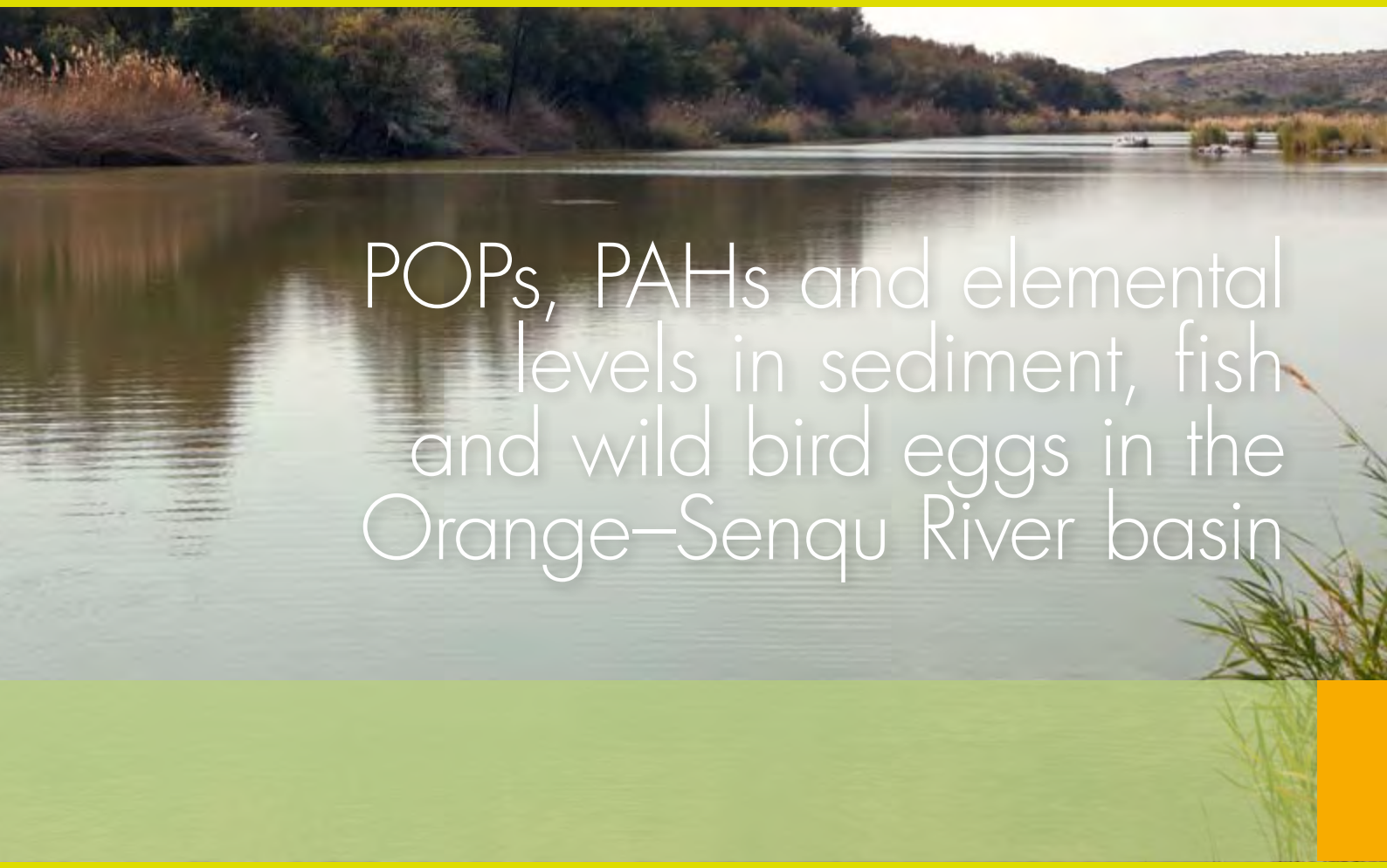


POPs, PAHs and elemental levels in sediment, fish and wild bird eggs in the Orange–Senqu River basin

ORANGE - SENQU RIVER COMMISSION
BOTSWANA LESOTHO
ORASECOM
NAMIBIA SOUTH AFRICA
Established 2000

UNDP partners with people at all levels of society to help build nations that can withstand crisis, and drive and sustain the kind of growth that improves the quality of life for everyone. On the ground in 177 countries and territories, we offer global perspective and local insight to help empower lives and build resilient nations. www.undp.org

Empowered lives.
Resilient nations.

The GEF unites 182 countries in partnership with international institutions, non-governmental organisations (NGOs), and the private sector to address global environmental issues while supporting national sustainable development initiatives. Today the GEF is the largest public funder of projects to improve the global environment. An independently operating financial organisation, the GEF provides grants for projects related to biodiversity, climate change, international waters, land degradation, the ozone layer, and persistent organic pollutants. Since 1991, GEF has achieved a strong track record with developing countries and countries with economies in transition, providing $9.2 billion in grants and leveraging $40 billion in co-financing for over 2,700 projects in over 168 countries. www.thegef.org

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.

POPs, PAHs and elemental levels in sediment, fish and wild bird eggs in the Orange–Senqu River basin. Report 002/2013.

Produced by the UNDP–GEF Orange–Senqu Strategic Action Programme
Published by the Orange–Senqu River Commission (ORASECOM), www.orasecom.org

ISBN 978-0-620-56533-2

Prepared by Prof. Hindrik Bouwman and Dr Rialet Pieters of the School of Environmental Sciences and Development, North-West University, Potchefstroom, South Africa, and Dr Bettina Genthe and Dr Jessica Chamier of the Council for Scientific and Industrial Research, Stellenbosch, South Africa

Final Report submitted November 2011

Published June 2013

Suggested citation: ORASECOM, 2013. *POPs, PAHs and elemental levels in sediment, fish and wild bird eggs in the Orange–Senqu River basin.* Report 002/2013, prepared by Bouwman, H, Pieters, R, Genthe, B and Chamier, J for ORASECOM, Pretoria.

Updating and editing by Sue Matthews
Design and layout by Handmade Communications
Proofreading by Liz Haines

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

EXECUTIVE SUMMARY

© Ian Smith

INTRODUCTION AND METHODOLOGY

The four southern African countries that share the basin of the Orange–Senqu River – Botswana, Lesotho, Namibia and South Africa – are all parties to the Stockholm Convention on Persistent Organic Pollutants (POPs), which currently targets 22 chemicals and classes of chemicals. Previously, research on POPs in the Orange–Senqu River basin concentrated on pesticides such as DDT. Only recently has more attention been given to POPs such as dioxins and polybrominated diphenyl ethers (PBDEs). Little is known about polycyclic aromatic hydrocarbons (PAHs) in the catchment, and there are very few studies available on levels of elements, including heavy metals, in sediments and biota.

The original scope of this study was to undertake a survey and assessment of POPs and heavy metals in water bodies and riverine sediments, under the umbrella of ORASECOM's 2010 Joint Basin Survey and as a contribution to the transboundary diagnostic analysis (TDA) of the Orange–Senqu River basin. During the study, PAHs were added as an additional research topic because of their detrimental effects to humans and wildlife. Sediments were sampled in September 2010 at 61 sites, 33 of which were in the Vaal River catchment. The remaining 28 sites were along the Orange–Senqu River and its other tributaries, with one site in Namibia and five in Lesotho. These sites largely conform to the sites used by other components of the Joint Basin Survey. Fish and wild bird eggs were sampled at four sites each to investigate the levels of the compounds and elements in the biota of the Orange–Senqu River basin.

Samples for POPs and PAHs were sent to an accredited laboratory in Germany for analyses on high-resolution gas chromatography and mass spectrometry (HRGC-MS), while samples for elemental composition were analysed at North-West University in Potchefstroom, using inductively coupled plasma mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

Organic pollutants

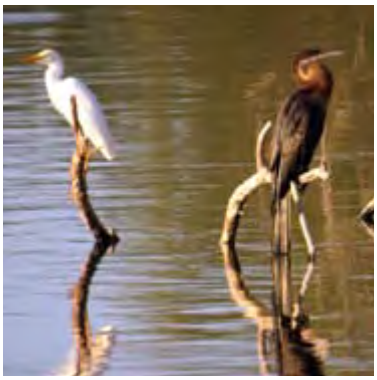
Levels of dioxin-like toxic equivalents (TEQ) were low in all media. In sediments, TEQ levels were higher in the east, and mostly undetectable towards the mouth. The relatively higher TEQ level in fish from Rooipoort requires further investigation, and a species-specific analysis is needed for birds.

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.



© Henk Bouwman

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_{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

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
	I_{geo}	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
	γ-HCH	gamma-hexachlorocyclohexane
	Ag	silver
	Al	aluminium

As	arsenic
Au	gold
B	boron
Ba	barium
BaP	benzo(a)pyrene
Be	beryllium
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
HCl	hydrochloric acid
Hg	mercury
HxCDD	hexachlorodibenzo-*p*-dioxin
I	iodine
K	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
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
Pd	palladium
PeCDD	1,2,3,7,8-pentachlorodibenzo-*p*-dioxin
PFOS	perfluorooctane sulfonate
PFOSF	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-*p*-dioxin
Ti	titanium
Tl	thallium
U	uranium
V	vanadium
Zn	zinc

1. INTRODUCTION

1.1 THE ORANGE–SENQU RIVER BASIN

© UNOPS/Christoph Mor

The 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^2. 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.

© Ian Smith

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 γ-HCH), alpha-hexachlorocyclohexane (α-HCH), beta-hexachlorocyclohexane (ß-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 22nd 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, fluorene, fluoranthene, *benzo(a)anthracene, chrysene, pyrene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k) fluoranthene, dibenz(a,h)anthracene,* benzo(g,h,i)perylene 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	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminum	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	57–71 Lanthanides	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	89–103 Actinides	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cp Copernicium	113 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium

Lanthanides	57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu Lutetium
Actinides	89 Ac Actinium	90 Th Thorium	91 Pa Protactinium	92 U Uranium	93 Np Neptunium	94 Pu Plutonium	95 Am Americium	96 Cm Curium	97 Bk Berkelium	98 Cf Californium	99 Es Einsteinium	100 Fm Fermium	101 Md Mendelevium	102 No Nobelium	103 Lr Lawrencium

Alkali metals | Alkaline earth | Basic metal | Halogen | Noble gas | Non-metal | Rare earth | Semi-metal | Transition metal

Figure 1: The Periodic Table of elements.

1.3 PREVIOUS RESEARCH

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).

© UNOPS/Christoph Mor

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 (Σt-PAH) ranging between 44 and 39,000 ng/g dw and the concentration of carcinogenic PAHs (Σc-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 ΣPAHs 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

© Ian Smith

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

Sediments 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.

Site number	River	Coordinates		Country	River system
		Longitude	Latitude		
1	Mooi River (Potchefstroom)	27.10	-26.68	SA	Vaal
2	Orange River (Upington)	21.24	-28.47	SA	Orange–Senqu
3	Hartbees River	20.64	-28.86	SA	Orange–Senqu
4	Orange River	20.15	-28.50	SA	Orange–Senqu
5	Orange River (Onseepkans)	19.30	-28.74	SA	Orange–Senqu
6	Orange River (Vioolsdrif)	17.61	-28.75	SA	Orange–Senqu
7	Orange River (Mouth)	16.47	-28.60	SA	Orange–Senqu
8	Orange River (Sendelingsdrif)	16.89	-28.12	SA	Orange–Senqu
9	Orange River (Prieska)	22.75	-29.66	SA	Orange–Senqu
10	Brak River	23.02	-29.62	SA	Orange–Senqu
11	Orange River (Douglas)	23.70	-29.16	SA	Orange–Senqu
12	Vaal River (Douglas)	23.84	-29.04	SA	Vaal
13	Orange River (Hopetown)	24.11	-29.60	SA	Orange–Senqu
14	Riet River	24.50	-29.04	SA	Vaal
15	Vaal River	24.07	-28.72	SA	Vaal
16	Harts River	24.30	-28.38	SA	Vaal
17	Vaal River (Warrenton)	24.87	-28.09	SA	Vaal
18	Vet River	26.13	-27.94	SA	Vaal
19	Vaal River	26.22	-27.52	SA	Vaal
20	Vals River	26.81	-27.49	SA	Vaal
21	Renoster River	27.00	-27.04	SA	Vaal
22	Skoon Spruit (Klerksdorp)	26.66	-26.93	SA	Vaal
23	Vaal River (Orkney)	26.68	-27.01	SA	Vaal
24	Vaal River (Parys)	27.40	-26.91	SA	Vaal
25	Klip River (West)	28.06	-26.55	SA	Vaal
26	Suikerbosrand River	28.38	-26.65	SA	Vaal
27	Blesbok Spruit	28.43	-26.48	SA	Vaal
28	Waterval River	29.03	-26.63	SA	Vaal
29	Vaal 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
37	Suikerbosrand River	28.05	-26.68	SA	Vaal
39	Modder River	26.11	-28.81	SA	Vaal
40	Kaal River	25.77	-28.95	SA	Vaal
41	Koranna Spruit	26.64	-29.09	SA	Vaal
42	Modder River	26.52	-29.10	SA	Vaal
43	Riet River	25.20	-29.47	SA	Vaal
44	Kromellenboog 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	Orange River	26.71	-30.68	SA	Orange–Senqu
52	Orange River	27.34	-30.40	SA	Orange–Senqu
53	Leeu River	27.14	-29.53	SA	Orange–Senqu
54	Caledon River	27.32	-29.49	SA	Orange–Senqu
55	Caledon River	28.15	-28.72	SA	Orange–Senqu
56	Molopo Eye	25.89	-25.89	SA	Orange–Senqu
57	Malibamatso River	28.55	-29.02	Lesotho	Orange–Senqu
58	Matsuko River	28.56	-29.23	Lesotho	Orange–Senqu
59	Senquenyane River	28.15	-29.55	Lesotho	Orange–Senqu
60	Kelekequ River	27.45	-29.34	Lesotho	Orange–Senqu
61	Senqu River	28.51	-30.06	Lesotho	Orange–Senqu
62	Fish River	17.79	-26.80	Namibia	Orange–Senqu

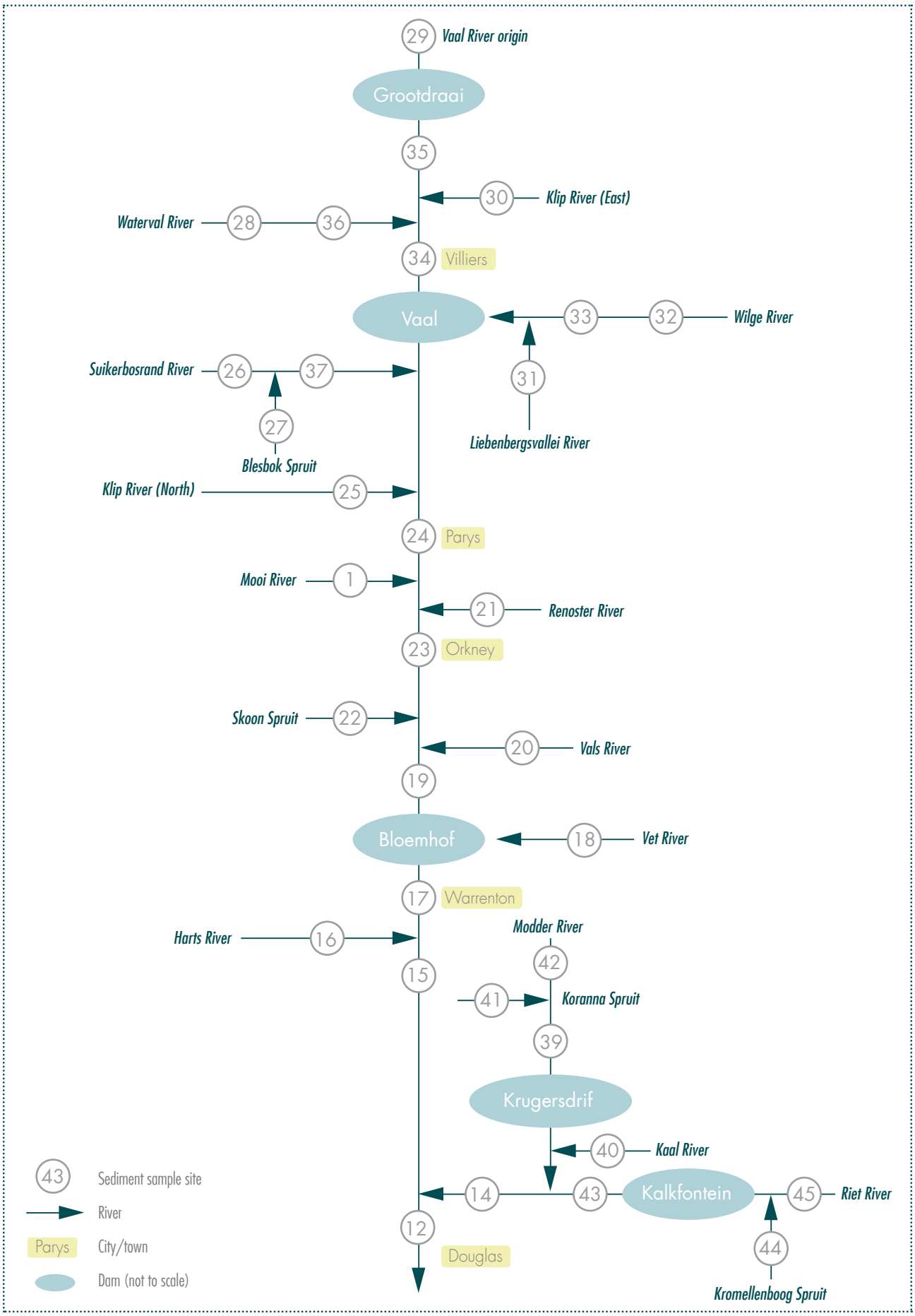


Figure 3: A diagrammatic representation of the Vaal River catchment (also see Figure 2).

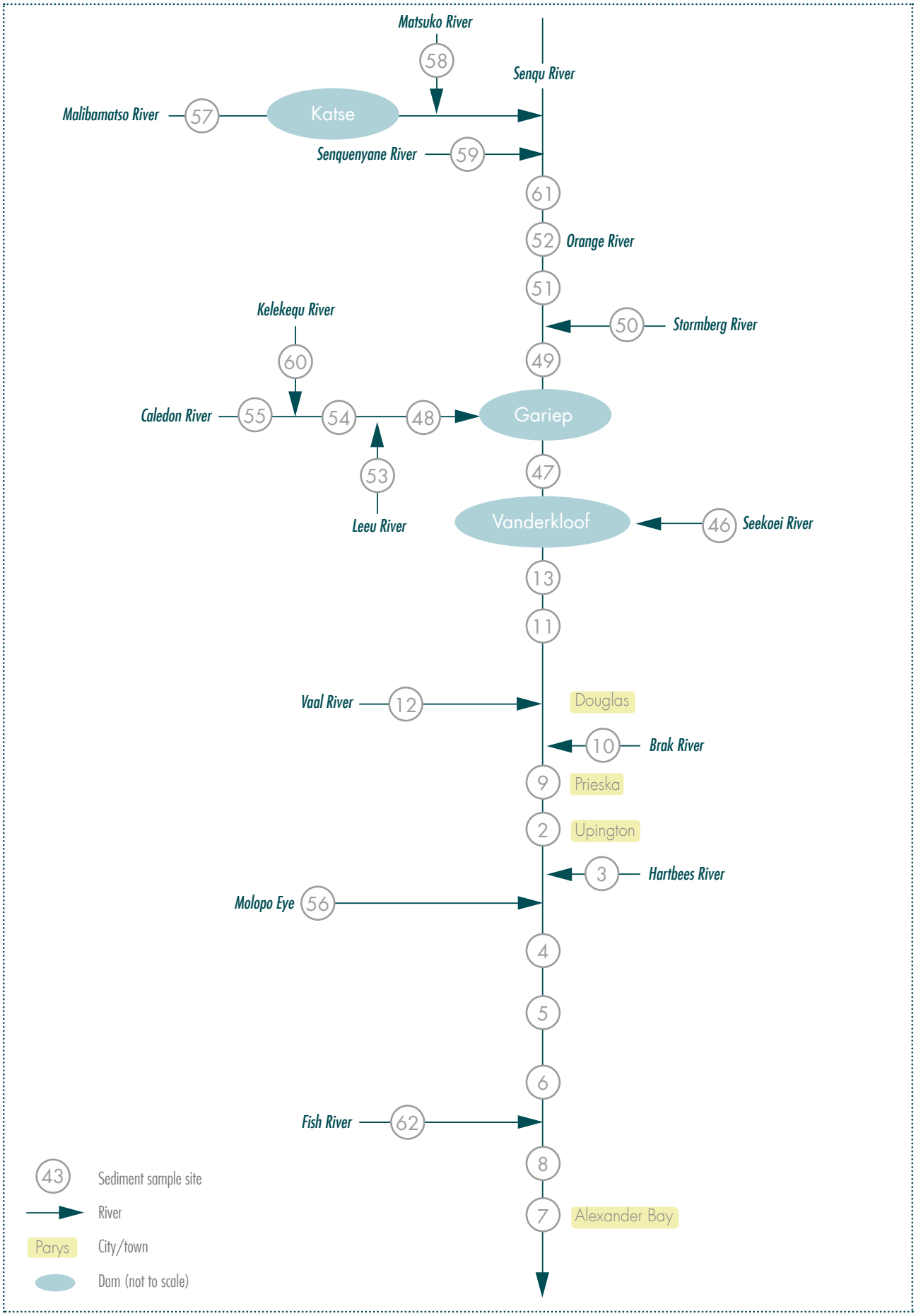


Figure 4: A diagrammatic representation of the Orange–Senqu River catchment excluding the Vaal River catchment (also see Figure 2).

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

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.

© Ian Smith

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.

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

		Coordinates			
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	V1	29.51	-26.86	Standerton	Vaal River
	V2	27.40	-26.92	Parys	Vaal River
	V3	24.16	-28.56	Rooipoort	Vaal River
	O1	26.71	-30.68	Aliwal North	Orange River
	O2	22.21	-29.21	Boegoeberg	Orange River

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_3 at 50–60°C and allowed to evaporate to 5 mℓ. The samples were further treated with H_2O_2 and

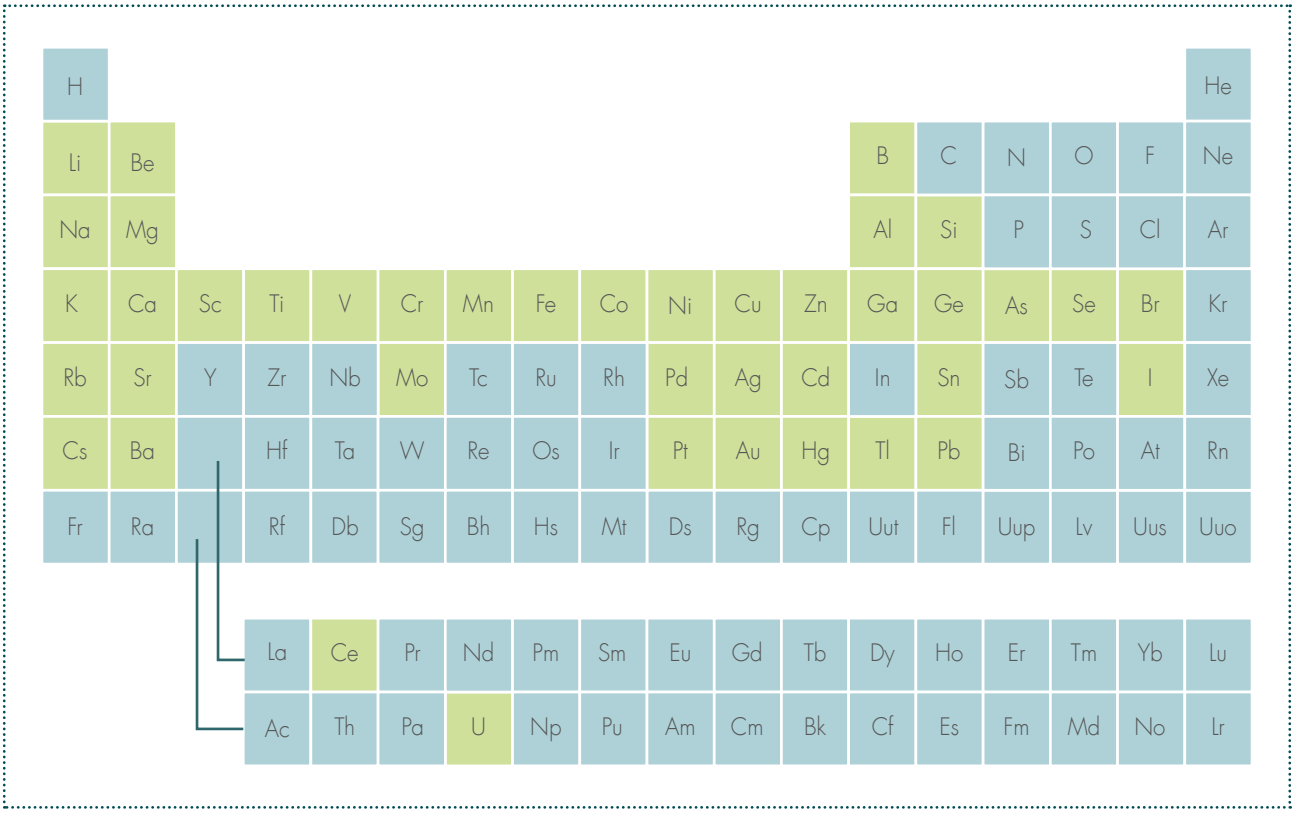


Figure 6: Samples were analysed for the elements highlighted in green.

allowed to cool before the addition of 3 mol/ℓ 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

the dissection process were followed. Fillets for POPs analysis were wrapped in pre-cleaned (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.

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

Pool number	Site label	Body mass (g)	Gender	Total length (mm)	Standard length* (mm)	Girth (mm)
Pool 1	O2	1,920	Male	670	610	290
		1,540		610	550	260
		3,020		790	720	330
		3,280		795	710	335
		2,880		560	500	260
Pool 2		2,240	Female	700	640	300
		1,300		570	530	255
		2,340		730	680	300
		2,740		710	640	320
		2,240		740	670	295
Pool 3	V1	3,160	Male	780	690	340
		2,950		760	730	300
		5,900		1,030	930	490
		4,900		1,040	930	375
		4,260		810	740	360
Pool 4		3,280	Female	760	690	360
		6,400		990	890	300
		3,800		860	790	345
		2,700		760	680	310
Pool 5	V2	4,200	Male	800	730	345
		4,340		790	700	350
		4,140		850	770	350
		4,700		790	760	340
Pool 6		3,520	Female	720	660	320
		3,960		760	690	340
		4,140		770	700	340
		4,150		770	750	330
		3,560		750	660	320
		4,560		830	760	340
Pool 7	V3	3,660	Male	820	740	370
		9,060		1,070	980	505
		12,380		1,200	1,060	555
		11,000		1,200	1,070	560
		2,960		745	660	335
Pool 8		7,560	Female	980	890	500
		2,940		750	670	335
		3,860		840	760	370

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

Bird egg sampling


© Ian Smith

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.

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

Location	Pools	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*

3. RESULTS

© Ian Smith

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).

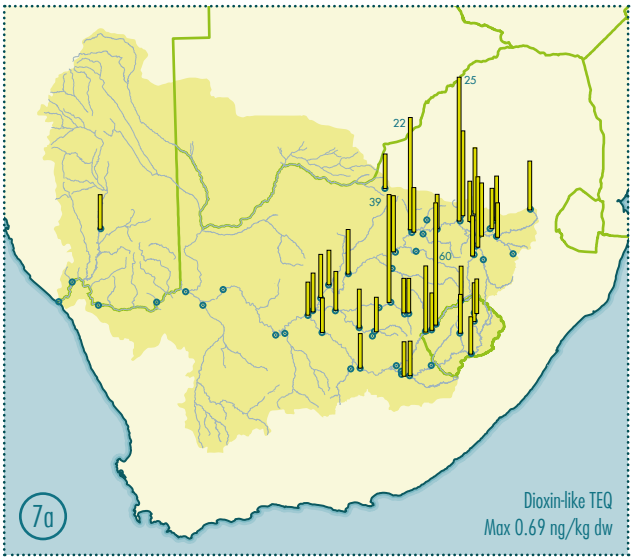
The distribution of PCBs (Figure 7b) largely reflects the TEQ distribution, and it is presumed that the same pollution sources are involved. However, site 56, at the Molopo Eye, had relatively high PCBs compared to dioxin-like TEQs, and this difference cannot yet be explained.

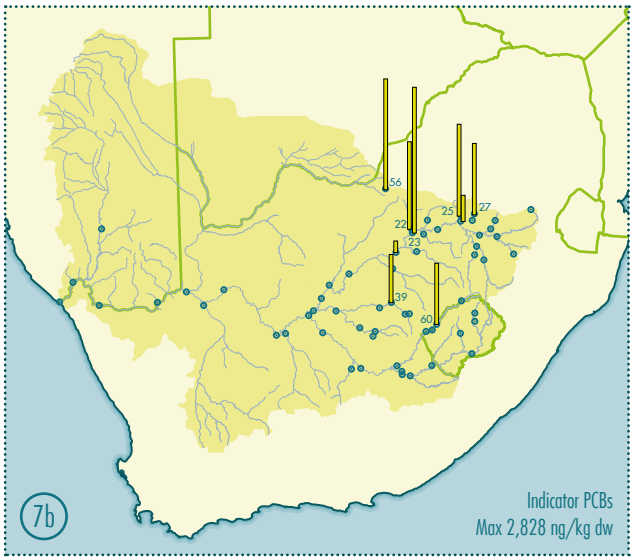
Blesbok Spruit (site 27), Suikerbosrand (37), Potchefstroom (1) and Klerksdorp (22) had the highest levels of OCPs, mainly in the form of legacy DDT. This pollution seems to be isolated in distribution, as neighbouring sites downstream generally had low or undetectable levels of OCPs (Figure 7c).

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

The highest ∑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).

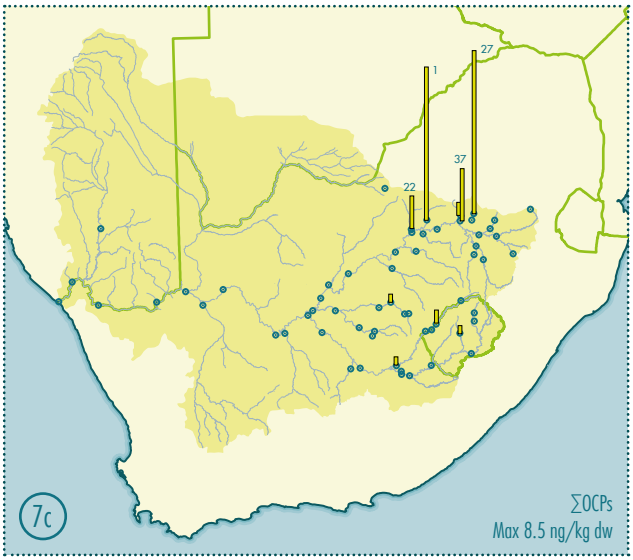
Table 5: The mean concentrations and other summary statistics for PAHs in the sediment at all sites. Units are mg/kg dw.

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

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.



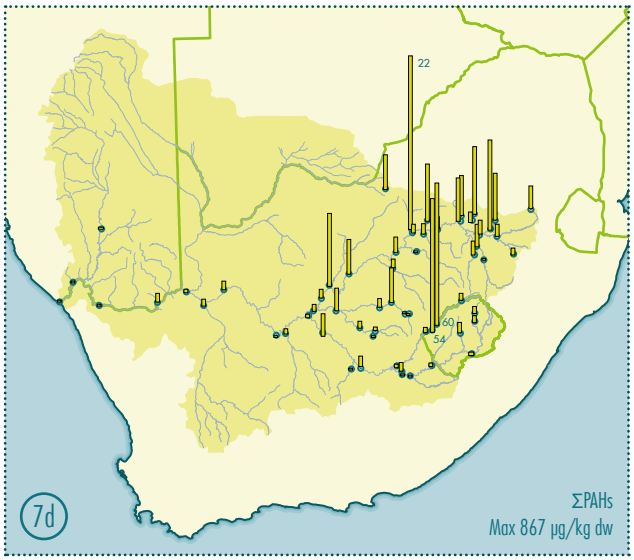


Table 6: The PAH ratios of the sediment sites according to pyrogenic or petrogenic origin. The shaded cells in columns 1 and 2 indicate predominant pyrogenic origin, and shaded cells in column 3 indicate contributions from coal/coke sources or smelters.

flu fluoranthene
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	11.7	1.0
10	1.0	7.9	1.3
11	2.7	9.5	1.0
12	1.3	10.9	1.1
13	1.6	10.9	1.2
14	1.5	14.1	1.1
15	1.3	8.9	1.0
16	1.3	3.6	1.0
17	1.1	5.9	0.9
18	2.3	37.0	1.0
19	1.3	7.1	1.0
20	1.0	12.3	1.0
21	1.0	9.0	1.1
22	1.3	6.4	0.8
23	1.3	7.2	1.5
24	1.3	5.8	1.2
25	0.9	4.3	1.0
26	1.9	10.3	1.8
27	1.3	6.3	0.9
28	1.3	3.2	0.8
29	1.3	8.2	0.8
30	1.0	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	1.1
36	1.5	6.4	0.7
37	1.3	5.5	1.0
39	1.2	5.5	0.8
40	1.4	7.0	1.3
41	1.0	8.3	1.0
42	1.0	7.7	1.0
43	1.2	8.8	1.0
44	1.0	6.3	1.0
45	1.8	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	1.1	6.3	0.7
60	1.5	8.2	0.9
61	1.6	7.4	1.4
62	1.0	2.3	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

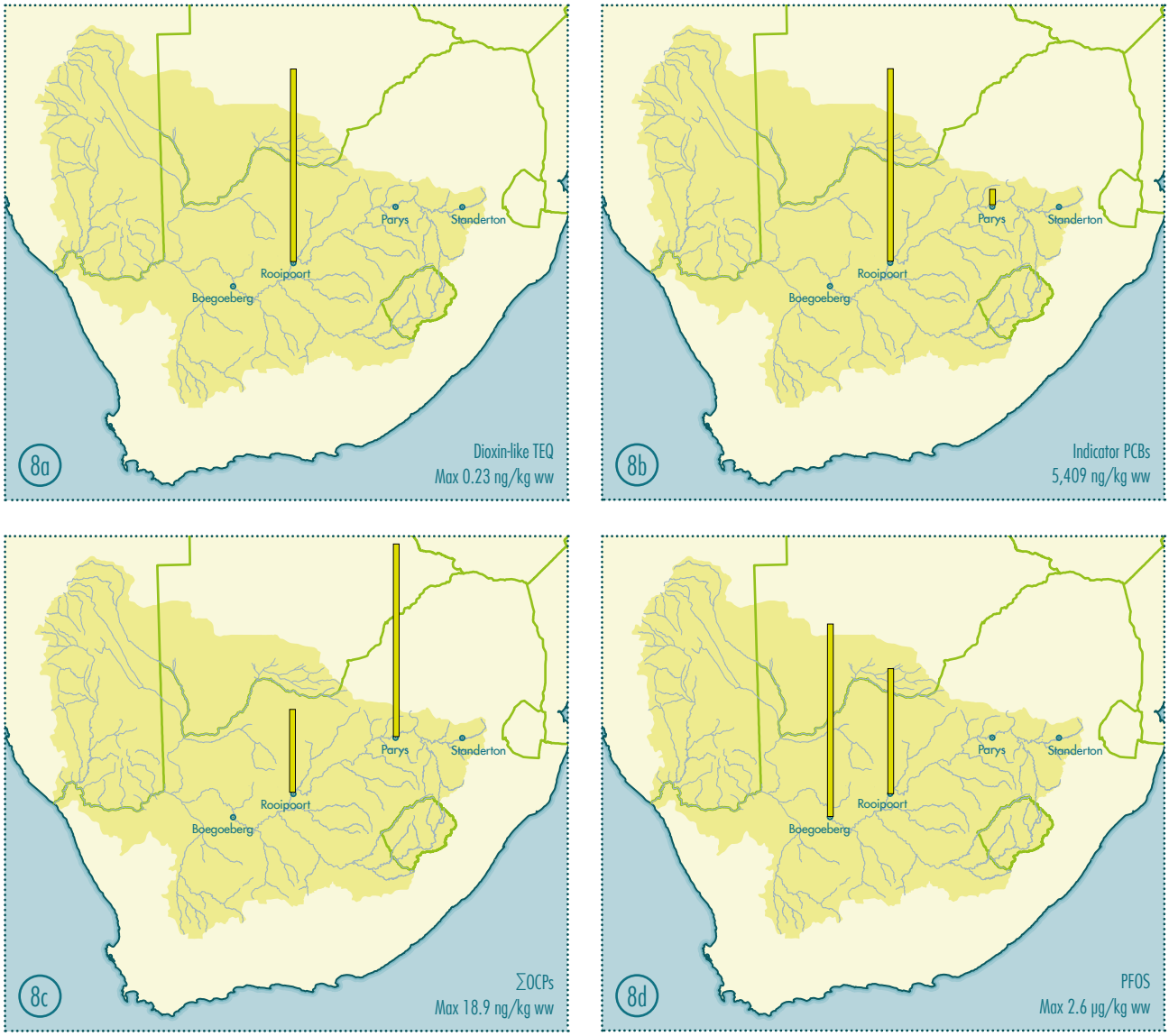


Figure 8: Distribution of pollutants in fish from the sampling sites. Sites indicated with small dots have pollutant levels at or below detection limit. Bar scale is relative. Max = maximum concentration at any of the sites.

© Henk Bouwman

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.