Orange-Senqu River Basin

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

UNDP-GEF
Orange-Senqu Strategic Action Programme
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Survey Design Report

2010 Joint Orange-Senqu Survey
Survey of Persistent Organic Pollutants and Heavy Metals

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2010 Orange-Senqu Survey
Survey of Persistent Organic Pollutants and Heavy Metals

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Revision	Description	Date	Signed
0	Draft for internal review	24 Aug 2010	HB, RP, mor
1	Updating fish survey	02 Sep 2010	HB, RP, GOB, mor
2	Including the locations of fish survey, map of survey locations	20 Sep 2010	HB, RP, GOB, mor

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Contents

1. Review of previous research

1.1 Research on POPs

The four southern African countries, Botswana, Lesotho, Namibia and South Africa, which each has a contribution to the Orange-Senqu River Basin, have all consented to the Stockholm Convention on Persistent Organic Pollutants. Botswana and Namibia expressed their consent to be bound by the treaty by accession. South Africa and Lesotho are signatories and have ratified the Stockholm Convention. Despite their intentions to participate in this treaty and fulfil their obligations towards the stipulations of the Convention, very little is known about levels, distribution and behaviour of the persistent organic pollutants (POPs) in these countries.

The Stockholm Convention originally focused on 12 chemicals or chemical classes, the so called dirty dozen. Initially included in this list were polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzo furans (PCDFs), aldrin, dieldrin, 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane (DDT) and its major metabolites 1,1-dichloro-2,2-bis (p-chlorophenyl) ethane (DDD) and 1,1-dichloro-2,2 (p-chlorophenyl) ethylene (DDE), endrin, chlordane, hexachlorobenzene (HCB), mirex, toxaphene and heptachlor. Nine new POPs were added to the SC in May 2009. They are chlordecone, hexabromobiphenyl, hexabromodiphenyl ether (hexaBDE), tetrabromodiphenyl ether (tetraBDE), pentabromodiphenyl ether (pentaBDE) heptabromodiphenyl ether (heptaBDE), HCH (including α-HCH, β-HCH and γ-HCH), pentachlorobenzene, perfluorooctane sulfonic acid (PFOA) and perfluorooctane sulfanyl fluoride (Stockholm Convention on POPs, 2010).

Compared to the amount of literature available on heavy metals in general for the four countries, very little is known regarding POPs. This brief literature overview include all the POPs literature available for the four countries and does not focus on the Orange-Senqu system exclusively.

In 2001-2002 two of the authors of this report, Prof H Bouwman and Dr R Pieters (then Vosloo) participated in a Global Environment Fund (GEF) web based survey to create a database of all the information published on persistent toxic substances for South Africa, Lesotho, Botswana, Namibia, Swaziland and Zimbabwe (Bouwman et al.,. 2002). This 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 1970's. Until then, Lesotho had no environmental data that could be traced. It still does not have any. For all the countries, the most data were obtained for the organochlorine pesticides (OCs). Including HCB, 93% of the scant 43 publications was on the OCs, with DDT (26%) and dieldrin (17%) leading. The focus on DDT was expected as it was used for vector control in malaria and tsetse-fly areas. DDT is still sprayed in northern KwaZulu-Natal and the Limpopo Province in South Africa for malaria control after it was proven that replacing DDT by

pyrethroids (end 1996 to start of 1999) was not successful (Bouwman, 2003). Very little was known for PCBs (8.5%) and PCDD/Fs (0.2%). Of these, some work has 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: The presence of these classes of compounds was established in human breast milk, and showed that urban women had higher levels than rural women (Schecter et al., 1990).

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

Since the GEF survey and the O'Donoghue and Marshall (2003) review paper, more publications appeared on levels of POPs in humans in South Africa, particularly DDT levels (Bouwman et al., 2006), but also selected PCBs, HCH, 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 to (Van Dyk et al., 2010).

Recent reports of POPs in wildlife include the organic chlorine levels in Cape fur seals harvested commercially in southern Africa (Koep et al., 2007) and HCB, DDTs, HCHs, chlordanes and PCBs in South African birds (Bouwman et al., 2008). This latter paper has data on birds from the Vaal River, which is one of the tributaries of the Orange River and as such included in the present study. The same group of researchers also published a paper on the polybrominated diphenyl ethers and hexabromocyclododecane (HBCD) in birds' eggs. The highest levels were found for eggs collected close to the Vaal River (Polder et al., 2008). DDT and its metabolites' levels were reported for water, sediment, fish, chickens and wild birds in an area still sprayed for malaria (Barnhoorn et al., 2009).

Environmental levels (soils and sediment) for POPs published in the past 5 years include levels of PCDD/Fs and dioxin-like PCBs for 22 aquatic sites in South Africa (Vosloo and Bouwman, 2005). This survey also included a few sites from the Orange River, the Vaal River 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 through which the Vaal River travels (Pieters et al., 2008). Levels of PAHs, PCBs, dioxin-like chemicals and OCPs are also reported for a central part of South Africa, including the Vaal Trianle (Quinn et al., 2009). Another paper that also appeared in 2009 compared specifically dioxin-like chemicals in the soil and sediment from residential and industrial areas in central South Africa (Nieuwoudt et al., 2009).

Ambient air in Durban were analysed for the OCs 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 (GAPS) study (Pozo et al., 2009). Levels for PAHs, PCDD/Fs, PCBs, HCH, endosulfans and DDT and its metabolites were reported. Compared to the other African sites, the three South African sites were at the lower end. All three the areas are within the Orange-Senqu Basin.

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

No recent (since the GEF survey) publications on POPs were found for Namibia, Lesotho or Botswana.

1.2 Research on heavy metals

Whereas very little is known regarding POPs levels and distributions for the four countries, much more is known about heavy metals. It was therefore possible to focus on literature that specifically contained information on heavy metals in the Orange-Senqu Basin. This include references to heavy metals in biota, air and sediment. The literature search was by no means meant to be exhaustive. No publications could be traced for Namibia, Botswana and Lesotho that directly link heavy metal contributions to the Orange-Senqu Basin. Therefore, the overview contains references to mainly South African sites.

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

A study on the Natal Spruit (Naicker et al., 2003) (which is in the catchment of the Vaal River) showed that shallow ground water is contaminated as a result of mining activities. Mining activities impacts on the quality of the water from the Witwatersrand watershed. The type of pollution is not

only affecting the pH of the water but contributes heavy metals to surface water. Evaporation of ground water off the capillary zone above the water table creates a surface soil layer along the banks of the Natal Spruit which is extremely enriched in heavy metals. During the dry winter months a gypsum crust develops on this surface. This also adds to the metal load in the stream when surfaces soil and the crust dissolves.

The Witwatersrand basin is also a source of low grade uranium. Because of the low grade, uranium is mainly produced as a by-product of gold. 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 slime dams is 100 ppm. In a case study in the North West Province it was found that dissolved uranium and other heavy metals move along with seepage from tailings deposits of, the now closed Stilfontein gold mine, into groundwater, which finally seeps into the Koekemoer Spruit (tributary of the Vaal River). This study proved 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 the 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 most enriched, often by a factor of 20–400. Significant enrichment of uranium, mercury, vanadium, chromium, cobalt, copper and sink was also observed in the sediments. Although the geo-accumulation 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 indexes (MPI) values were found at sites that were close to tailings dams.

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

It is also possible that heavy metals suspended as air particles might contribute to the loads in the aquatic systems. The lead that was monitored in the atmosphere of Johannesburg, mainly came from the 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 the mine tailings dumps seemed to be geographically limited. Domestic coal burning only contributed a small portion of the total lead in the atmosphere.

Although the focus of this survey is not on air pollution, one should not forget about the possible contributing sources of heavy metals when results have to be interpreted. Coal from the Highveld coal field were analysed for 14 trace elements because of the perception that they are hazardous to human and animal life (Wagner and Hlatshwayo, 2005). The concentrations of chromium and manganese were 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 emitted to our atmosphere.

South Africa is regarded as the country with the second highest mercury emissions in the world. This assumption is based on estimates of total mercury emissions derived from gold mining and coal combustion. Mercury emissions from coal-fired power plants range between 2.6 and 7.6 t/a (Dabrowski et al., 2008).

Some of these air borne mercury and other heavy metal particles are bound to be deposited again and carried to rivers and streams when it rains.

2. Survey design

2.1 2010 Joint Orange-Senqu Survey

ORASECOM intends to undertake a basin wide water quality and aquatic ecosystem health survey in September / October 2010 – the 2010 Joint Orange-Senqu Survey. The Survey shall provide a comprehensive baseline of the chemical, physical, and ecological condition of the Orange-Senqu River System. The following investigations shall be carried out:

- Sampling and analysis of physical and chemical water quality parameters, following the methodology and identified 12 sampling points proposed in the report "Framework for Water Resource Quality Monitoring". To be conducted by the GTZ supported project and the respective line agencies of the ORASECOM member States.
- Sampling and analysis of bio-indicators, following the methodology and identified 52 sampling points proposed in the report "Aquatic Ecological Health Monitoring Programme". To be conducted by the EU supported project.
- Sampling and analysis of POPs and heavy metals in water bodies and sediment, methodology and sampling points to be determined. To be funded by the UNDP-GEF Project.

The Survey will be supported by the respective line departments of the governments of the ORASECOM member States. Further technical expertise may be provided by seconded experts from the International Commission for the Protection of the Danube River (ICPDR).

2.2 Roles and responsibilities

The North-West University, South Africa assigned the following roles and responsibilities for the implementation of the survey:

- Project management: Prof H Bouwman and Dr R Pieters;
- Conceptualization and detailed survey design: Prof H Bouwman, Dr R Pieters, Mr I Smith;
- Sampling of sediment and bird eggs in the field: Prof H Bouwman, Dr R Pieters, Mr I Smith;
- Sampling of fish in the field: Dr R Pieters, Mr G O'Brian;
- Sample handling and shipping: Laboratory of North-West University;
- Chemical analysis of POPs: Accredited laboratory, to be determined;
- Chemical analysis of heavy metals: Laboratory of North-West University;
- Interpretation of results and reporting: Prof H Bouwman and Dr R Pieters.

2.3 Sampling sites

POPs and heavy metal sampling will be conducted as part of the monitoring of water resource quality under the 2010 Joint Orange-Senqu Survey. Sampling sites will follow those 56 sites proposed and outlined in the report: OSAEH Programme – Orange-Senqu Aquatic Ecosystem Health Monitoring Programme (2009). An additional six sites will be added to these, which are regarded as important and relevant in elucidating the current POPs and heavy metal status in the basin (a list of the sites with their coordinates is included as Appendix A).

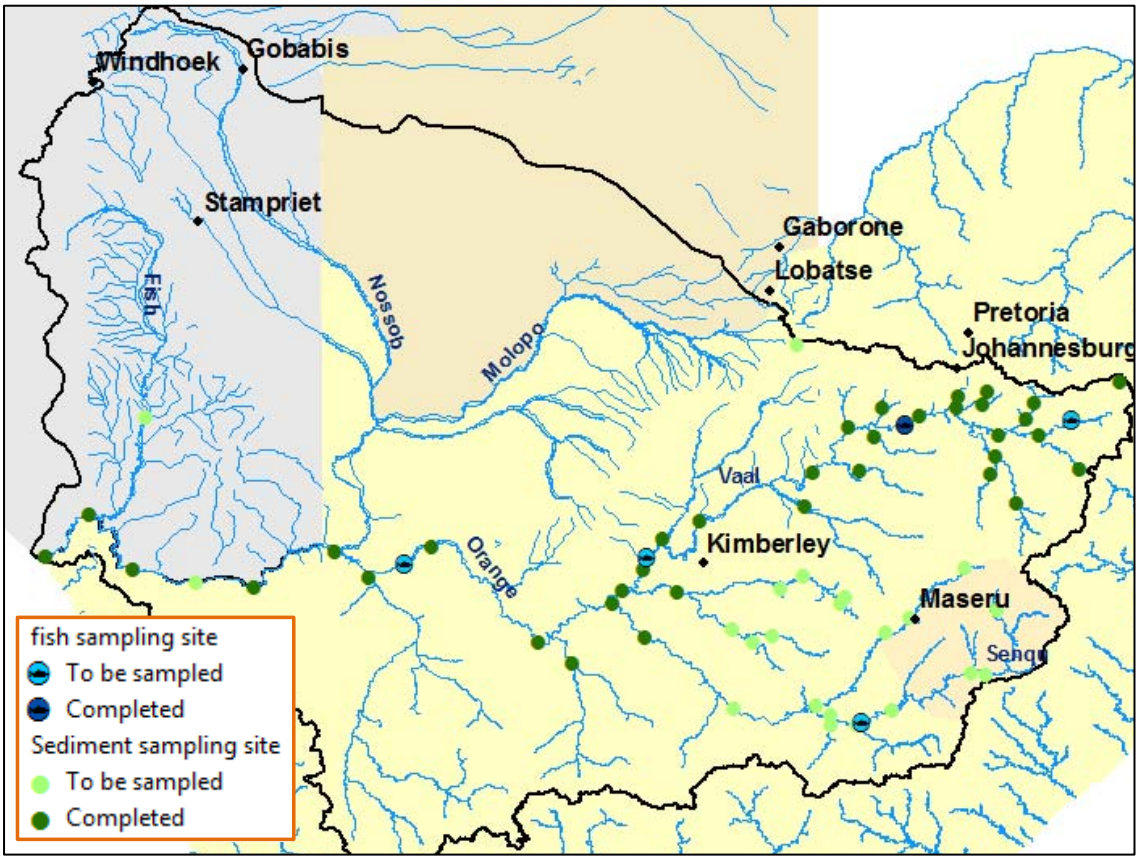

Figure 1. Sampling sites and progress as per 20 Sep 2010.

POPs and heavy metal sampling will focus on riverbed sediments at all sixty predetermined sites.

Aquatic bird eggs will also be sampled at two to three sites. Identification of these sites will depend on the breeding colonies spotted during the sediment collection trip and from information obtained from other sources. The aim is to collect eggs from an area at the Orange River mouth, the middle region, and close to the origin in Lesotho. Should breeding activity not coincide with sediment sampling effort, another period will be set aside for such sampling.

The fish survey is planned to be carried out at four to five sites along the Orange-Senqu River System in South Africa. Local anglers with a wealth of local fisheries knowledge have been

contacted for advice, and access to sites has been arranged. The sites are: (1) site NWU 7 on the Upper Vaal River above the Vaal Dam in the vicinity of Standerton in Mpumalanga; (2) site NWU 8 on the Vaal River downstream of the Vaal River Barrage in the vicinity of Parys; (3) site NWU 9 is proposed on the Upper Orange-Sengu River above or in the vicinity of the Gariep Dam, ideally close to Aliwal North; and (4) site NWU 10 located on the Lower Orange-Sengu River in the vicinity of Keimoes downstream of Upington. Time permitting (5) site NWU 11 at Rooiport will be sampled (a list of the sites with their coordinates is included as Appendix A).

Additional fish samples may be obtained from the Aquatic Ecosystem Health Monitoring team. Again, the approach is to obtain fish samples from the mouth, the middle and the origin. Sample locations, fish species and numbers to be collected are yet to be determined.

2.4 Sampling methods

The sampling methods described are focused on POPs because sampling for them is more complex than sampling for heavy metals. Samples for heavy metal analysis will therefore be collected, stored and transported in the same manner as for POPs.

Sediment samples

Sediment samples will be collected following standardised protocols (US EPA, 2004). All equipment that come into contact with the sediment samples will be of glass or stainless steel and pre-cleaned as follows: washed with warm water and phosphate-free soap, rinsed with tap water, followed with de-ionised water (18 MΩ), acetone (Burdick and Jackson), and hexane (Burdick and Jackson). Both the acetone and hexane must be of the quality used in high pressure liquid chromatography. The acetone removes all polar contaminants and the hexane all non-polar contaminants.

All the sites will be sampled from the bank of the river or stream, i.e. where the water is accessible to humans on foot. Where applicable, slow flowing stretches of the rivers will be chosen and where the bottom is visible, sampling will focus on pockets of silt and fine sediment.

Equal volumes of individual sediment samples from four different locations at a particular site will be pooled to obtain a composite sample. Core samples will be taken of the top 50cm. The entire core will be used to create a composite sample. The composite sample will be stirred vigorously before three sub-samples are transferred into pre-cleaned, labeled glass jars. Each sample will be covered with cleaned aluminum foil to prevent possible contamination by the lining of the screw top of the jars. The samples will be protected from ultraviolet and microbial breakdown by storing in the dark and at 4°C. The samples will be stored temporarily at the North-West University in Potchefstroom before it will be shipped to the POPs laboratory. The sediment will be air dried or freeze dried depending on the requirements of the analytical laboratory. The heavy metal analysis will be done by the North-West University. This laboratory participates in the following quality

control schemes: (1) Agricultural Laboratory Association of Southern Africa and (2) International Soil-Analytical Exchange (ISE), Wageningen, The Netherlands.

The sediment samples will be acid digested using concentrated nitric acid, hydrogen peroxide and diluted hydrochloric acid in a sand bath close to boiling point. The extracts will be analyzed through inductively coupled plasma mass spectrometer (ICP MS), an Agilent 7500C.

Sampling of birds' eggs

Before any eggs are collected, permits will be obtained from the Lesotho government as well as the respective provincial Directorates for Nature Conservation of Mpumalanga, North-West, Gauteng, Free State and the Northern Cape, South Africa.

Breeding roosts of the following fish eating bird species will be targeted for egg collection: White breasted cormorant *(Phalacrocorax lucidus)*, reed cormorant *(Phalacrocorax africanus)*, African darter *(Anhinga rufa)*. Where feasible only the c-egg (or last egg laid) will be collected. C-eggs usually have a weaker chance of survival and have been found to contain a larger amount of pollutants. The earlier eggs are mainly produced through energy derived through the female's food intake and the fatty tissue is more strongly utilized when the last eggs of the clutch are laid since food intake is normally reduced during laying periods (Nisbet, 1982). No more than one egg per clutch will be collected.

Collected eggs will be stored at –20 ºC until the eggs can be thawed and the contents separated from the shell. The contents will be homogenised (Jaspers et al., 2005) and the eggshell left to air dry until completely dry. The thickness will be measured till the nearest 0.001 mm (Fernie et al., 2000).

The contents of the eggs will be placed in pre-cleaned high-density polyethylene bottles and shipped to the analytical laboratory for POPs analysis. Lipid content of the eggs will be determined gravimetrically. Pollutant concentrations of specifically the POPs are expressed as unit mass per lipid content. Heavy metal analysis will be done by the North-West University's laboratories following a similar protocol as described for sediment.

Sampling of fish

Preferably the fish species collected at each of the sites should be the same species and it should be a species consumed by humans. In this way, possible human risk assessment can be done once the concentration data had been compiled. The species must also be distributed through out the entire Orange-Senqu Basin. Three species suggested are: (1) Vaal-Orange largemouth yellowfish *(Labeobarbus kimberleyensis)* which is a predator; (2) Vaal-Orange smallmouth yellowfish *(Labeobarbus aeneus)* which is omnivorous and (3) sharptooth catfish *(Clarias gariepinus)* which is completely omnivorous (Skelton, 2001). The advantage of selecting the catfish is that it is widely distributed in

southern Africa, making comparisons between the Orange-Senqu Basin and rivers from other parts of southern Africa possible (Skelton, 2001).

The survey will include at least two nights and one day of sampling effort at each site. Attempts will be made to collect 10 Orange-Vaal largemouth yellowfish and either 10 Orange-Vaal smallmouth yellowfish or 10 sharptooth catfish from each site. The sampling effort will include the use of active and passive netting techniques where applicable, electrofishing, and angling techniques.

Once collected the fish will be maintained in a large steel holding contained submerged into the river in a quiet area. The team will ensure that no fish are unnecessarily destroyed in nets etc. by observing the sampling methods constantly and then removing desired specimens and relocating them into large floating holding containers and releasing undesirable species.

Once sufficient individual have been collected dissections will take place and include the following:

- Individuals will be weighed (to the nearest 10g), photographed and lengths and girth taken.
- Individuals will be killed and dissected and various tissues for histopathology will be collected including gill, heart, liver, spleen, kidney, muscle tissues and stored in buffered formalin, then gonads will be collected and stored in Bouin's solution.
- Then, after "washing" dissection equipment two fat samples will be collected weighed and stored in cleaned aluminium foil (for organic analyses) and plastic bags (for heavy metal analyses). Muscle will also be collected and weighed in a similar manner.
- Finally a genetic sample will be collected and stored in 96% ethanol.
- All histopathology samples will be stored in labeled boxes and tissues will be stored on ice in the field and frozen within six hours. Frozen tissues will then be kept frozen until delivery to the North West University with other tissues.

Composite samples will be prepared in the North-West University's laboratories and distributed to the analytical laboratories. The samples will be stored at -20°C until analysis can be performed by the respective laboratories.

Samples will be sent to a POPs analytical laboratory and heavy metal analysis will be done by the North-West University's laboratories. A similar protocol as for sediment analysis will be followed.

Total organic carbon analysis

It is necessary to determine the total organic carbon (TOC) content of the sediment samples specifically to make better sense of the POPs data as these compounds tend to adhere to the carbon particles in the sediment. Biological responses of benthic organisms to non-ionic organic chemicals in sediments are different across sediments when the sediment concentrations are expressed on a dry weight basis, but similar when expressed on an organic carbon normalised basis (US EPA, 2000). By measuring the TOC in sediments and soils, concentrations can be expressed as normalised concentrations, i.e. what the concentration would have been if the entire sediment

sample consisted of only organic carbon. Normalised concentrations allow for comparison between sites without considering the characteristics of each site (Froese et al., 1998). Knowing the TOC content of a sediment sample also allows for interpreting the results in terms of 1g TOC which is the unit in which international sediment quality guidelines (such as the Canadian sediment quality guidelines, 2002) are made available.

Measuring the %TOC will be done by using a TruSpec CN analyser. Organic carbon is determined gravimetrically by loss-on-ignition at 850 to 950°C. The mass of the sample only need to be 0.2g.

2.5 Quality Assurance / Quality Control

The complete POPs analysis will be executed under a joint and unique QA/QC-protocol under the ISO 17025 accreditation covering:

- Sample logistics;
- Sample preparation;
- Sample storage;
- Method of analysis (calibration, extraction, cleanup, measurement, quantification, QC);
- Calculation;
- Reporting.

Consequently, all analyses will be executed under the accreditation acc. DIN EN ISO/IEC 17025:2005, and the complete project will be controlled by one quality manager of the accredited POPs laboratory. QA/QC covers (among others):

- All analyses are controlled – among others - by regular and successful participation in inter-laboratory comparisons.
- Furthermore, reference material (either certified reference material or stable internal reference materials) are analysed regularly and together with the project samples. These levels have to be within given limits to demonstrate constant analytical conditions.
- Corresponding control charts illustrate the long term behaviour of the analysis.
- Beyond this, regularly – and also within the project – selected individual samples are analysed in double to control sample to sample deviations. Deviations has to be within given limits.
- The general and extended uncertainty of measurement is determined for every analytical parameter.
- Analytical blank levels are determined regularly – and within the project - covering the complete method (pretreatment, extraction, clean-up, measurement).
- In case of unexpected high levels of individual samples, closely related samples (both at pretreatment, extraction, clean-up, measurement) will be completely re-analysed to control for cross contamination. Additional blank level tests will be executed, and analytical work will proceed only in case of approval by QA.

- All analyses are based on isotope dilution method, using isotope labelled internal standards. This allows the control of the recovery ratios (to be within given limits)
- For the analysis of dioxins, furans and PCBs the analysis by high resolution GC / high resolution MS (HRGC/HRMS) is regarded as mandatory.
- For the analysis of POPs-pesticides and brominated POPs low resolution mass spectrometry is applied, for confirmatory cases, high resolution methods are available. Fluorinated POPs are analysed via LC/MS/MS.
- For all analytical parameters calibration has to cover at least six calibration levels covering the complete concentration level of the samples. If the concentration level of the samples range over several decade, number of calibration steps has to be extended accordingly.
- Extraction efficiencies for the individual sample matrix of the used method are demonstrated within the validation data of the individual methods.
- Internal standards will be added prior to extraction in each cases in order to control the complete analysis (recovery ratios has to be within given limits).
- In case of deviation from the given QC limits, an analysis has to be repeated completely.

2.6 Public participation and training

The public communication and outreach events will be attended as required by prior arrangement.

Professionals or the respective government departments and academia have been invited to join (some of) the field work. These professionals will have to be independently mobile. Convenient localities shall be arranged at which on-the-job training for POPs sampling can be conducted.

Even though some of these activities may overlap with other line-functions, the team will endeavor to meet the expectations of ORASECOM.

2.7 Logistics

An estimated distance of 10,500 km will be covered by the team sampling sediment and bird eggs, in order to visit and sample the 60 sites once, within a time frame of 25 days. Most sampling sites are close to roads and bridges, allowing relatively easy access. Additional arrangements will be made on site or by prior arrangement where appropriate. Many of these sites have been visited previously.

The sediment and bird egg sampling effort will start on 6 September 2010. The team envisages breaking up the trip into three legs:

- Orange River Mouth to Potchefstroom;
- Potchefstroom to Senqu River source (Lesotho);
- Potchefstroom to Vaal River source.

Independently, a second team will be sampling fish and the four predetermined sites. This effort will also start on 6 September 2010, and is scheduled to continue for 14 days. From their base at Potchefstroom this team will conduct four trips to the individual sites. An estimated distance of 1,600km will be covered.

Collected samples will be stored in a portable freezer, and then either deposited on return trips at the University facilities, or couriered (cool box with ice packs) from field positions to the North-West University, South Africa, should freezer capacity run out during a trip.

Requirements:

- Vehicles (4x4 pickup or similar);
- Vehicle recovery equipment (e.g. compressor, snottplugs, spade, jack etc);
- Sample collecting equipment;
- Fishing gear;
- GPS with relevant software installed (Tracks4Africa);
- Video camera;
- Tent and sleeping bags (should camping be required);
- Assistant/technician;
- Handheld maps/fact sheets of the different monitoring sites;
- Funds/budget for fuel, sustenance, toll roads, accommodation, etc.;
- Laptop;
- Cellular phones and two-way radios;
- First-aid kit.

Samples will be couriered to the POPs laboratory using our normal courier for this purpose.

Appendix A: Sampling sites

Adapted from: OSAEH Programme - Orange - Senqu Aquatic Ecosystem Health Monitoring Programme, Report No. ORASECOM 009/2009, November 2009.

No	*OSAEH code*	*Site category*	*Catchment*	*Lat*	*Long*
1	OSAEH 11 1	Monitoring Site P	Vaal	-27.51729	26.21604
2	OSAEH 11 2	Monitoring Site P	Vaal	-27.03820	28.57393
3	OSAEH 11 3	Monitoring Site C	Vaal/Mooi	-26.68283	27.09856
4	OSAEH 11 4	Monitoring Site C	Vaal/Skoonspruit	-26.93333	26.66527
5	OSAEH 11 5	Monitoring Site C	Vaal/Vals	-27.48683	26.81305
6	OSAEH 11 6	Monitoring Site P	Vaal/Renoster	-27.05286	27.00991
7	OSAEH 11 7	Monitoring Site P	Vaal	-27.03040	29.08733
8	OSAEH 11 8	Ecological Reserve Site	Vaal/Blesbokspruit	-26.47500	28.43194
9	OSAEH 11 9	Reference Site	Vaal/Klip	-27.47008	29.60048
10	OSAEH 11 10	Ecological Reserve Site	Vaal/Waterval	-26.63518	29.02262
11	OSAEH 11 11	Ecological Reserve Site	Vaal/Waterval	-26.83428	28.92836
12	OSAEH 11 12	Monitoring Site C	Vaal/Klip	-26.54934	28.06435
13	OSAEH 11 13	Reference Site	Vaal/Kromellenboogspruit	-26.80030	27.58428
14	OSAEH 11 14	Monitoring Site C	Vaal/Suikerbosrand	-26.68122	28.0501 1
15	OSAEH 11 15	Reference Site	Vaal/Suikerbosrand	-26.64672	28.38197
16	OSAEH 11 16	Monitoring Site P	Vaal/Wilge	-27.30700	28.54195
17	OSAEH 11 17	Monitoring Site P	Wilge/Liebenber	-27.53083	28.47556
18	OSAEH 11 18	Monitoring Site P	Riet/Modder	-29.16111	26.57194
19	OSAEH 11 19	Monitoring Site P	Riet/Modder	-28.80722	26.10694
20	OSAEH 11 20	Ecological Reserve Site	Caledon/Leeuspruit	-29.52197	27.13561
21	OSAEH 11 21	Reference Site	Modder/Karonnaspruit	-29.08107	26.62615
22	OSAEH 11 22	Monitoring Site P	Orange	-30.50472	27.21889

No	*OSAEH code*	*Site category*	*Catchment*	*Lat*	*Long*
23	OSAEH 15 1	Ecological Reserve Site	Caledon	-28.72231	28.15083
24	OSAEH 15 2	Reference Site	Malibamatso/Matsuko	-29.25583	28.56417
25	OSAEH 15 3	Monitoring Site P	Senqu	-30.06556	28.40770
26	OSAEH 15 4	Reference Site	Malibamatso	To be decided	To be decided
27	OSAEH 15 5	Monitoring Site P	Malibamatso	-30.03630	28.22250
28	OSAEH 15 6	Monitoring Site P	Caledon	-29.35434	27.44597
29	OSAEH 26 1	Ecological Reserve Site	Vaal	-29.00083	23.80646
30	OSAEH 26 2	Reference Site	Orange	-29.60070	24.09160
31	OSAEH 26 3	Monitoring Site P	Orange	-29.16207	23.69651
32	OSAEH 26 4	Monitoring Site P	Orange/Hartbees	-28.84095	20.61190
33	OSAEH 26 5	Reference Site	Modder/Kaalspruit	-28.97005	25.80632
34	OSAEH 26 6	Ecological Reserve Site	Riet	-29.48389	25.19861
35	OSAEH 26 7	Monitoring Site P	Orange/Brak	-29.91500	23.17031
36	OSAEH 26 8	Monitoring Site P	Caledon	-30.45233	26.27088
37	OSAEH 26 9	Reference Site	Riet/Krom elenboogspruit	-29.64470	25.46472
38	OSAEH 26 10	Ecological Reserve Site	Riet	-29.57528	25.70805
39	OSAEH 26 11	Monitoring Site P	Orange/Kraai	-30.70364	26.77132
40	OSAEH 26 12	Monitoring Site P	Orange/Seekoei	:30.38766	25.00357
41	OSAEH 26 13	Monitoring Site P	Orange/Stormbergspruit	-30.70364	26.44681
42	OSAEH 26 14	Monitoring Site P	Orange	-30.57305	26.45305
43	OSAEH 26 15	Monitoring Site P	Orange	-30.50305	25.22555
44	OSAEH 26 16	Monitoring Site P	Orange	-29.66075	22.75574
45	OSAEH 26 17	Monitoring Site P	Orange	-28.43861	21.40583
46	OSAEH 26 18	Monitoring Site P	Fish	-26.80313	17.78942
47	OSAEH 28 1	Monitoring Site P	Orange	-28.9641 1	19.14531

No	*OSAEH code*	*Site category*	*Catchment*	*Lat*	*Long*
48	OSAEH 28 2	Monitoring Site P	Orange	-28.51115	20.17482
49	OSAEH 28 3	Ecological Reserve Site	Orange	-28.90205	18.42036
50	OSAEH 28 4	Ecological Reserve Site	Orange	-28.73645	17.61856
51	OSAEH 28 5	Ecological Reserve Site	Orange	-28.04051	17.06967
52	OSAEH 29 1	Monitoring Site P	Vaal/Harts	-28.35124	24.31354
53	OSAEH 29 2	Monitoring Site P	Vaal	-28.11097	24.80193
54	OSAEH 29 3	Monitoring Site C	Vaal/Vet	-27.93412	26.12094
55	OSAEH 29 4	Monitoring Site C	Vaal	-28.72533	24.07293
56	OSAEH 29 5	Ecological Reserve Site	Riet	-29.02805	24.51250
57	NWU1	NWU sediment site POPs	Orange	28°34'14.90"S	16°30'19.01"E
58	NWU2	NWU sediment site POPs	Wilge	27°54'12.01"S	28°48'25.91"E
59	NWU3	NWU sediment site POPs	Vaal	26°21'46.20"S	30°6' 31.04"E
60	NWU4	NWU sediment site POPs	Molopo	25°53' 1.50"S	26°1' 20.56"E
61	NWU 5	NWU sediment site POPs	Vaal	-27.01357	26.67980
62	NWU 6	NWU sediment site POPs	Tweelopie spruit	-26.14622	27.71625

Sampling sites fish survey:

No	*OSAEH code*	*Site category*	*Catchment*	*Lat*	*Long*
63	NWU 7	NWU fish sampling site	Vaal	26°50'49.50"S	29°29'19.44"E
64	NWU 8	NWU fish sampling site	Vaal	26°54'55.65"S	27°23'53.65"E
65	NWU 9	NWU fish sampling site	Orange	30°40'14.29"S	26°50'22.41"E
66	NWU 10	NWU fish sampling site	Orange	28°40'17.58"S	21° 3'37.73"E
67	NWU 11	NWU fish sampling site	Orange	28°35'50.31"S	24° 7'18.83"E

Appendix B: References

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