# POPs, PAHs and elemental levels in sediment, fish and wild bird eggs in the Orange–Senqu River basin





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The Orange–Senqu River Commission – ORASECOM – was established by the governments of Botswana, Lesotho, Namibia and South Africa to promote equitable and sustainable development and management of the resources of the Orange–Senqu River. This joint commitment was sealed through an Agreement on the Establishment of the Orange–Senqu River Commission signed in November 2000 in Windhoek, which conforms with best international practices regarding the joint management of shared rivers.

The highest body of ORASECOM is the Council, consisting of delegations from each country, supported by various 'Task Teams' that manage projects, and a Secretariat. The Council serves as technical advisor to the member states on matters related to development, utilisation and conservation of water resources of the Orange–Senqu River system. The Secretariat, established by agreement with South Africa in 2006 and hosted there, coordinates ORASECOM activities, implements ORASECOM decisions and is the focal point of the institution.

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# EXECUTIVE SUMMARY



### INTRODUCTION AND METHODOLOGY

he 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 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 ( $I_{geo}$ ) values were determined the same site had the most elements with  $I_{geo}$  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  $I_{\rm geo}$  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 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

This study 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.

# CONTENTS

Abbreviations and acronyms	2
1. Introduction	5
<ul><li>1.1 The Orange–Senqu River basin</li><li>1.2 POPs, PAHs and heavy metals</li><li>1.3 Previous research</li></ul>	5 6 7
2. Materials and methods	11
<ul><li>2.1 Site selection</li><li>2.2 Sampling and sample preparation</li></ul>	11 16
3. Results	20
3.1 Organic pollutants 3.2 Heavy metals and trace elements	20 26
4. Discussion	43
<ul><li>4.1 Organic pollutants</li><li>4.2 Heavy metals and trace elements</li></ul>	43 44
5. Risk assessment	45
5.1 Background and methods	45 47 51
6. Concerns and recommendations	52
6.1 Areas of concern	52 53
References	55
Addendum	60

ABBREVIATIONS AND	
ACRONYMS	

General	∑c-PAH	concentration of carcinogenic PAHs
	∑t-PAH	total concentration of PAHs
	ADD	average daily dose
	ATSDR	Agency for Toxic Substances and Disease Registry
	BSAF	biota-sediment accumulation factor
	CAC	Codex Alimentarius Commission
	CMR	Creamer Media Reporter
	CRESP	Consortium for Risk Evaluation with Stakeholder Participation
	dw	dry weight
	EC	European Commission
	EU	European Union
	FAO	Food and Agricultural Organisation
	GAPS	Global Atmospheric Passive Sampling
	GEF	Global Environment Facility
	HQ	hazard quotient
	HRGC-MS	high-resolution gas chromatography and mass spectrometry
	IARC	International Agency for Research on Cancer
	ICP-MS	inductively coupled plasma mass spectrometry
	lgeo	geoaccumulation index
	LADD	lifetime average daily dose
	MBF	mean bioaccumulation factor
	MPI	metal pollution index
	NTA	National Toxicology Program
	ORASECOM	Orange–Senqu River Commission
	RfD	reference dose
	SADC	Southern African Development Community
	SADF	South African Defence Force
	SSBF	species-specific bioaccumulation factor
	TDA	transboundary diagnostic analysis
	TEQ	toxic equivalent
	UNDP	United Nations Development Programme
	USEPA	United States Environmental Protection Agency
	UV	ultraviolet
	vol.	volume
	WHO	World Health Organisation
	WRC	Water Research Commission
	WW	wet weight
Units of measure	μg	microgram(s)
	cm	centimetre(s)
	d	day(s)
	g	gram(s)
	kg	kilogram(s)
	km	kilometre(s)
	l	litre(s)
	mg	milligram(s)
	ml	millilitre(s)
	mm	millimetre(s)
	mol	mole(s)
	ng	nanogram(s)
	ppm	part(s) per million
Elements and compounds	α-HCH	alpha-hexachlorocyclohexane
	ß-HCH	beta-hexachlorocyclohexane
	ү-НСН	gamma-hexachlorocyclohexane
	Ag	silver
	AĬ	aluminium

As	arsenic
Au	gold
В	boron
Ba	barium
BaP	benzo(a)pyrene
Be	bervllium
Br	bromine
Ca	calcium
Cd	cadmium
Ce	cerium
Co	cobalt
Cr	chromium
Cs	caesium
Cu	copper
DDT	dichloro-diphenyl-trichloroethane
Fe	iron
Ga	gallium
Ge	germanium
HCB	hexachlorobenzene
HCH	hexachlorocyclohexane
HC1	hydrochloric acid
Hg	mercury
HxCDD	hexachlorodibenzo-p-dioxin
Ι	iodine
К	potassium
Li	lithium
Mg	magnesium
Mn	manganese
Mo	molybdenum
Na	sodium
Ni	nickel
OCP	organochlorine pesticide
PAH	polycyclic aromatic hydrocarbon
Pb	lead
PBDE	polybrominated diphenyl ether
PCDD	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzoruran
	1.2.3.7.8-peptachlorodihenzo-a-diovin
PFOS	perfluorooctane sulfonate
PFOSE	perfluorooctane sulfonyl fluoride
POP	persistent organic pollutant
Pt	platinum
Rb	rubidium
Rh	rhodium
Sc	scandium
Se	selenium
Si	silicon
Sn	tin
Sr	strontium
TCDD	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin
Ti	titanium
T1	thallium
U	uranium
V	vanadium
Zn	zinc

# 1. INTRODUCTION

### 1.1 THE ORANGE-SENQU RIVER BASIN

he Orange–Senqu River rises in the Lesotho Highlands, from where it flows westwards to discharge into the Atlantic Ocean between the settlements of Alexander Bay and Oranjemund on the West Coast. The river basin is the third largest in southern Africa, after the Zambezi and the Congo, covering an area of approximately 1,000,000 km<sup>2</sup>. Four countries – Botswana, Lesotho, Namibia and South Africa – share the basin.

Lesotho lies entirely within the basin and makes up less than 5% of the total basin area. It contributes over 40% of the stream flow, but uses little of this water. South Africa, with more than 60% of the basin area, is by far the biggest user of the basin's water, which supports the economic heartland of the country. The Botswana part of the basin, making up 7.9% of its area, is entirely covered by the Kalahari Desert so there is very little surface runoff, and water demand is largely met by groundwater abstraction. Namibia contributes 24.5% of the basin's area but less than 5% of the runoff, and is heavily dependent on the basin's water to support agricultural activities along the lower Orange River.

Indeed, irrigation demands from both Namibia and South Africa largely determine the water requirements in the lower reaches of the river, but there is also a need to maintain sufficient flow to safeguard the environment of the estuary. The Orange River estuary is ranked as one of the most important wetland systems in southern Africa and is designated a Ramsar site, but it was placed on the Montreux Record following recognition of its environmental degradation.

The middle and lower reaches of the river are subject to periodic and often devastating floods, while agricultural, urban and industrial activities throughout the basin potentially impact upon water quality. The effective management of the Orange–Senqu River basin is therefore particularly complex, but is also vital to the economy of the region. Recognising this, the riparian states prioritised the basin for the establishment of a Shared Watercourse Institution under the revised Southern African Development Community (SADC) Protocol on Shared Watercourses. The Orange–Senqu River Commission (ORASECOM) was established under the Protocol in 2000, and the Orange–Senqu River Basin Environment Programme was agreed at the ORASECOM Council Meeting in April 2007. The programme covers six thematic areas: institutional and organisational strengthening; capacity building on shared watercourse management; information system; communication and awareness building; transboundary projects and studies; and conservation and environmental strategies and policies.

The preliminary transboundary diagnostic analysis (TDA) of the basin, compiled during the preparation of the UNDP-GEF Orange-Senqu Strategic Action Programme and adopted by ORASECOM in April 2008, noted several knowledge gaps, among them the lack of basin-wide and consistent information on persistent organic pollutants (POPs) and heavy metals. These areas were addressed in this study. During the course of the work, polycyclic aromatic hydrocarbons (PAHs) and a human health risk assessment were added to the study's scope.





### 1.2 POPS, PAHS AND HEAVY METALS

The four countries that share the catchment of the Orange–Senqu River system are all parties to the Stockholm Convention on Persistent Organic Pollutants (POPs). The Stockholm Convention originally focused on 12 chemicals or chemical classes, the so-called 'dirty dozen'. Included in this list were eight pesticides (aldrin, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene and dichloro-diphenyl-trichloroethane, better known as DDT), the industrial chemicals polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB), and a family of unintended by-products of industrial processes, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs), commonly known as dioxins and furans.

Nine additional POPs were listed by the Stockholm Convention in May 2009. They are chlordecone, lindane (gamma-hexachlorocyclohexane or  $\gamma$ -HCH), alpha-hexachlorocyclohexane ( $\alpha$ -HCH), beta-hexachlorocyclohexane ( $\beta$ -HCH), hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, tetrabromodiphenyl ether and pentabromodiphenyl ether, pentachlorobenzene, as well as perfluorooctane sulfonate (PFOS), its salts and perfluorooctane sulfanyl fluoride (PFOSF). In 2011, endosulfan became the 22<sup>nd</sup> POP to be listed under the Stockholm Convention.

Polycyclic aromatic hydrocarbons (PAHs) are composed of carbon and hydrogen atoms in fused benzene rings (Sims and Overcash, 1983). The widespread occurrence of PAHs is largely due to their formation and release during the incomplete combustion of organic materials in furnaces, fireplaces, gas and oil burners, in the production of coke and carbon, in petroleum processing and aluminium sintering, in coal power plants and in mobile sources such as cars, lorries and trains (Maliszewska-Kordybach, 1999). Direct releases from petroleum and coal are also possible. Natural sources such as volcanic activity contribute only slightly to environmental levels of PAHs, although the role of vegetation fires in this regard is currently unknown in southern Africa.

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

The term 'heavy metals' is typically used to describe elements that exhibit metallic properties, have relatively high density and are toxic at low concentrations, but there is no standardised definition of the term. Some metals with low density are toxic, while some with high density are not. Heavy metals generally include the transition metals, certain metalloids, lanthanides and actinides, but some non-metals and halogens are also toxic. The term 'toxic elements' is therefore often used instead.

Heavy metals are natural constituents of the Earth's crust and some, in small quantities and particular forms, are essential to life. However, human activities have altered their biochemical and geochemical cycles with the result that they have accumulated in the environment and now pose a health risk. Combustion and industrial processes are the main anthropogenic sources of heavy metals, which can be widely dispersed throughout the atmosphere, often being deposited thousands of miles from the site of initial release.

IA																	VIIIA
1																	2
Hudrogon	11.6											111A	IVA	VA	VIA	VIIA	Helium
3	4											5	6	7	8 8	9	10
Li	Be											В	С	N	0	F	Ne
Lithium	Beryllium											Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
11	12											13	14	15	16	17	18
Na	/V\g											AI	SI	P	5	C	Ar
Sodium	Magnesium 20	21	IVB	VB	VIB	VIIB	26	- VIIIB -	28	1 IB	30	Aluminum	Silicon	Phosphorus	Sultur 3.4	Chlorine 35	Argon
K	Ca	Sc	Ti	V	Cr.	Mn	Fe	Co	Ni	Ću	Zn	Ga	Ge	Δs	Se	Br	Kr
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te		Xe
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine	Xenon
55	56 D =:	57–71	72 LJL	73 T	74	75 D -	76	77	78 Di	79	80	81 TI	82 Dl-	83	84 D-	85	86 D
CS	DQ	Landaratidae	Hafnium	I Cl Trantalum	V V Tungston	Ke Phonium	Osmium	[ Iridium	Platinum	AU	Пg	 Thallium	L D	Bicmuth	FO Polonium	Actation	R I I Padon
87	88	89–103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra		Rf	Db	Sa	Bh	Hs	Mt	Ds	Ra	Ср	Uut	FI	Uup	lv	Uus	Uuo
Francium	Radium	Actinides	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meitnerium	Darmstadtium	Roentgenium	Copernicium	Ununtrium	Flerovium	Ununpentium	Livermorium	Ununseptium	Ununoctiur
			57	50	50	(0)	()	(0	(0		15		(7	(0	(0	70	71
	т		5/	58	59 Pr	Nd	Pm	62 Sm	63 Fu	64 Gd	os Th	00 Dv	6/ Ho	68 Fr	oy Tm	70 Vh	
	Lantho	anides	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	LU
			89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Ac	tinides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
			Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrenciur
			Alkali metak	Alkaline earth	Rasic metal	Halogen	Noble ans	Non-metal	Rare earth	Semi-metal	Transition						

# 1.3 PREVIOUS RESEARCH

Figure 1: The Periodic Table of elements.

#### POPs

Two of the authors of this report, Prof. H Bouwman and Dr R Pieters (then Vosloo), participated in a Global Environment Facility (GEF) web-based survey in 2001–2002 to create a database of all information published on persistent toxic substances for Botswana, Lesotho, Namibia, South Africa, Swaziland and Zimbabwe (Bouwman et al., 2002). The survey involved all of the original POPs as well as mercapthion and nonylphenol, and the period investigated was for the preceding 30 years, i.e. from the 1970s. For all the countries, the most information was obtained for the organochlorine pesticides, particularly DDT and its degradation products. The focus on DDT was expected as the pesticide was used for vector control in malaria and tsetse-fly areas. It is still applied in northern KwaZulu-Natal and the Limpopo Province in South Africa for malaria control after it was shown that replacing DDT with pyrethroids (end of 1996 to start of 1999) was not successful (Bouwman, 2003).

The survey revealed that very little was known about PCBs or dioxins and furans. Some work had been done on PCBs in the Isipingo Estuary (Grobler et al., 1996) and Wilderness Lakes (De Kock and Randall, 1984). Only one study could be traced that investigated dioxins and furans in South Africa; this established their presence in human breast milk, and showed that urban women had higher levels than rural women (Schecter et al., 1990).



In another review of available scientific literature on marine pollution in South Africa, 20% of the 284 publications dating between 1960 and 2002 were on halogenated hydrocarbons such as PCBs and DDT (O'Donoghue and Marshall, 2003).

Since the GEF survey and the marine pollution review paper, more studies have been published on levels of POPs in humans in South Africa, particularly DDT (Bouwman et al., 2006), but also selected PCBs, hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), heptachlor, chlordanes, nanochlors and mirex in the blood plasma of delivering women (Röllin et al., 2009) and levels in matrices to which humans are exposed (van Dyk et al., 2010).

A previous study involving one of the authors of this report revealed that bird eggs from the Vaal River have detectable levels of DDT and its degradation products, as well as some other organochlorines, PCBs and polybrominated diphenyl ethers (PBDEs), used as flame retardants (Bouwman et al., 2008; Polder et al., 2008). The study focused on the stretch of the Vaal River flowing through the Vaal Triangle in order to target industrial and urban areas suspected as being hotspots for sources of POPs, but no part of the Vaal River catchment in an area where DDT is sprayed for malaria control. Levels of DDT and its metabolites were also reported for water, sediment, fish, chickens and wild birds in an area still sprayed for malaria in Limpopo Province (Barnhoorn et al., 2009).

Environmental levels (soils and sediment) of POPs reported in recent years include levels of dioxins/furans and dioxin-like PCBs for 22 aquatic sites in South Africa (Vosloo and Bouwman, 2005). This survey incorporated a few sites from the Orange and Vaal rivers, as well as some of the smaller tributaries of the catchment. The highest levels were measured for a site in the industrial Vaal Triangle area (Pieters et al., 2008). Levels of PAHs, PCBs, dioxin-like chemicals and organochlorine pesticides were reported for the central part of South Africa, including the Vaal Triangle (Quinn et al., 2009), and dioxin-like chemicals in the soil and sediment from residential and industrial areas in this region were compared (Nieuwoudt et al., 2009).

In addition, ambient air in Durban was analysed for organochloride pesticides (OCPs) and measurable levels of DDT, lindane, aldrin, chlordane, HCB and dieldrin were found (Batterman et al., 2008). Air, soil and milk from urban and industrial areas of KwaZulu-Natal were also sampled for PCB levels (Batterman et al., 2009). Air samples from passive samplers from two rural areas and one urban area in South Africa (Klánová et al., 2009) were analysed as part of the continent-wide monitoring in 2008 for the Global Atmospheric Passive Sampling study (Pozo et al., 2009). Levels for PAHs, PCBs, HCH, endosulfans, dioxins/furans, and DDT and its metabolites were reported. The three South African sites, all of which were within the Orange–Senqu River basin, had low levels compared to the other African sites.

Other urban areas such as Durban, Cape Town, Bloemfontein, Richard's Bay and Soweto are included in a current Water Research Commission project report in which the authors are involved. Organochlorine pesticides (OCPs) and PCBs were present in intermediate concentrations, while PBDEs were the least abundant and present in the lowest concentrations. Aldrin and chlordane were not detected anywhere, while nonachlor, chlordane and oxychlordane were only detected at a few sites. HCB, HCH and DDT were the predominant OCPs, while heptachlor and mirex were present in lower concentrations. This was ascribed to the fact that HCB is still produced for industrial applications, and HCH and DDT are still used in some parts of the country, while heptachlor and mirex have been banned (Roos et al., 2012).

#### PAHs

Polycyclic aromatic hydrocarbons have been recorded in sediment from the Vaal River catchment of the Vaal Triangle (Nieuwoudt et al., 2011), with total concentration of PAHs ( $\Sigma$ t-PAH) ranging between 44 and 39,000 ng/g dw and the concentration of carcinogenic PAHs ( $\Sigma$ c-PAH) ranging between 19 and 19,000 ng/g dw. Pyrogenic (burning) processes were the most likely sources, with minimal petrogenic (derived from fuels and oils) contributions. PAH levels were in the same range as levels reported from other countries. For freshwater sediments, Roos et al. (2012) found that PAHs were the most abundant of all the groups of organic compounds investigated, also occurring at the highest levels of all the compounds analysed. In general, 4-ringed PAHs were the most abundant, followed by 5-ringed congeners, followed by 3- or 6-ringed congeners. Two-ringed PAHs were the least abundant. One of the sites with the highest PAH levels was in Soweto/Lenasia with  $\Sigma$ PAHs of 5,528,000 ng/kg (Roos et al., 2012).

#### **Heavy metals**

Whereas very little is known regarding levels of POPs and PAHs and their distributions for the four countries, much more is known about heavy metals. The literature search conducted for this study therefore focused on publications containing information on heavy metals in the biota, air and sediment of the Orange–Senqu River basin. No publications could be traced for Botswana, Lesotho and Namibia that directly link heavy metal contributions to the Orange–Senqu River basin, so this overview contains references to South African sites only.

Gold is one of the main mineral commodities mined in South Africa, and the Witwatersrand's very deep gold mines are known to be contaminating groundwater that drains into the Vaal River (Duane et al., 1997). Water collected from four of the mines contained lead, copper, zinc, chromium, iron, cadmium, uranium, arsenic and manganese, as well as other trace elements. It is not only the water from the active mines that pollutes groundwater, but also water from the mine tailings dumps and abandoned shafts. A study on the Natal Spruit, which is in the catchment of the Vaal River, showed that shallow groundwater is contaminated as a result of mining activities, impacting the quality of water from the Witwatersrand watershed (Naicker et al., 2003). This pollution is not only affecting the pH of the water, but contributing heavy metals to surface water.

The Witwatersrand Basin is also a source of low-grade uranium, mainly produced as a by-product of gold mining. About 6,000 tonnes of uranium are annually disposed onto slimes dams by gold mining activities (Winde and De Villiers, 2002). The average concentration of uranium in these slimes dams is 100 ppm. In a case study on the (now closed) Stilfontein gold mine in North West Province, it was found that dissolved uranium and other heavy metals moved along with seepage from the mine's tailings deposits into groundwater, which then seeped into the Koekemoer Spruit, a tributary of the Vaal River. This study showed that the increased uranium concentration in tailings, as a result of the abandonment of uranium production by many mines, has significantly elevated the potential of slimes dams for uranium pollution of adjacent streams (Winde and van der Walt, 2004).

Trace metals were analysed in water and sediment samples from the Blesbok Spruit, a Ramsar-listed riparian wetland (Roychoudhury and Starke, 2006), to assess the impact of mining on sediment quality and the fate of trace metals in the environment. The



Blesbok Spruit joins the Suikerbosrand River, which confluences with the Vaal River at the city of Vereeniging. Compared to their regional background, gold and silver in the sediment were particularly enriched, often by a factor of 20–400. Significant enrichment of uranium, mercury, vanadium, chromium, cobalt, copper and zinc was also observed in the sediments. Although the geoaccumulation indices suggested very light to light pollution with respect to most of the trace metals, the river was highly polluted with gold and silver. The highest metal pollution index (MPI) values were found at sites that were close to tailings dams.

Heavy metals have also been measured in biota, and their bioaccumulation calculated. For example, studies carried out on the Vaal River have shown that fish accumulate heavy metals released by industries and other sources (Crafford, 2000; Groenewald, 2000; Kotze, 2003; Retief et al., 2006). Internal parasites (tapeworm) of yellowfish from the Vaal Dam have also been found to bioconcentrate many of the heavy metals (Retief et al., 2006).

It is also possible that heavy metals suspended as air particles might contribute to the loads in the aquatic systems. Lead monitored in the atmosphere of Johannesburg mainly came from vehicle exhaust fumes, as leaded antiknock additives were still in use in South Africa at the time of the study (Monna et al., 2006). The contribution of dust emissions from mine tailings dumps seemed to be geographically limited, while domestic coal burning only contributed a small portion of the total lead in the atmosphere. In another study that analysed coals from the Highveld coal field for 14 trace elements (Wagner and Hlatshwayo, 2005), the concentrations of chromium and manganese were found to be higher than the global averages, cadmium and copper were lower, and arsenic, molybdenum, lead, selenium, antimony and zinc were low to very low. Since South Africa's main electricity source is coal-fired power plants, high levels of these heavy metals are likely emitted to the atmosphere.

Indeed, South Africa was listed as the country with the second highest mercury emissions in the world (Pacyna et al., 2006), based on estimates of total mercury emissions derived from gold mining and coal combustion. However, a national survey of mercury levels in South African water resources involving collection and analyses of surface water, sediment and biota samples from 65 sites between 2007 and 2009 revealed that guideline levels for mercury were exceeded at only a few sites. These were in the Olifants, Upper Vaal and Inkomati water management areas (Walters et al., 2011).

# 2. MATERIALS AND METHODS

# 2.1 SITE SELECTION

### **Sediment samples**

ediments were sampled from 61 sites in the Orange–Senqu River catchment in September 2010. Of these sites, 33 were in the Vaal River catchment and the remaining 28 were in the Orange River or its other tributaries, with one site in Namibia and five in Lesotho (Figure 2 and Table 1). The relationships between tributaries are indicated in the schematic diagrams (Figures 3 and 4).



Figure 2: Sediment sampling sites.

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

Cito		Coord	inates		
number	River	Longitude	Latitude	— Country	River system
1	Mooi River (Potchefstroom)	27.10	-26.68	SA	Vaal
2	Orange River (Upington)	21.24	-28.47	SA	Orange—Senqu
3	Hartbees River	20.64	-28.86	SA	Orange—Senqu
4	Orange River	20.15	-28.50	SA	Orange—Senqu
5	Orange River (Onseepkans)	19.30	-28.74	SA	Orange—Senqu
6	Orange River (Vioolsdrif)	17.61	-28.75	SA	Orange—Senqu
7	Orange River (Mouth)	16.47	-28.60	SA	Orange—Senqu
8	Orange River (Sendelingsdrif)	16.89	-28.12	SA	Orange—Senqu
9	Orange River (Prieska)	22.75	-29.66	SA	Orange—Senqu
10	Brak River	23.02	-29.62	SA	Orange–Senqu
11	Orange River (Douglas)	23.70	-29.16	SA	Orange–Senqu
12	Vaal River (Douglas)	23.84	-29.04	SA	Vaal
13	Orange River (Hopetown)	24.11	-29.60	SA	Orange—Senqu
14	Riet River	24.50	-29.04	SA	Vaal
15	Vaal River	24.07	-28.72	SA	Vaal
16	Harts River	24.30	-28.38	SA	Vaal
17	Vaal River (Warrenton)	24.87	-28.09	SA	Vaal
18	Vet River	26.13	-27.94	SA	Vaal
19	Vaal River	26.22	-27.52	SA	Vaal
20	Vals River	26.81	-27.49	SA	Vaal
21	Renoster River	27.00	-27.04	SA	Vaal
22	Skoon Spruit (Klerksdorp)	26.66	-26.93	SA	Vaal
23	Vaal River (Orkney)	26.68	-27.01	SA	Vaal
24	Vaal Kiver (Parys)	27.40	-26.91	SA	Vaal
<u></u> 24	NIID KIVEL (WEST)	20.00 28.38	-20.00	SA CA	Vaal
20	Rlashak Saruit	20.30	-20.05	SA SA	Vaal
27	Waterval River	20.43	-26.63	SA SA	Vaal
20	Vaal River origin	30.03	-26.31	SA	Vaal
30	Klip River (East)	29.60	-27.47	SA	Vaal
31	Liebenbergsvallei River	28.48	-27.53	SA	Vaal
32	Wilge River	28.75	-27.65	SA	Vaal
33	Wilge River	28.53	-27.31	SA	Vaal
34	Vaal River (Villiers)	28.60	-27.02	SA	Vaal
35	Vaal River	29.10	-27.04	SA	Vaal
36	Waterval River	28.91	-26.85	SA	Vaal
3/	Suikerbosrand River	28.05	-26.68	SA	Vaal
39	Modder Kiver	20.11	-20.01	SA	Vaal
40 /1	Koranna Spruit	25.11	-20.75	SA SA	Vaal
47	Modder River	20.04	-2910	SA SA	Vaal
43	Riet River	20.32	-29.47	SA SA	Vaal
44	Kromellenboog Spruit	25.59	-29.68	SA	Vaal
45	Riet River	25.65	-29.56	SA	Vaal
46	Seekoei River	24.96	-30.53	SA	Orange—Senqu
47	Orange River	25.24	-30.51	SA	Orange—Senqu
48	Caledon River	26.31	-30.43	SA	Orange—Senqu
49	Orange River	26.46	-30.57	SA	Orange-Senqu
50	Stormberg Spruit	26.47	-30.65	SA	Orange-Senqu
51	Urange Kiver	26.71	-30.68	SA	Urange-Senqu
52	Urange Kiver	27.34	-30.40	SA SA	Urange-Senqu
50 51	LEEU KIVEI Caladan Rivar	27.14 27.20	-27.33 _70 /0	AC A	
55 55	Caledon River	27.32	-27.47	SA SA	
56	Molono Eve	20.15	-25.89	SA SA	Orango-Sonau
57	Malihamatso River	23.07	-29.07	lesotho	
58	Matsuko River	28.56	-29.23	Lesotho	Oranae-Senau
59	Senguenyane River	28.15	-29.55	Lesotho	Oranae—Senau
60	Kelekequ River	27.45	-29.34	Lesotho	Orange—Senau
61	Senqu River	28.51	-30.06	Lesotho	Orange—Senqu
62	Fish River	17.79	-26.80	Namibia	Orange—Senqu



Figure 3: A diagrammatic representation of the Vaal River catchment (also see Figure 2).



Figure 4: A diagrammatic representation of the Orange-Senqu River catchment excluding the Vaal River catchment (also see Figure 2).



#### Fish and bird egg collection

Fish and eggs from wild birds were collected to investigate the levels of POPs, PAHs and elements in the biota of the Orange–Senqu River basin (Figure 5 and Table 2). The sampling was done with the appropriate ethical clearance by the North-West University and permits from the provinces.

Fish sampling was conducted at three sites (V1, V2 and V3) in the Vaal River, the main tributary of the Orange–Senqu River. V1 was at Standerton in Mpumalanga and thus upstream of Gauteng's urban and industrial hub, which potentially contributes to most of the pollution in the basin. V2 was downstream of Gauteng, at the Free State town of Parys, allowing the influence of pollution from Gauteng on contaminant levels in fish to be assessed. V3 was at Rooipoort in the Northern Cape, in an undeveloped area close to the confluence with the Orange River. Two sites were selected in the Orange River, one close to the Lesotho border at Aliwal North (O1), and another at Boegoeberg, downstream of the Orange River's confluence with the Vaal River (O2). Unfortunately, insufficient fish for laboratory analyses could be collected at O1.

Eggs of wild aquatic birds were collected at four sites in the Vaal River catchment, at Potchefstroom, Barbers Pan, Bloemhof Dam and Eldorado Park. Breeding colonies were located during a low-flying aerial survey and by visiting known sites.

Figure 5: Sampling sites for fish and wild bird eggs.



Bird eggs are regarded as good indicators of organic pollutants in the environment because they provide a reflection of such compounds in the female bird (Braune, 2007; van den Steen et al., 2006). They are ideal monitoring tools (Medvedev and Markove, 1995; Lebedev et al., 1998) because they:

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

		Coordi	inates		
Sample type	Site name/label	Longitude	Latitude	Location name	River
Wild bird eggs	Potchefstroom	27.09	-26.78		Mooi River
	Barbers Pan	25.57	-26.60		Harts River
	Bloemhof Dam	25.64	-27.70		Vaal River
	Eldorado Park	27.88	-26.30		Klip River (West)
Fish	٧1	29.51	-26.86	Standerton	Vaal River
	V2	27.40	-26.92	Parys	Vaal River
	V3	24.16	-28.56	Rooipoort	Vaal River
	01	26.71	-30.68	Aliwal North	Orange River
	02	22.21	-29.21	Boegoeberg	Orange River

Table 2: Sampling sites for fish and wild bird eggs.

## 2.2 SAMPLING AND SAMPLE PREPARATION

#### 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, which removed polar organic contaminants and non-polar organic contaminants respectively.

Sediment samples were prepared at each site by collecting the top 5 cm of five collection points within a 10 m radius and stirring the pooled mixture thoroughly. Sub-samples were stored in high-density polyethylene bottles at -20°C and protected from UV degradation. While sampling, the pH level of the sediment was determined. Unfortunately, the pH meter malfunctioned halfway through the sampling campaign, so the pH of the remaining samples was determined after thawing of sediment in the laboratory at North-West University.

The sediment samples were air-dried, ground and sieved (mesh size 0.5 mm), before being sent to an accredited laboratory in Germany (Oekometric GmbH in Beyreuth) for analyses. Analyses were done for the 21 POPs then listed under the Stockholm Convention, as well as the 16 PAHs identified as priority pollutants by the USEPA.

Duplicate sediment samples were analysed for 42 elements (Figure 6), using inductively coupled plasma mass spectrometry (ICP-MS) at North-West University. The samples were completely digested with concentrated HNO<sub>3</sub> at  $50-60^{\circ}$ C and allowed to evaporate to 5 m $\ell$ . The samples were further treated with H<sub>2</sub>O<sub>2</sub> and

Н																	He
Li	Be											В	С	Ν	0	F	Ne
Na	Mg											Al	Si	Р	S	Cl	Ar
К	Са	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	$\mathbb{W}$	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
Fr	Ra	1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Ср	Uut	Fl	Uup	Lv	Uus	Uuo
			La	Ce	Pr	Nd	Pm	Sm	Ευ	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

allowed to cool before the addition of 3 mol/ $\ell$  HCl. The samples were gently heated for another hour, and then diluted and injected into the ICP-MS. Complete digestion was chosen as an exhaustive search of the literature revealed very little knowledge of elemental bioavailable levels in the Orange–Senqu River basin. Since sediments are derived from the rock and soils from particular drainage areas, the natural elemental composition of sediments at each site is unknown, making it impossible to attribute high levels of certain elements to pollution or disturbance. The elemental levels at each site were therefore assessed in terms of the geology of the area.

#### **Fish sampling**

After obtaining the necessary provincial permits, sharptooth catfish (*Clarias gariepinus*) were sampled at each of the sites. Fillet was collected for chemical analysis because this is the tissue likely to be consumed by humans. Sharptooth catfish are omnivores, preying and scavenging on any available organic food source including fish, birds, frogs, small mammals, reptiles, molluscs, crustaceans, seeds, fruit and even plankton. They feed close to the bottom and sometimes hunt in packs, herding and trapping small fish in shallower water (Skelton, 2001). They are ideal for determining the levels of pollutants in fish because the higher an animal is in the food chain, the more likely it is to bioaccumulate pollutants. Being hardy fish that survive conditions inhospitable to many other species, sharptooth catfish live long enough to reveal any bioaccumulation. They also have a large distribution and occur throughout the basin, which allows a comparison between sites using the same species. In addition, the species is often consumed by subsistence fisherman.

Fish were caught using fyke nets and electrofishing, and temporarily held in a keep net until at least ten per site were caught. The fish were measured (Table 3) before being killed and the fillet sampled. Protocols to prevent cross-contamination during Figure 6: Samples were analysed for the elements highlighted in green.

the dissection process were followed. Fillets for POPs analysis were wrapped in precleaned (rinsed with acetone and hexane) aluminium foil, and were transported and stored frozen until analysed. Fillets destined for elemental analysis were stored in plastic bags, and transported and stored frozen until analysed.

The fish were pooled in the laboratory at North-West University, but with males and females separated for each site (Table 3). Approximately the same mass of flesh was cut from each fillet. Samples for POPs analysis were kept frozen and sent to the German laboratory. Samples for elemental analysis were freeze-dried before undergoing the same acid- and heat-digestive treatments described for the sediment samples.

		Body mass		Total length	Standard		
Pool number	Site label	(g)	Gender	(mm)	length* (mm)	Girth (mm)	
		1,920		670	610	290	
		1,540		610	550	260	
Pool 1		3,020	Male	790	720	330	
		3,280		795	710	335	
	00	2,880		560	500	260	
	02	2,240		700	640	300	
		1,300		570	530	255	
Pool 2		2,340	Female	730	680	300	
		2,740		710	640	320	
		2,240		740	670	295	
		3,160		780	690	340	
		2,950		760	730	300	
Pool 3		5,900	Male	1,030	930	490	
		4,900		1,040	930	375	
	V1	4,260		810	740	360	
		3,280		760	690	360	
D 14		6,400	E 1	990	890	300	
Pool 4		3,800	Female	860	790	345	
		2,700		760	680	310	
		4,200		800	730	345	
D 15		4,340		790	700	350	
Pool 5		4,140	Male	850	770	350	
		4,700		790	760	340	
	10	3,520		720	660	320	
	VZ	3,960		760	690	340	
		4,140	<b>F</b> 1	770	700	340	
Pool 6		4,150	Female	770	750	330	
		3,560		750	660	320	
		4,560		830	760	340	
		3,660		820	740	370	
		9,060		1,070	980	505	
Pool 7		12,380	Male	1,200	1,060	555	
	110	11,000		1,200	1,070	560	
	V3	2,960		745	660	335	
		7,560		980	890	500	
Pool 8		2,940	Female	750	670	335	
		3,860		840	760	370	

Table 3: Dimensions and gender of the sharptooth catfish individuals that constituted the pools.

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

#### **Bird egg sampling**

Eggs were collected at four breeding colonies of wild birds. Attempts were made to locate more colonies, without success, and two known breeding colonies at Upington were washed away by floods during the study. Eggs were sampled from nests by either climbing trees using rock-climbing gear, or using ladders on smaller trees. Eggs were carefully stored and transported to the laboratory, where they were photographed before being frozen. On the day of sample preparation, eggs were measured and thawed. Eggs from the same species at 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 homogenisation. A subsample was taken for elemental analysis. Samples of the 16 pools were sent to various laboratories with all the necessary permits.



Location	ocation Pools Common name	Common name	Scientific name
Barbers Pan	1	Grey heron	Ardea cinerea
	5	African darter	Anhinga rufa
	14	Black-headed heron	Ardea melanocephala
Bloemhof Dam	2	Great white egret	Ardea alba
	3	Grey heron	Ardea cinerea
	6	African darter	Anhinga rufa
	8	Reed cormorant	Microcarbo africanus
	10	Sacred ibis	Threskiornis aethiopicus
	11	Little egret	Egretta garzetta
	16	Cattle egret	Bubulcus ibis
Eldorado Park	4	Sacred ibis	Threskiornis aethiopicus
Potchefstroom	7	Reed cormorant	Microcarbo africanus
	9	Glossy ibis	Plegadis falcinellus
	12	Black-headed heron	Ardea melanocephala
	13	Black-headed heron	Ardea melanocephala
	15	Cattle egret	Bubulcus ibis
	••••••		•

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

# 3. RESULTS

The results of the analyses are discussed below. Raw data are available in the addendum.

# 3.1 ORGANIC POLLUTANTS

#### Sediment

In general, the levels of POPs detected in sediments were low. Detectable levels of dioxin-like toxin-equivalent (TEQ) – the toxic equivalent for a mixture of dioxins, furans or dioxin-like PCBs relative to 2,3,7,8 tetrachlorodibenzo-p-dioxin – occurred at sites in Gauteng, Klerksdorp, Orkney, Modder River and Kelekequ River (Figure 7a). At the first three of these, elevated levels can be associated with pollutants from industry, urban activities and mining. Pollution sources for the last two (sites 39 and 60) are unknown, but may be associated with smaller industry and urban activities. Dioxin-like TEQ seems to be confined to certain hotspots and either is not transferred downstream, or is diluted or broken down very quickly, but the hotspots are nevertheless a concern, particularly those in Soweto and Klerksdorp (sites 25 and 22 respectively).

The distribution of PCBs (Figure 7b) largely reflects the TEQ distribution, and it is presumed that the same pollution sources are involved. However, site 56, at the Molopo Eye, had relatively high PCBs compared to dioxin-like TEQs, and this difference cannot yet be explained.

Blesbok Spruit (site 27), Suikerbosrand (37), Potchefstroom (1) and Klerksdorp (22) had the highest levels of OCPs, mainly in the form of legacy DDT. This pollution seems to be isolated in distribution, as neighbouring sites downstream generally had low or undetectable levels of OCPs (Figure 7c).

No PFOS was detected in sediment, so a map is not shown.

The highest  $\Sigma$ PAH concentration (867 µg/kg dw) was measured in the Skoon Spruit (site 22), which is downstream of Klerksdorp, followed by sites in the Kelekequ (60) and Caledon rivers (54), both downstream of a large city in Lesotho (Figure 7d). The most common PAH was fluoranthene, followed by phenanthrene and benzo(b+k) fluoranthene (Table 5). The highest concentrations of the carcinogenic benzo(a)pyrene were found in the Harts River, Vaal River at Warrenton, Skoon Spruit near Klerksdorp, Caledon River and Kelekequ River (sites 16, 17, 22, 54 and 60 respectively). The







Figure 7: Distribution of pollutants in sediment from the sampling sites. Sites indicated with small dots have pollutant levels at or below detection limit. Bar scale is relative. Numbers on the maps refer to the sites where the highest

levels were measured. Max = maximum concentration at any of the sites.

sources of PAHs at all these sites were pyrogenic in nature, but only at site 60 was the pyrogenic origin predominantly coal- or smelter-related (Table 6).

Name	Mean	Standard deviation	Minimum	Maximum	Median
Naphthalene	20.8	36.8	0.6	244.2	10.2
Acenaphthylene	3.2	4.8	0.5	23.6	1.4
Acenaphthene	7.7	7.3	1.1	39.1	5.2
Fluorene	4.9	12.0	0.6	88.7	1.8
Phenanthrene	25.6	57.9	0.7	362.2	8.4
Anthracene	6.9	20.4	0.5	130.8	1.4
Fluoranthene	51.6	156.0	0.8	1,001.2	7.6
Pyrene	41.0	125.0	0.6	798.6	6.0
Benz(a)anthracene	24.3	71.7	0.5	394.3	3.1
Chrysene	25.2	75.9	0.6	454.4	4.6
Benzo(b+k)fluoranthene	46.6	132.3	0.7	669.4	7.6
Benz(a)pyrene	23.6	60.9	0.6	329.0	4.0
Indeno(1,2,3-cd)pyrene	23.7	64.9	0.8	304.0	3.7
Benzo(ghi)perylene	27.9	78.8	0.5	406.8	3.8
Dibenz(ah+ac)anthracene	6.9	15.3	0.5	59.9	1.9

Table 5: The mean concentrations and other summary statistics for PAHs in the sediment at all sites. Units are mg/kg dw.

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

• if fluoranthene/pyrene (pyr) > 1 and phenanthrene/anthracene < 30 = pyrogenic origin;

• if fluoranthene/pyrene (pyr) < 1 and phenanthrene/anthracene > 1 = petrogenic origin;

• if indeno(1,2,3-cd)pyrene)/benzo(ghi)perylene > 1 = coal/coke sources or smelters.

The main origin of PAHs was pyrogenic for two-thirds of the sediment sites, as shown by those sites with shaded cells in both the first and second columns of Table 6. The specific pyrogenic origin was likely to be coal/coke sources or smelters for those sites with shaded cells in the third column.





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

61		1	'I										
+		÷		11	n	r	n	n	t	h	۵	n	۵
	U	I	I	υ	υ	L.		ш			G		G

- pyr pyrene
- phe phenanthrene
- ant anthracene
- ind indeno(1,2,3-cd)pyrene
- ben benzo(ghi)perylene

Site number	flu/pyr > 1	phe/ant < 30	ind/ben > 1
1	1.3	5.8	1.0
2	1.5	10.5	1.0
3	1.9	14.0	1.0
4	1.0	11.3	1.0
5	1.3	8.3	1.2
6	1.0	16.3	1.0
7	1.0	9.3	1.0
8	1.0	14.7	1.0
9	1.0	./	1.0
10	1.0	7.9	1.3
10	<u> </u>	9.5	1.0
12	1.3	10.7	,  1 0
13	1.0	10.9	I.Z 11
14		14.1 8 0	1.1
17	1.0	2 4	1.0
17	1.0	5.0	1.0 0.9
17	1.1 2 2	37.0	1.0
19	13	71	1.0
20	1.0	12.3	1.0
21	1.0	90	1.0
22	1.3	6.4	0.8
23	1.3	7.2	1.5
24	1.3	5.8	1.2
25	0.9	4.3	1.0
26	1.9	10.3	1.8
27	1.3	6.3	0.9
28	1.3	3.2	0.8
29	1.3	8.2	0.8
30	1.0	17.0	1.0
31	1.8	11.3	1.7
32	1.0	8.3	1.0
33	1.6	8.8	0.9
34	1.2	10.7	1.0
35	1.6	11.6	.
36	1.5	6.4	<u>U./</u>
3/	1.0	5.5	1.0
39	I.Z	5.5	0.8
40	1.4	7.0	1.0
41	1.0	0.0	1.0
42	1.0	8.8	1.0
- <del>1</del> 3 ΔΔ	1.2	6.3	1.0
45	1.0	10.0	1.0
46	1.0	4.3	1.0
47	1.5	7.2	1.4
48	1.0	7.0	1.0
49	1.8	5.3	1.1
50	1.0	7.3	1.0
51	1.0	1.0	1.0
52	1.0	1.0	1.0
53	1.0	1.0	1.0
54	1.2	3.4	0.8
55	1.6	8.7	0.9
56	0.8	5.6	1.3
57	1.3	6.3	2.2
58	2.1	7.2	2.0
59	.  1.5	6.3	U./
60	1.5	8.2	0.9
61	1.6	/.4	1.4
02	1.0	Ζ.ΰ	1.0

### Fish

Dioxin-like TEQ was detected in sharptooth catfish (*Clarias gariepinus*) from only one of the four collection sites, namely Rooipoort (Figure 8a). The reason for the higher levels at this site is not known. Potential upstream sources include mining, urban and industrial activities, and sewage associated with Kimberley and smaller centres, but since Figure 7a indicates no apparent downstream movement of dioxin-like TEQ in sediment, the relatively higher level in fish indicates a local source. This highlights the need to sample fish closer to Soweto and Lenasia and downstream of Orkney, where there are dioxin-like TEQ hotspots in sediments.

The distribution of PCBs in fish (Figure 8b) reflects the dioxin-like TEQ distribution, as it did in sediments, but there is little agreement between the distribution pattern in sediment and fish.

Parys and Rooipoort had the highest levels of OCPs (Figure 8c), mainly DDT and degradation products, as for sediments. The origin of these degradation products is



Figure 8: Distribution of pollutants in fish from the sampling sites. Sites indicated with small dots have pollutant levels at or below detection limit. Bar scale is relative. Max = maximum concentration at any of the sites.



not known and needs further investigation. Since there is intensive recreational and subsistence fishing along these rivers, the health risks should be assessed.

The distribution of PFOS, detected only at Rooipoort and Boegoeberg (Figure 8d), cannot be explained, given that PFOS is an industrial and consumer chemical that would have been expected at higher concentrations near centres of industry. However, PFOS is very persistent, so the distribution pattern might be due to residues of past use having found their way downstream. Alternatively, it may reflect local use of unknown source, but further investigation is required.

#### **Bird eggs**

The survey results indicated widespread distribution of dioxin-like TEQ (Figure 9a) in eggs from wild birds. The levels were an order of magnitude higher than the single positive value recorded in fish (Figure 8a). Higher levels were expected in eggs from birds from Eldorado Park, but levels here were lowest. However, the data needs further interpretation as the bars represent maxima from each site, and not all species were represented at each site.

Levels of PCBs seemed to increase along the Vaal River from Eldorado Park towards Bloemhof Dam (Figure 9b), which may represent a retaining effect of PCBs in biota. Confirmation is needed, as well as a more in-depth species assessment.

It was expected that bird eggs would have higher levels of OCPs than sediment, but it was not anticipated that the highest level would be from Bloemhof Dam (Figure 9c). As with PCBs, it seems that Bloemhof Dam might retain OCPs, but a more precise species assessment needs to be done.

The levels of PFOS in bird eggs were found to be relatively high (Figure 9d). The distribution pattern was unexpected, with much higher levels at Bloemhof Dam than at Eldorado Park. It was unfortunate that eggs could not be collected at Upington further downstream, as PFOS levels there could have indicated if aquatic transport of this pollutant via water and biota is involved, before it accumulates in higher trophic levels. The PFOS levels at Bloemhof Dam are among the highest measured anywhere in the world, and need much closer scrutiny as to source and impact.



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



# 3.2 HEAVY METALS AND TRACE ELEMENTS

#### Sediment

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





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

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

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

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

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

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

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

	Mean	Standard deviation	Minimum	Maximum	Median
Li	5.7	4.6	1.1	25	3.8
Be	0.9	0.6	0.2	3	0.6
Na	1,203.3	858	250	4,750	925
Mg	12,199.6	10,194.9	1,125	50,000	9,000
Al	22,315.6	15,284.6	3,500	72,500	20,750
K	2,093.3	1,577.3	240	7,000	1,500
Са	17,357.8	21,941.6	1,650	110,000	11,000
Ga	11.9	37.7	0.8	300	7.3
Ge	2.2	1.3	0.5	6	2.1
Rb	9.4	6.5	1.7	27.5	6.8
Sr	35.1	30	5.5	155	27.5
Cs	0.9	0.7	0.2	3.5	0.6
Ba	277.2	1,073	23.5	8,500	145
TI	0.3	0.4	0.1	3.3	0.2
Pb	12.1	10.9	3.5	80	10
Sc	6.8	4.6	1.1	21.3	6.3
Ti	713.4	806.1	50	4,250	425
٧	69	44.3	15.8	207.5	60
Cr	73.4	60.9	10.5	450	70
Mn	1,725.2	7,603.7	105	60,000	750
Fe	25,975.4	14,959.1	5,000	72,500	25,000
Со	23.7	16.9	3.5	117.5	21.5
Ni	85	52.4	14	250	75
Си	47.3	28.1	8.8	137.5	42.5
Zn	74.3	55.6	22	300	57.5
Мо	0.5	0.5	0.1	4	0.3
Rh	0.4	0.3	0.1	2.2	0.4
Pd	0.4	0.3	0.1	1.8	0.4
Ag	5.6	4.3	1	23	4.3
Cd	0.1	0.1	0.04	0.9	0.1
Sn	0.9	0.5	0.2	2.8	0.8
Pt	0.04	0.1	0.003	0.2	0.01
Au	0.2	0.3	0	2.3	0.1
Hg	0.5	0.5	0.1	3.5	0.3
В	12.6	9	4.5	67.5	10
Si	31	5.4	14.3	37.5	32.5
As	6.1	3.7	2.5	19.3	5.3
Se	10.3	3.9	0.7	13.8	11.8
Br	3.9	3.2	1.1	16.3	3
	2.3	4.2	0.1	25	1.1
Ce	18.6	21.1	4.8	170	15
U	1.9	6.3	0.3	50	11

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



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

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

$I_{\text{geo}} < 1$ :	unpolluted
$1 < I_{geo} < 2$ :	very lightly polluted
$2 < I_{geo} < 3$ :	lightly polluted
$3 < I_{geo} < 4$ :	moderately polluted
$4 < I_{geo} < 5$ :	highly polluted
I <sub>geo</sub> > 5:	very highly polluted

The  $I_{geo}$  classification of the elements at each of the sites is summarised in Tables 8 and 9. As for the MPI, the highest  $I_{geo}$  value was calculated for site 56 at the Molopo Eye, the origin of the Molopo River. This finding is difficult to explain because this is a rural area with only agricultural activities in the immediate vicinity. The geology of the site comprises the dolomite rock formations belonging to the Malmani Subgroup of the Transvaal Supergroup. It is possible that underground water from mines in the area found its way to underground caverns close to the site, or simply that the groundwater has naturally high elemental levels.
	Site	Li	Be	Na	Mg	Al	K	Ca	Ga	Ge	V	(r	Mn	Fe	Co	Ni	Cu	Zn	Мо	Ag	Cd	Sn	Hg	Se	Br	I	Sr	Cs	Ba	Tl	Pb	Ce	U
1	Mooi River																																
12	Vaal River																																
14	Riet River																																
15	Vaal River																																
16	Harts River																																
17	Vaal River																																
18	Vet River																																
19	Vaal River																																
20	Vals River																																
21	Renoster River																																
22	Skoon Spruit																																
23	Vaal River																																
24	Vaal River																																
25	Klip River West																																
26	Suikerbosrand River																																
27	Blesbok Spruit																																
28	Waterval River																																
29	Vaal River origin																																
30	Klip River (East)																																
31	Liebenbergsvallei River																																
32	Wilge River																																
33	Wilge River																																
34	Vaal River																																
35	Vaal River																																
36	Waterval River																																
37	Suikerbosrand River																																
39	Modder River																																
40	Kaal River																																
41	Koranna Spruit																																
42	Modder River																																
43	Riet River																																
44	Kromellenboog Spruit																																
45	Riet River																																

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



	Site	Li	Be	Na	Mg	Al	K	Ca	Ga	Ge	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Мо	Ag	Cd	Sn	Hg	Se	Br	Т	Sr	Cs	Ba	Tl	Pb	Ce	U
2	Orange River																																
3	Hartbees River																																
4	Orange River																																
5	Orange River																																
6	Orange River																																
7	Orange River																																
8	Orange River																																
9	Orange River																																
10	Brak River																																
11	Orange River																																
13	Orange River																																
46	Seekoei River																																
47	Orange River																																
48	Caledon River																																
49	Orange River																																
50	Stormberg Spruit																																
51	Orange River																																
52	Orange River																																
53	Leeu River																																
54	Caledon River																																
55	Caledon River																																
56	Molopo Eye																																
57	Malibamatso River																																
58	Matsuko River																																
59	Senquenyane River																																
60	Kelekeque River																																
61	Senqu River																																
62	Fish River	1																															

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

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

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

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

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

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

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

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

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

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



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



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



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

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

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

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

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

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

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

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

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

Uranium (U) was the only actinide analysed and was either undetectable or found in low concentrations except for site 15 in the lower catchment of the Vaal River, where the level was 50 mg/kg (Figure 151). This site is at a small town called Schmidtsdrift where alluvial diamond mining takes place (CMR, 2008), and the river here also receives drainage from lime-mining activities to the north. Furthermore, in 1974 the South African Defence Force (SADF) acquired the Schmidtsdrift farms and established a military training base, which was occupied by the SADF for the next 20 years (Kleinbooi, 2007). The high levels of U at this site might therefore be associated with military activities.



Figure 14: A geological map of southern Africa.



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





Figure 16: Levels of elements in fish from the sampling sites. Bar scale is relative for each element, but not between elements. Range = range of all samples.

### Fish

The investigation of elements in fish focused on those with known toxic effects and for which guideline levels in fish fillet (i.e. considered safe for human consumption) were found. Values for the heavy metals chromium (Cr), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd) and lead (Pb) were sourced from Wagner and Boman (2003), who cited a 'range of international standards' compiled by the Food and Agricultural Organisation (FAO) from different countries for contaminants in fresh fish. Wagner and Boman (2003) also noted that values expressed as dry weight (dw) could be converted into wet weight (ww) by dividing them by factors ranging from four to six. This conversion factor is supported by the US-based Consortium for Risk Evaluation with Stakeholder Participation, which recommends multiplying wet weight values of contaminants in fish by five to give an approximate conversion to dry weight values (CRESP, 2006).

In recent years, food standards have been revised by individual countries and by the Codex Alimentarius Commission (CAC), an inter-governmental body to implement the Joint FAO/WHO Food Standards Programme. In the current (2010) version of



the Codex General Standard for Contaminants and Toxins in Food and Feed, the only heavy metals for which Standards in fish products are provided are lead (0.3 mg/kg ww) and methylmercury (0.5 mg/kg ww) (Codex Standard 193). The European Union has food safety limits for cadmium (0.05 mg/kg ww), lead (0.3 mg/kg ww) and mercury (Hg) (0.5 mg/kg ww) in freshwater fish (EC 2006).

According to Wagner and Boman (2003), the range of international standards for Cu in fish fillet is 10 to 100 mg/kg and for Cr it is 1 mg/kg wet weight (ww). This means that the Cu and Cr levels measured for pooled fish fillets in this study were well within guideline levels (Figures 16a and b).

The Zn levels found in fish fillet in this study were far below that allowed by international standards, which varied between 40 and 100 mg/kg ww (Wagner and Boman, 2003). The concentrations were similar between the four sites (Figure 16c).

The highest As levels were found in the fillet of fish caught in the only Orange River site (O2). According to Wagner and Boman (2003), As may vary between 0.1 and



5 mg/kg ww depending on the fish species. The highest level for As in this study was 1.41 mg/kg dw, equivalent to approximately 0.28 mg/kg ww (Figure 16d).

Results for Se ranged between 2.3 and 5.4 mg/kg dw, with the highest measured in fish from site V3 (Figure 16e). The 'safe' range of 0.3 to 2 mg/kg ww (Wagner and Boman, 2003) would equate to 1.5–10 mg/kg dw, using a conversion factor of 5.

The international standards for Cd are 0.05 to 2 mg/kg ww (EC, 2006; Wagner and Boman, 2003), for Pb they are 0.5 to 10 mg/kg ww (Wagner and Boman, 2003), and for Hg they are 0.5 mg/kg ww (EC, 2006). The levels of Cd, Pb and Hg in fish analysed in this study (Figure 16f–h) were well within these thresholds. The highest Hg level was found in fish from the Orange River site (O2) and although the level was twice as high as fish from the other sites, it was still below international limits.

The elemental bioaccumulation factors for fish were determined from the data. A bioaccumulation factor is the ratio of the contaminant concentration in the organism to that of the potential ambient sources (Newman, 2010), in this case the sediment. The term biota-sediment accumulation factor (BSAF) is therefore used. The BSAF for each of the fish pools was calculated using the concentrations at one or two sediment sites closest to where the fish were sampled, and the mean BSAF determined. It was assumed that 100% of the measured concentration in the sediment was bioavailable to fish, which implies that BSAF would be much higher if bioavailability is in fact lower. Only elements for which the mean BSAF was found to be greater than one are reported, namely rubidium (Rb), rhodium (Rh), silver (Ag), tin (Sn), platinum (Pt) and gold (Au) (Table 11).

Fish pools	Sediment sites	Rb	Rh	Ag	Sn	Pt	Au
V1	35	0.3	2.9	1.2	0.9	5.6	2.3
V2	24	3.7	0.8	1.9	2.3	10.6	1.6
V3	12, 15	1.0	0.4	0.1	0.7	3.5	1.5
02	2, 9	2.8	0.3	1.5	1.5	3.3	0.2
Mean		1.9	1.1	1.2	1.3	5.8	1.4

Table 11: The BSAF of elements that showed accumulation in fish tissue.

For each element that showed bioaccumulation, the highest BSAF was at fish pool V1 or V2 (Table 11). The mean for all fish pools showed that Pt had the strongest bio-accumulation, more than double that of the element with the next highest BASF, Rb.

### **Bird eggs**

Only elements with the five highest concentrations at each site, irrespective of bird species, are reported here. The complete dataset is provided in the addendum. Blackheaded herons were not included in this assessment because they are mainly terrestrial feeders. Tin (Sn) had the highest level in bird eggs at all of the sites, followed by iron (Fe) (Table 12). These two elements, together with boron (B) and zinc (Zn), were ranked among the top four at each of the egg collection sites.

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

Barbers Pan			Bloemhof Dam			Eldorado Park*			Potchefstroom		
African darter	Sn	235	Great white egret	Sn	280.6	Sacred ibis	Sn	240	Reed cormorant	Sn	255.4
Grey heron	Fe	230	Little egret	Fe	230.0	Sacred ibis	Fe	205	Reed cormorant	Fe	204.1
Grey heron	В	115	Great white egret	Zn	75.0	Sacred ibis	Zn	65	Cattle egret	Zn	75.0
African darter	Zn	70	Great white egret	В	65.0	Sacred ibis	В	40	Reed cormorant	В	34.1
Grey heron	Au	70	Great white egret	Au	19.5	Sacred ibis	Al	21	Cattle egret	Ba	17.0

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

The bioaccumulation of elements from fish to birds was evaluated. This could only be done for elements analysed in both fish and bird eggs, and it is assumed that 100% of the measured concentration in fish will be bioavailable to birds, although fish and egg samples were not taken at the same sites. The bioaccumulation factors were calculated for each bird species relative to each of the fish samples. This approach was followed because the birds would not necessarily feed on the fish species collected for elemental analysis, nor would the birds' uptake of elements be through food only. It was assumed that all the bird species in this study would consume sharptooth catfish. The mean bioaccumulation factor (MBF) for each element was calculated to provide a broad indicator of the range of bioaccumulation factors, irrespective of the species. A bird species-specific bioaccumulation factor (SSBF) was also calculated for each element to assess if the different species would accumulate the elements differently.

The MBF showed that all the elements bioaccumulated (at levels higher than in fish) in the bird eggs, except Cs (Table 13). Sn had the highest MBF of 313.6, followed by Au at 108.1. Six elements – Be, B, Mo, Pd, Tl and U – had MBFs between 10 and 20, and the rest had MBFs less than 10. Grey herons accumulated the greatest percentage of elements to the highest extent (42%), followed by cattle egret (26%). These results should be treated with caution, however, as the diet of cattle egrets is dominated by insects.

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

Table 13: The MBF of elements in bird eggs as well as the SSBF for the different bird species. MBF and SSBF were calculated assuming the birds consume sharptooth catfish. The highest SSBF for each element is shaded.

# 4. DISCUSSION

# 4.1 ORGANIC POLLUTANTS

ioxin-like TEQ was found in sediments in the eastern parts of the Orange-Senqu River basin, but was undetectable in the western parts. The presence of dioxin-like TEQ in fish from Rooipoort needs further investigation, and a species-specific analysis is needed for birds. Fish from the Gauteng region were not sampled in this study, and it would be useful to do so in the future to investigate the impact of industrial activities.

PCBs in sediment were also higher towards the eastern than the western parts of the catchment, but levels in fish from Rooipoort were higher than in any of the sediment samples. Appreciable levels were also found in some bird eggs, especially at Bloemhof Dam.

In sediments, OCPs were highest in the Gauteng region, and mostly undetectable in the rest of the basin. Although the highest levels of OCPs in fish were from Parys, in birds the highest levels were from Bloemhof Dam, which could possibly be acting as a biological retainer of some compounds coming from upstream. It would have been instructive to sample fish and sediments from Bloemhof Dam as well, but the bird colony at Bloemhof Dam was only located after the fish sampling was completed.

None of the sediment samples had detectable levels of 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. This requires further exploration, and a species-specific assessment needs to be done.

The three sediment sites with the highest  $\Sigma$ PAH levels were downstream of urban and industrial areas in South Africa and Lesotho. The sources for PAHs were pyrogenic in nature, typically associated with coal combustion or smelter operations. The most common PAH was fluoranthene, followed by phenanthrene and benzo(b+k) fluoranthene.

In summary, sediment had higher levels of POPs towards the east, decreasing drastically downstream towards the west, but this distribution pattern was not reflected in biota. This study has shown that sediment analysis alone will not provide sufficient information to assess contaminant levels in biota and the risk to human health. However, using pollution distribution patterns on a basin scale assists in assessing the overall pollution picture and in identifying hotspots and areas of interest.

In order to clarify some aspects, it would be very informative to sample fish from a number of additional areas, including between Bloemhof Dam and Boegoeberg, Upington, Modder River, Klerksdorp, Potchefstroom, in or near Lesotho, and Gauteng, while bird eggs from the colony at Upington might yield helpful data, especially with regard to PFOS distribution.



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## 4.2 HEAVY METALS AND TRACE ELEMENTS

The MPI for sediment site 56, the Molopo Eye, was the highest, and when the  $I_{geo}$  values were determined the same site had the most elements with  $I_{geo}$  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.

Levels of the elements in the sediment warrant further investigation, especially in light of the  $I_{geo}$  values for Se, As and Hg. However, intensive investigation into the natural background levels for these elements is needed for clarification.

When the sediment levels are compared to sediment quality guidelines for the Netherlands (only for As, Ba, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni and Zn (Adriano, 2001), and U and Se (Hamilton, 2004; Sheppard et al., 2005), all of the sites had a value less than 0.5, which is considered to be a low probability of being toxic, apart from the site at the Molopo Eye. There, the value of 1.6 implies that the sediment levels of elements have a high probability of being toxic to the biota in the system.

The levels of Cu, Cr, Zn, As, Se, Cd, Pb and Ag in the fish fillets were compared to international food safety guidelines and standards, and were found to be well within acceptable limits, with the possible exception of Se. Those elements that seemed the most likely to bioaccumulate in the fish, if exposure to sediment is their only exposure pathway and 100% of the measured concentrations are bioavailable, were Pt > Rb > Au > Sn > Ag > Rh. None of the other elements had bioaccumulation factors greater than 1. Further assessment is needed on the bioavailable fractions of the elements at the sites identified.

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

# 5. RISK ASSESSMENT

## 5.1 BACKGROUND AND METHODS

human health risk assessment was conducted to determine if the contaminants in the sediment, fish fillets and bird eggs tested would be likely to cause adverse health effects to humans consuming the fish or eggs from these areas or being in regular skin contact with the sediment (dermal exposure). The methodology with which this human health risk was assessed is described by the USEPA (1987, 1992, 1996) and the WHO (2002). Human health risk assessment consists of four steps:

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

For agents that cause non-cancer toxic effects, a hazard quotient (HQ) can be calculated in order to compare the expected exposure to the agent to an exposure that is assumed not to be associated with toxic effects.

For oral or dermal exposures, the average daily dose (ADD) was compared to a reference dose (RfD):

HQ = ADD/RfD	Equation 1

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

For chemicals that may cause cancer if ingested, risk is calculated as a function of oral slope factor and dose, and can be calculated using the following formula:

$Risk = 1 - e^{-(oral \ slope \ factor \times \ lifetime \ average \ daily \ dose)}$	Equation 2
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In this report the human health risk assessment will be based on the HQ determined for toxic agents and risk calculated for the various carcinogens.

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

Cross-media transfer equations were used to determine the amount of contaminant that could transfer from the sediment into fish. The formulae used to generate the exposure concentrations based on sediment concentrations was that described by the USEPA (1990) for sediment to fish concentrations.



C(w) =	$\frac{C(sd)}{(K_{oc} \times OC \times DN)}$	Equation 3
BCF =	$(0.79 \times \log(K_{_{OW}})) - 0.40$	Equation 4
C(f) = ]	BCF $\times \left(\frac{\text{fat}}{3}\right) \times C(w)$	Equation 5
Abbrev	iations:	
C(w)	concentration in water	
C(sd)	concentration in sediment	
C(f)	concentration in fish	
DN	sediment density (relative to water density of 1.0 kg/ $\ell$ ) (1.9)	
OC	organic carbon fraction of sediment (4.0%)	
K <sub>OC</sub>	octanol-carbon partition coefficient of the compound	
K <sub>OW</sub>	octanol-water partition coefficient of the compound	
BCF	bioconcentration factor	

These calculations, however, restrict the number of contaminants that can be investigated as there are limited contaminants for which  $K_{OW}$  and  $K_{OC}$  values are available. To determine the risk posed by contaminants, various exposure parameters are used to assess the average exposure of humans. The exposure parameters used in this risk assessment are listed in Table 13.

Exposure parameterAmountEvents per year350kg per event (fish)0.054kg per event (eggs)0.060Body mass70 kg

Exposure duration

Table 13: Exposure parameters used to generate exposure estimates.

30 years

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

## 5.2 RESULTS

The results of the exposure calculations are presented as both average daily dose (ADD) and lifetime average daily dose (LADD) in mg/(kg × d) for fish, bird eggs and sediment (Tables 14 and 15). Based on the exposure assumptions described above, risks of developing cancer and toxic effects were calculated for those contaminants where sufficient data were available (Tables 14 and 15 and Figures 17 and 18). An HQ of less than 1 is considered to be safe for a lifetime exposure, with no negative health effects experienced (USEPA 1991). A cancer risk of greater than one in 100,000 is considered unacceptable (WHO 2002). Most of the chemicals were at concentrations below the 'unacceptable' risks level, as defined by both the WHO and USEPA.

Beryllium, and especially arsenic, presented high risks of developing cancer from all media investigated (Figure 17). The risk of developing cancer from the consumption of bird eggs is as high as one in 1,000. PAHs were only measured in sediment and the following pose between a two in 100,000 and five in 100,000 risk for the development of cancer: indeno(1,2,3-cd)pyrene, benz(a)anthracene, benzo(b)fluoranthene and benzo(k)fluoranthene. The other PAHs are still being investigated by the EPA and their slope factors are derived from other isomeric chemicals. Benzo(a)pyrene in sediment poses an 'unacceptable' cancer risk of one in 10,000. This sediment sample was collected from site 64 which also had significant pyrene, benz(a)anthracene, chrysene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene and pyrene concentrations. Of the POPs, PCBs in bird eggs pose a two in 10,000 cancer risk. This bird egg sample was taken from Bloemhof Dam, which also posed a significant arsenic cancer risk.

Arsenic in the bird eggs and fish samples presented a high toxic health risk too, with HQ values exceeding 3. The chromium and selenium HQ value in the bird eggs also exceeded 1, posing a possible health risk. These concentrations were measured in pool 15 and pool 1 respectively, and therefore pose individual risks. The only PAH which is an emerging health risk is indeno(1,2,3-cd)pyrene in sediment. The reference dose for this PAH is, however, still under investigation by the EPA, and is only derived from isomeric compounds.



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

Table 14: The ADDs, LADDs, toxic health risks and cancer risks associated with exposure to the maximum concentrations detected in bird eggs and fish.

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

Table 15: The ADDs, LADDs, toxic health risks and cancer risks associated with exposure to the maximum concentrations detected in sediment.



Figure 17: The risk of developing cancer determined from the maximum concentrations detected in wild bird eggs, fish and sediment.



Figure 18: The hazard quotient determined from the maximum concentrations detected in wild bird eggs, fish and sediment.

### 5.3 DISCUSSION

The human health risk assessment examined whether possible human health effects might be anticipated based on chemical contaminants detected in sediment, bird eggs and fish samples. The methods involved modelling the contaminant concentrations expected in fish based on levels detected in sediments. Trans-media calculations (sediment to fish) were conducted based on individual chemical parameters described in the earlier sections. These used partition coefficients from the literature, although reported values vary (Bowman and Sans, 1983; Ahangar, 2011).

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

This risk assessment has highlighted that possible health risks can be anticipated resulting from regular ingestion of fish or eggs collected from the wild. However, there are uncertainties in any health risk assessment, and this study represents a screening of human health risk. It was intended to provide an indication of potential health risks that would require further investigation.

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

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

*Polychlorinated biphenyls* usually occur as mixtures of a possible 209 individual chlorinated compounds (known as congeners), primarily originating from anthropogenic sources. Health effects that have been associated with exposure to PCBs include neurobehavioural and immunological changes in children. Developmental delays occur at all ages and are greater in children smaller in size (ATSDR, 2000). PCBs are known to cause cancer in animals, and the EPA, the International Agency for Research on Cancer (IARC) and the WHO have classified PCBs as probable human carcinogens.

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

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

# 6. CONCERNS AND RECOMMENDATIONS

### 6.1 AREAS OF CONCERN

### Organic compounds

n general, the sediment levels of all compounds except PAHs were fairly low, but the distribution patterns indicated that industrial activities and combustion (pyrogenic) processes contribute to PAH pollution in the basin. The risk assessment suggested that, at the maximum level recorded, benzo(a)pyrene poses an unacceptably high cancer risk. The highest concentrations (and therefore the higher risks) were found at sites 16, 17, 22, 54, 60 and 64. The sources of the PAHs at all these sites were pyrogenic in nature, but the exact type of activity needs further investigation.

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 (OCPs) were generally at low levels at the sediment sites sampled, which is a positive finding. However, detectable OCP levels found 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 the biota samples were not collected at sites that were sampled for sediments. The highest levels of dioxinlike TEQ, PCBs and PFOS were from isolated sites, far removed from industrial areas. The high levels of PFOS in fish at Boegoeberg and Rooipoort, and in bird eggs from Bloemhof Dam and Barbers Pan, suggest sources other than industry, possibly linked to unknown releases from agriculture (although PFOS should then be similar to OCP distribution), or unknown uses in mining in the drier, central parts of the country. The levels are quite high compared to European levels, so PFOS sources and environmental distribution demand closer scrutiny. Human consumption of PFOS via fish should be seen as a serious concern.

### 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.

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

The risk assessment suggested that arsenic, chromium and selenium levels are potentially hazardous to human health in terms of toxic effects, while arsenic and beryllium may pose significant cancer risks 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 may be related to local geology. The levels in bird eggs in particular need closer scrutiny, as very little data is available on the impacts of these elements on biota, or on rates of consumption by humans and other organisms. In fish, arsenic occurs predominantly in relatively non-toxic organic forms, such as arsenobetaine, rather than the highly toxic and carcinogenic inorganic arsenic (ATSDR, 2007).

## 6.2 RECOMMENDATIONS

### **Organic compounds**

Communities potentially exposed to hazardous levels of PAHs should be identified and the contributing pyrogenic sources investigated, so that interventions to reduce PAHs emissions 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 project 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.

### **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.



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# 60 ADDENDUM

Site number/ name Coordinates Sadiment ma/ka dw Re R Al Sc Ti V Cr Ma Eo Co Ni Cu Ta Co Ac So Ph So																						
Sediment mg/	kg dw		Be	В	Al	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb	Sr	r
1	27.099	-26.683	0.35	67.5	3750	2.425	62.5	17.75	57.5	475	7500	9	25	12	32.5	0.825	0.5	2.75	3.75	1.7	5.5	)
<u>2</u> 3	21.242	-28.858	0.35	32.5 25	5500	2.75	222.5	40	15 75	237.5	6750	12.5 3.5	42.5 14	24.5 9.75	37.5 25	2.5 1.4	0.55	3.25 2.75	2.075	2.75 6.25	27.5	5
4	20.042	-28.499	0.4	19.5	10500	2.325	700	32.5	18.5	177.5	12500	9.25	30	24.75	35	2.125	1.025	3	1.775	4.25	15.75	5
5	19.303	-28.737	0.235	16	6500	1.925	450	30	17	152.5	10750	6	20.25	13	25	1.5	0.9	2.475	1.775	4.5	10.5	)
6	17.608	-28.749	0.275	13.5	10000	2.175	575	27.5	20.25	170	12000	9	30	30	37.5	1.95	1	3.25	1.65	3.5	16.75	)
7	16.471	-28.602	0.215	11	2500	1.5	425	23.5	12.5	152.5	9500	6.25	22.75	25	27.5	1.65	0.775	3.25	1.525	2.025	10 75	)
9	22 748	-20.123	0.225	6 25	6000	1.075	450	30	16 75	182.5	9000	3.5 7	14.5 25	15 75	25	1.075	0.373	25	1 2 2 5	1775	10.75	5
10	23.016	-29.623	0.35	4.5	7750	2.5	172.5	19.75	25	192.5	8250	4.5	21.25	11.5	27.5	1.5	0.7	3.75	0.65	4.5	19	)
]]	23.699	-29.162	0.575	20.25	23250	6	925	62.5	50	325	24000	19.5	70	42.5	57.5	6	2	4.25	11.5	6.75	27.5	)
12	23.841	-29.039	1.225	21.5	27500	8.25	425	67.5	95	1000	30000	25	112.5	42.5	75	8.25	2.5	8.5	12.75	16.75	30	) -
13	24.111	-29.601	0.6	18.25	25000	5./5	725	07.5 75	47.5	500 875	27500	21 22	80 105	45 60	65 975	/.5 12	2.25	5.25	11.5	5.5 21.25	47.5	<u> </u>
15	24.067	-28.722	1.125	17	20750	7.5	300	55	85	725	23250	22	97.5	42.5	60	7.5	2.75	6.75	12.25	13.5	40	)
16	24.303	-28.377	0.85	18	21500	6.25	250	52.5	82.5	775	21500	18	105	30	47.5	7	1.7	5.75	10.75	9.25	70	)
17	24.867	-28.095	1.375	14	24750	8.25	450	52.5	72.5	825	25000	25	87.5	47.5	70	11	2.125	6.5	13.25	18.25	25	)
10	26.127	-27.936	0.425	12.5	24500	2.15	1/0	20	30	000	21000	7.25	22.5	15.25	27.5	3.25	0.6/5	3.5	12.25	6.5	14.25	1
20	26.813	-27.487	0.4	10.5	15750	2.5	275	47.5 55	77.5	650	16750	20.5	67.5	65	40	4.75	1.775	7.25	12.25	4.5	23.25	
21	26.998	-27.040	0.475	11.5	10000	1.975	227.5	40	90	350	11500	21.5	67.5	22.5	27.5	3.5	1	3.5	11.25	6.25	9	)
22	26.664	-26.935	0.8	13.75	16250	5.5	227.5	65	152.5	925	40000	32.5	172.5	47.5	122.5	7.5	3.25	11.75	11.75	11	16.25	)
23	26.680	-27.014	0.275	11.5	5250	1.975	120	24.25	45	400	7250	15	27.5	23	35	2.5	0.65	3.5	10.75	4.25	7.75	)
<u></u> 25	27.397	-26.714	0.200	10 75	11250	1.275	142 5	10.25	82.5	1375	20500	10.75 52.5	37.5 200	10 45	32.5 275	Z.I 4	0.4/5	2.75	10.75	3.25 5.5	0.20	<u>,</u>
26	28.381	-26.647	0.975	9	20500	11	247.5	85	112.5	625	30000	32.5	147.5	65	42.5	7.75	2.5	4	12.25	9	14.5	)
27	28.426	-26.479	0.525	9.25	8000	3	50	25	57.5	1075	11250	40	160	32.5	300	2.75	0.95	4.75	11.25	3.5	6.75	,
28	29.025	-26.629	0.275	9	7000	2.25	185	55	57.5	1050	11500	32.5	87.5	30	47.5	2.5	1	3.25	10.75	3.25	8.75	) -
<u></u> 30	29.600	-26.313	1.3 0.5	0./5 8	21500	9.75	575 90	152.5	67.5 25	325 775	32500	30 12	32.5	92.5	45 22	6./5 3.5	2.5	5 25	11.75	3 25	1.15	<u> </u>
31	28.475	-27.531	1.525	7	27500	11.75	400	75	95	1225	27500	25	80	52.5	57.5	12.5	2.4	4.25	12.5	17	25	<u>,</u>
32	28.750	-27.647	0.625	8	19250	3.5	1050	60	40	500	27500	21	60	45	50	7	2.325	9	12.5	3.5	30	)
33	28.534	-27.310	2.275	8	37500	14.25	450	77.5	92.5	1975	37500	30	85	57.5	110	19	3.25	8.25	13.5	25	40	)
<u>34</u> 25	28.598	-27.023	1.075	7.5	2/500	1Z	275	67.5 57.5	87.5	900 725	2/500	23 25	110 75	57.5	92.5 52.5	8 25	2.5	5.25	12.5	21.75	27.5	! {
36	28.914	-26.846	0.675	8.75	17000	'. 7	245	50	65	750	16250	20.75	60	40	47.5	6.25	1.0	3.25	13	15.25	14.75	
37	28.050	-26.682	1.05	8.5	17250	9.75	182.5	67.5	95	1175	30000	55	187.5	57.5	185	7	2.5	6.5	12	10	19.25	)
39	26.107	-28.807	1.575	16.75	27500	9.25	350	55	90	1700	27500	21.5	95	50	120	15.25	2.475	8.25	11.75	19	52.5	) 
40 11	25.773	-28.945	0.5/5	16.25	25000	6.25	350	102.5	62.5	525	30000	21.25	167.5 87.5	//.5	/5 70	1.25	2.5	16 5	12.25	1/ 25	155	!
42	26.525	-29.101	1.3	10.5	23750	6.25	750	62.5	72.5	825	24000	24.75	72.5	35	60	8.25	2.125	8	12.23	14.75	30	)
43	25.202	-29.474	2.3	17.25	45000	10.75	1150	115	85	800	52500	23	110	62.5	147.5	15.25	4.5	17	12.75	27.5	77.5	)
44	25.587	-29.681	1.35	15.75	37500	10	1400	82.5	87.5	600	32500	19.5	75	42.5	105	11.5	2.75	10.25	12.75	21.25	72.5	)
45	25.649	-29.563	1 425	12	21500	5.25	1000	60	4/.5	350	22250	21.25	50	45	60 105	6./5	2 2 25	7.25 5.25	11 75	12.75	55	1
40	25.242	-30.507	1.425	8.5	32500	14.25	1000	75	77.5	1175	32500	21.25	85	47.5	80	9.5	2.75		12.75	13.5	40	)
48	26.306	-30.428	0.625	6.5	19000	4.25	1175	67.5	35	800	25000	23.5	72.5	45	50	8.5	2.325	7.25	11.75	4.5	30	)
49	26.459	-30.575	1.325	10	50000	14.5	1150	92.5	97.5	875	42500	27.5	117.5	77.5	85	12	3.5	6.5	12	18	40	)
50 51	26.465	-30.650	0.55	9.25	2/500	6.5 5	55U 875	85 60	27.5	1425	40000	25	72.5	37.5	90 175	5 25	3.25	12	13	8 25	27 5	1
52	27.337	-30.405	0.375	6.25	19750	4.75	1500	85	30	525	25000	19	65	45	50	5.25	2.275	4.25	12.25	3.75	27.5	
53	27.137	-29.528	1.325	6.5	19750	5.75	350	97.5	117.5	850	35000	23	72.5	50	72.5	8	3	10.5	12	9.5	27.5	)
54	27.316	-29.490	0.275	5.75	8250	2.5	425	35	24.25	195	11500	8.75	30	22.75	27.5	3	1.05	3.25	11.5	3.5	8.75	)
55	28.151	-28.724	1.1/5	8 75	42500	12.75	1600	207.5	140	2400	52500	4/.5	135	/5 80	/U 55	16.25	4.5 1	9.25	12 12	6 /	57.5 80	/ }
 57	28.551	-29.020	1.05	14	35000	7.75	1250	87.5	62.5	2500	37500	23.75	100	67.5	207.5	11.75	3	6.75	11.75	10.5	82.5	5
58	28.563	-29.230	0.6	6.75	72500	21.25	4250	205	112.5	1325	72500	45	147.5	137.5	127.5	12	6	2.75	12.5	5.25	120	)
59	28.148	-29.553	0.425	5	57500	16	2500	170	97.5	1025	57500	40	150	117.5	105	8.25	4.75	2.75	12	3	75	)
<u>60</u> 41	27.454	-29.336	0.525	5.5	62500	13.25	4000	1/5	02 5	050	62500	37.5	1/5	137.5	125 87.5	10 8	5.25	2.5	12.25	8 25	92.5	! }
62	17.79	-26.8	0.525	7.75	8750	2.3	2000	32.5	18.25	425	18500	<u> </u>	32.5	42.5	47.5	4.75	1.625	13.75	11.75	5.25	24	, 
										. 20												
Fish		2/ 0/	0.00	ז ר	10.00	0.00	<u> </u>	1.00	0/0	114	10 50	0.07	0.00	07/	20 50	0.07	0.00	1.97	4.50	105	0.70	)
V2	27.51	-26.97	0.00	3.75 3.25	4 88	0.09	∠5.03 22.00	1.20	3.03 3.75	0.94	50.00	0.08	0.77	2.70	20.50 19.50	0.07	0.02	1.20	4.50	4.25	0.70	! }
V3	24.16	-28.56	0.01	3.50	6.00	0.09	24.13	1.16	3.38	0.93	53.75	0.05	0.30	2.10	20.38	0.07	0.02	1.13	5.38	15.00	0.79	1
02	22.21	-29.21	0.01	3.38	10.38	0.08	23.50	1.11	3.50	0.96	52.50	0.03	0.33	2.91	20.50	0.07	0.02	1.41	4.13	6.25	0.88	}
Rird eags	ma/ka du	v																				
Barberspan	25.53	-26.59	0.153	115	16	0.23	7.5	2.95	9	4.25	230	0.35	2.05	8.5	70	0.095	0.039	2.25	10	2.4	2.95	)
Bloemhof Dam	25.67	-27.69	0.083	65	16.664	0.244	8.5	2.95	9	3.749	230	0.125	1.525	9.15	75	0.115	0.045	2.562	6.71	2.604	3.489	)
Eldorado Park	27.89	-26.3	0.095	40 21 DE	21	0.195	5	2.2	7 05	3.75	205	0.205	1.25	10	65 75	0.11	0.039	1.8	5.5	5 10 1	2.9	1

																	Total PAHs	Dioxin TFQ	Indic PCRs	Sum OCPs	PFOS
Мо	Rh	Pd	Aa	Cd	Sn	(s	Ba	Ce	Pt	Au	Ha	TI	Pb	U	1	MPI	ma/ka dw	na/ka dw	na/ka dw	na/ka dw	ua/ka dw
1.65	0.245	1.325	4.25	0.153	0.975	0.173	23.5	4.75	0.148	2.3	3.5	1.825	5.25	0.65	0.85	8.681	0.290	0.17		<b>g</b> / <b>g</b> u.!	0
0.725	0.75	0.85	4	0.093	0.6	0.325	90	7.5	0.173	0.675	1.525	0.5	5.75	0.475	0.4	10.598	0.046	0.16	0	0	0
0.425	0.218	0.475	2.5	0.055	0.675	0.55	40	8.75	0.015	0.35	]	0.3	4	1.5	1.1	6.841	0.035	0.16	0	0	0
0.35	0.4	0.475	2.375	0.07	0.65	0.425	62.5	9.75	0.018	0.213	0.9	0.275	4.25	1.5	0.3	8.230	0.021	0.16	0	0	0
0.233	0.12	0.3	2.3	0.048	0.675	0.325	40	11.5	0.105	0.18	0.65	0.21	3.5	0.8	0.525	6.790	0.050	0.16	0	0	0
0.235	2.15	0.325	1.7	0.053	0.375	0.4	55	7.5	0.168	0.108	0.65	0.195	4.25	1.275	0.1675	7.846	0.014	0.16	0	0	0
0.223	0.275	0.3	2	0.07	0.275	0.225	55	7	0.138	0.095	0.575	0.143	4.25	1.025	0.1725	6.313	0.009	0.16	0	0	0
0.22	0.148	0.218	2.45	0.038	0.75	0.3	37.5	6.5	0.04	0.128	0.4	0.108	4.75	0.45	0.14	4.936	0.017	0.16	0	0	0
0.138	0.13	0.17	1.5	0.035	0.245	0.228	42.5	5.5	0.010	0.063	0.3	0.09	3.5	0.3	0.1475	4.655	0.012	0.16	0	0	0
0.108	0.158	0.168	]	0.04	0.3	0.5	45	5	0.008	0.04	0.213	0.1	5	0.4	1.3	5.224	0.029	0.16	0	0	0
0.325	0.425	0.475	4.75	0.108	0.85	0.8	117.5	14.25	0.014	0.098	0.575	0.233	8.5	0.825	1.175	13.176	0.020	0.16	0	0	0
0.45	0.5	0.525	5	0.168	1.05	1.475	157.5	19.75	0.015	0.128	0.575	0.35	13.5	1.5	6	18.478	0.043	0.19	0	0	0
0.375	0.575	0.525	9	0.108	1.425	0.7	150	13	0.019	0.08	0.5	0.2	8.75	0.575	0.9	14.704	0.116	0.17	0	0	0
0.35	0.5	0.575	6.5	0.155	1.5/5	1.8	202.5	25	0.014	0.105	0.5/5	0.4	17.5	2.225		22.225	0.11/	0.19	0		0
0.55	0.45	0.475	14.75	0.118	0.975	1.025	155	17.5	0.025	0.09	0.525	0.275	12.5	50	6./5	19.605	0.04/	0.21	0	<u> </u>	0
0.3	0.725	0.5	3.75	0.128	0.725	1.075	160	12.5	0.006	0.088	0.4/5	0.218	1./5	0.925	6.25	15.444	0.365	0.17	U	<u> </u>	U
0.325	0.35	0.4/5	0.	0.125	1.35	1.3/5	212.5	21.75	0.1/5	0.2	0.5	0.35	ا/ ر ۵۲	1 2 2	5./5	18.586	0.1/9	0.22	0	<u> </u>	0
0.1/3	0.1/5	0.25	L./5	0.045	0.45	0.625	15	12.75	0.103	0.06	0.3/5	0.18	6.25	1.325	0.8/5	/.5/5	0.047	0.16	0	<u> </u>	U
0.325	0.24	0.35	4./5	0.155	1.15	1.225	150	19.5	0.014	0.098	0.4	0.3	IZ.5	1./	2.75	14.00/	0.003	0.27	244	U	U
0.3	0.275	1.025	1.75	0.00	0.3/5	0.3/5	77.5	1U 0 E	0.125	0.4	0.95	0.25	5./5	4./5	0.525	0 102	0.015	0.16	0	U0	U 0
0.225	0.210	0.215	2.4/5	0.003	0.475	0.00	//.J	7.5	0.014	0.00	0.323	0.213	2./2 10.25	0.020	0.00	0.173	0.000	0.10	U 1702	U 17	0
0.020	0.00	0.323	10.20	0.02	0.525	0.323	147.D	17.20 2 E	0.014	0.0	0.775	0.205	10.23	1.0/ 3	رن 11	7.014	0.007	0.04	1/02	1./	0
0.373	0.13	0.245	ა ე 75	0.003	0.323	0.00	57.5	0.J 4 5	0.017	0.105	0.373	0.120	4.75	0.775	0.575	5 336	0.032	0.22	2020		0
0.130	0.130	0.140	12.75	0.045	2 25	0.5	80	0.J 8 75	0.013	0.033	0.35	0.113	14 75	1 15	0.575	12 821	0.007	0.17	1807	0	0
0.323	0.4	0.235	12.25	0.45	0 725	0.45	152.5	15 25	0.011	0.00	0.35	0.173	14.75	0 775	1.0	12.001	0.207	0.41	1007 N	0.7	0
0.25	0.23	0.323	5 25	0.05	0.725	0.475	60	13.25	0.023	0.03	0.375	0.2	11.75	23	1 575	10.012	0.037	0.2	1389		0
0.175	0.148	0.21	3.5	0.05	0.025	0.233	60	9 7 5	0.00	0.100	0.025	0.113	3 5	0.5	0.45	7187	0.013	0.02	0007	0.5	0
0.205	0.110	0.215	6 25	0.053	0.05	0.200	115	25	0.007	0.010	0.25	0.325	23 25	1 175	1 125	11 969	0.117	0.22	0	0	0
0.325	0 103	0 135	2 75	0.038	0.725	0.323	97.5	85	0.007	0.00	0.123	0.023	6	0.375	0.3	5 7 2 5	0.035	0.21	0	0	0
0.023	0.325	0.4	5 75	01	0.95	13	227.5	25	0.009	0.038	0 375	0 325	16 75	1 175	13	14 961	0 074	0.2	0		0
0.35	0.45	0.3	3.25	0.08	0.5	0.325	167.5	13	0.012	0.03	0.275	0.11	9.75	0.525	0.4	10.689	0.015	0.16	0	0	0
0.55	0.45	0.625	8.5	0.223	1.625	2.075	350	37.5	0.035	0.06	0.3	0.425	27.5	2.15	2.75	21.523	0.117	0.34	0	0	0
0.325	0.45	0.5	5.25	0.153	1.3	1.65	245	30	0.008	0.068	0.275	0.375	17.5	1.925	1.825	16.864	0.074	0.26	0	0	0
0.195	0.213	0.325	3.5	0.078	0.85	1.1	182.5	24.25	0.03	0.043	0.25	0.25	14.25	1.1	0.75	12.331	0.068	0.17	0	0	0
0.275	0.235	0.275	3.75	0.055	0.675	0.575	135	13.75	0.003	0.063	0.275	0.19	7.25	0.8	0.8	10.063	0.454	0.2	0	0	0
0.3	0.3	0.4	21.75	0.208	1.125	1.675	150	17	0.038	0.125	1.6	0.193	15.5	1.975	3.75	17.551	0.225	0.69	531	2.8	0
0.475	0.5	0.5	8.75	0.143	1.775	1.7	300	22.25	0.012	0.068	0.4	0.3	21.5	1.15	20.75	21.302	0.174	0.52	953	0.5	0
0.35	1.225	0.65	3	0.115	0.775	1.125	165	8.5	0.014	0.07	0.325	0.3	6.25	0.875	6	18.199	0.050	0.16	0	0	0
0.55	0.6	0.5	12.75	0.11	1.075	1.45	227.5	27.5	0.010	0.043	0.4	0.245	19	1.225	2.125	17.896	0.012	0.17	0	0	0
0.275	0.35	0.4	4.25	0.098	1.05	1.4	177.5	23.75	0.010	0.145	0.238	0.245	15.5	1.325	1.4	14.817	0.016	0.17	0	0	0
0.425	0.675	0.55	4.5	0.163	1.625	3.5	250	30	0.013	0.048	0.22	0.45	24.25	1.825	5.5	24.597	0.043	0.19	0	0	0
0.325	0.625	0.55	5.25	0.12	1.55	1.975	210	25	0.088	0.14	0.21	0.275	17.25	1.625	1.925	20.465	0.016	0.16	0	0	0
0.375	0.525	0.375	11.25	0.12	0.925	1.3	145	18.5	0.014	0.043	0.208	0.22	11	1.275	1.925	14.412	0.024	0.17	0	0	0
0.218	0.5	0.45	8	0.123	1.35	2.075	100	20.25	0.021	0.035	0.213	0.275	16.25	1.025	1.55	17.798	0.011	0.16	0	0	0
0.375	0.45	0.4	8.25	0.118	1.125	1.625	195	24	0.013	0.038	0.228	0.235	13.75	1.5	0.925	16.427	0.060	0.17	0	0	0
0.4	0.6	0.525	3.5	0.085	0.625	0.5	200	18.75	0.020	1	0.203	0.113	11	0.65	0.325	12.827	0.024	0.16	0	0.5	0
0.3	0.425	0.425	4./5	0.138	1.15	2.15	210	25	0.038	0.058	0.25	0.248	15	1.2	1.6/5	18.908	0.044	0.16	0		0
0.4	0.6/5	0.6	2.75	0.3	1.15	1.9	250	27.5	0.011	0.035	0.1/5	0.25	24.5	2.225	0.775	18.400	0.013	0.17	0	<u> </u>	0
0.228	0.325	0.25	3.5	0.070	0.65	1.0/5	97.5	22.25	0.053	0.03	0.155	0.138	1.15	0.95	0.45	11.3/9	0.013	0.1/	0	<u> </u>	U
0.3	0.245	0.25	4	0.073	0.33	0.075	102 5	12	0.010	0.03	0.1/3	0.000	2./2	1 275	0.25	7./70 10.00E	0.022	0.10	0	U0	0
U.S 0 175	0.35	0.3/5	4./) 275	0.070	U.//)	0.7/5	172.5 27 E	10 75	0.010	0.033	0.175	U.1/3	17.23 17.2	1.3/3	U.00 0 0 C	10.070	0.000	U.JZ	U ^	U ^	0
0.175	0.11	0.140	J.7 J A 25	0.030	0.33	0.373	225	20.25	0.000	0.023	0.170	0.070	4.75	0.323	1.25	0.000	0.073	0.10	0	0	0
U.33 /	U.020	0.423 0.475	4.20 00	U.12 0 100	U./ 1	U.323 ດາ	27C 82UU	20.23 170	0.00/	U.UZŬ 0.02	0.200	U.100 2 75	13.5 00	U.7 1575	۱.۲۵ ۱۳۲۲ ۱	1/.103	0.037	0.1/	U 2150	U 0	U ^
4	0.475	0.475	5 25	0.100	ا 2 75	1 225	240	170	0.17.5	0.03	0.103	0.20	14 75	1.373	0 075	20 200	0.177	0.17	2130	0	0
0.475	0.075	0.45	J.2J Q	0.100	0.0	0.22	152.5	12 25	0.000	0.03	0.100	0.200	10.75	0 375	1.8	18 / 52	0.037	0.17	0	0	0
0.475	0.05	0.075	/ 7	0.170	0.7	0.22	102.5	13.23	0.03	0.03	0.0	0.070	ч. J 2 5	0.375	1.0	14 585	0.030	0.17	0	0.5	0
0.425	0.55	0.5	5 25	0.133	0.7	0.135	102.5	11 75	0.010	0.020	0.2	0.073	4 25	0.325	1.075	15 786	0.033	0.17	1204	0.5	0
0.13	0.025	0.525	5.25	0.143	0.875	0.10	110	14 25	0.020	0.020	0.103	0.000	1.23	0.03	1 475	15.705	0.033	0.37	1201	0.7	0
1 15	0.3	0.3	1,875	0 115	0.6	0 75	125	15 5	0 003	0 0 2 3	0 135	011	10 25	0 775	0.35	9 7 7 8	0.006	0 17	0 N		0 0
1.13	0.0	0.0		5.115	0.0	0.13	123			5.020	3.105	0.11		3.773	0.05			5.17	U		
																		ng/kg ww	ng/kg ww	ng/kg ww	µg/kg ww
0.10	0.63	0.12	4.11	0.02	0.75	0.02	5.75	0.03	0.17	0.10		0.08	0.44	0.04				0.16	0	1.6	0
0.11	0.13	0.08	5.25	0.01	0.79	0.03	6.38	0.01	0.14	0.09		0.12	0.25	0.01				0.16	454	18.9	0
0.10	0.21	0.11	1.28	0.01	0.66	0.21	6.50	0.02	0.07	0.16		0.10	0.34	0.10				0.23	5409	8.2	1.7
0.08	0.13	0.09	3.99	0.01	0.65	0.01	6.25	0.01	0.30	0.07		0.10	0.34	0.07				0.16	0	1.4	2.6
																			-		
	<b>A</b> :			0.1.1	0.1.7	0.000		0.000		- 1							r	ng/kg ww	ng/kg ww	ng/kg ww	µg/kg ww
2.6	0.105	6.5		0.148	235	0.003	12.5	0.022	2.95	70		8.5	1.6	2.9				0.2	6077	90.8	846
2.604	0.125	2.Z		0.072	200.6	0.005	13.017 19 r	0.015	0.0	19.5	9.5 2 0 F	1.75	0.65	0.55				1.61	0/646	۲5 ۱ <i>۲۲</i> ۶	2330
1.55	0.125	1.1		0.038	240	0.005	13.5	0.019	0.36	0.5	2.05	0.010	0.6	0.007				0.44	52627	155./	69
٥.١	U.3	1.0		0.021	200.0/0	0.000		0.010	0.33	J.03Z	J.ZJJ	0.312	U.33	0.071			<u>.</u>	U.3Z	44741	103.0	201

