource for resource for future trend analyses, as well as identifying general areas of concern that needs details follow-up studies for data that will inform interventions, where possible. The ORASECOM has now provided enough data to identify and motivate detailed studies of specific areas. Based on the 2010 data for instance, a detailed study of PAHs in the Soweto and Lenasia regions of the Klip Spruit is now ongoing. Similar studies can be considered in the other areas of concern. The more remote regions are likely to undergo land use changes, increased population densities, mining, and industrialisation. Monitoring and detailed studies should therefore continue to track and identify impacts in a timely manner. New POPs are likely to be added to the Stockholm Convention and these may need additional attention.

The extent and impacts of plastic and microplastic pollution is virtually unknown in the system. Given the millions of people living in and depending on the Basin, it is likely that the impact will be of concern. A more detailed exposition of the problem is given in Appendix A. ORASECOM would be a globally leading organisation if it were to assess this issue on a Basin scale.

The strong indications of bio-accumulation of POPs and some heavy metals is very concerning as the biota in the arid regions of the basin is almost entirely dependent on the riverine water, and any impacts from long-range transport is a major issue that needs much better understanding. The high concentrations of pollutants in birds and fish may affect sustainability and ecosystem function. Many people depend on their food and water directly from the rivers, and may be exposed to pollutants that may be harmful. It is therefore recommended that a more detailed animal and human study be considered.

Other organic threats have been detected in the Basin, outside the scope of the previous and current studies. Endocrine disruption has been detected in water and sediment. This may also affect the biology and ecologies of the basin, and, potentially also human health. Pharmaceuticals, specifically HIV-antiretrovirals, have also been detected in river water, ground water, and fish (WRC study in prep). There are also strong indications of many other pharmaceuticals such as pain killers and anti-depressants.

The ORASECOM member states can also use the data generated by the current and previous studies for reporting purposes to international bodies such as the Stockholm and Minamata conventions.

#### *Summarised recommendations*

- ORASECOM States may consider using the available data in their international reporting obligations.
- The next five-year survey should cover the initial sites, as well as additional ones that may come to the fore. Compounds that have been shown not to be an issue need not be analysed again, but new POPs should be checked at least once.

- The areas that have been identified should be subjected to detailed investigations for the compounds of concern. This will inform well-motivated interventions. For example, interventions to reduce PAHs could consider source reductions such as open fires at waste dumps.
- A detailed and in-depth study of the bio-accumulation of POPs and mercury should be undertaken. This will have two purposes. It will inform on threats to the long-term sustainability of the ecosystems involved, and it will provide information on possible health threats due to water and fish consumption.
- Plastic and micro-plastic pollution in the aquatic environment has not been assessed for the entire Basin. This threat is potentially huge and may remain so for a long time. A better understand of the situation may motivate targeted interventions. An exposition of plastics as a pollutant is provided in Appendix B.
- Endocrine disrupting activity and pharmaceuticals in water, biota, and sediments of the Basin needs more attention.

## 5 LITERATURE

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Appendix A : Map of sediment sampling sites with site numbers corresponding to the same numbers used in this report



## Appendix B : Plastics in freshwaters - H. Bouwman & Rialet Pieters

### H Bouwman & Rialet Pieters

**Background:** Pollution by plastics in the marine environment has been in the news lately. Plastics production has increased globally from 5 million tons in the 1960s to 280 million tons now. Large volumes of plastics, mainly from shore-based sources, are entering the marine environment and ending up as “garbage patches” in the oceanic gyres, on the ocean floor, and on distant shores. There are a number of major immediate impacts: entanglement and strangling of animals (at least 663 impacted species have now been documented<sup>2</sup>), intake by biota, destruction of corals, fouling of ships propellers, and loss of income from fishing and tourism. The ability and impacts of both floating and sunken plastics to act as rafts and new habitats for biota is not well understood. In addition, other impacts such as transport of persistent or of ever smaller particle sizes are increasingly recognised as areas of concern. As plastics disintegrate due to physical and biological actions on them, the smaller particles release of POPs, inherent chemicals such as plasticisers, and heavy metals, and they become easier to be taken up by smaller animals. The potential impacts of these micro- and nano-plastics are not well understood, but research on this “hot” topic progressively provides a stronger basis to show that concerns are valid and the impact potentially vast. More on this can be gleaned from two recent documents produced by the Scientific and Technical Advisory Panel (STAP) of the Global Environment Facility (GEF).<sup>1,2</sup>

Together with other impacts on the world’s oceans such as acidification, loss of biodiversity, and climate change, plastics pollution is now recognised as one of the major stressors of the oceanic environment.

**Plastics in freshwaters:** Compared to knowledge on plastics in marine environments, comprehension about plastics in freshwaters is very limited. Recently, a “garbage patch” in the Great Lakes in the USA, similar in concept to the patches in the five oceanic gyres, was discovered.<sup>3</sup> Concern about micro-plastics was also expressed in this case. Plastics and micro-plastics pollution in Lake Geneva<sup>4</sup> has also drawn attention.

It is therefore very likely that the same problems and impacts of plastics pollution in the oceans are also present in freshwaters. In developing countries with deficient waste control, the problems might be greater than in developed countries and even in coastal countries. In addition, human consumption of natural freshwater polluted by micro-plastics might be a concern not associated with the marine environment.

Many plastics are also likely to be on the bottom of streams, rivers and lakes, and may pose a significant hazard by acting as a source and sink of POPs, heavy metals, and polycyclic aromatic hydrocarbons (PAHs), as well as inherent chemicals such as plasticisers and UV-protectors, all compounds known or suspected to be endocrine disruptive and/or carcinogenic. The plastics in freshwaters are also likely to be a continuous source of micro-plastics for as long as it remains in the freshwater environment.

Plastics pollution in freshwaters is a visible reality in many developing countries, but the more subtle and insidious problems with chemicals and micro-plastics remain largely unknown. Based on the concerns from the marine environment, research on plastics in the freshwater environment is urgently needed.

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<sup>1</sup> STAP (2011). *Marine Debris as a Global Environmental Problem: Introducing a solutions based framework focused on plastic*. A STAP Information Document. Global Environment Facility, Washington, DC.<http://www.unep.org/stap>.

<sup>2</sup> Secretariat of the Convention on Biological Diversity and the Scientific and Technical Advisory Panel—GEF (2012). *Impacts of Marine Debris on Biodiversity: Current Status and Potential Solutions*, Montreal, Technical Series No. 67, 61 pages. <http://www.unep.org/stap>

<sup>3</sup> <http://newswatch.nationalgeographic.com/2013/04/12/new-concerns-about-plastic-pollution-in-great-lakes-garbage-patch/>

<sup>4</sup> <http://planetsave.com/2013/05/30/micro-plastic-pollution-is-prevalent-in-lakes-too-not-just-the-oceans/>