Executive summary

1. Introduction and historical background

The eastern catchment of the Mooi River, also known as the Wonderfonteinspruit, has been identified in a number of studies as the site of significant radioactive and other pollution, generally attributed to the mining and processing of uraniferous gold ores in the area.

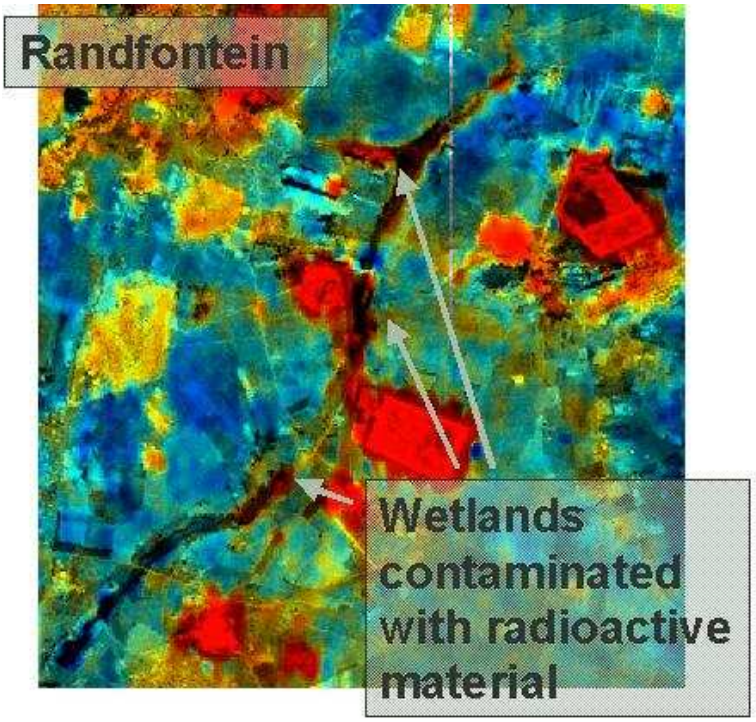
With the establishment of West Rand Consolidated in 1887 gold mining reached the Wonderfonteinspruit catchment only one year after the discovery of gold on the Witwatersrand. By 1895 five more gold mines had started operations in the (non-dolomitic) headwater region of the Wonderfonteinspruit as the westernmost part of the West Rand goldfield. Except for one, today all of these early mines are closed and/or abandoned .

Attempts at gold mining further downstream the Wonderfonteinspruit valley, and to access known gold reefs below water-bearing dolomite, failed because of flooding. With appropriate technology becoming available some 40 years later, a second phase of gold mining started in the study area with three more gold mines being established during the 1930s (Venterspost, Libanon and Blyvooruitzicht). A third phase of mining commenced some 20 years later during the 1950s/early 1960s when the newly developed magnetic prospecting led to seven more gold mines coming into operation in and around the study area. Between 1968 and 1991 a further eight mines were established.

Mining in the study area is spatially concentrated at two major goldfields, namely the West Rand covering a large portion of the non-dolomitic headwater region of the Wonderfonteinspruit catchment, with many dysfunctional and abandoned mining sites, and the Far West Rand in the upper part of the lower Wonderfonteinspruit, consisting of the 'West Wits Line' (mines around the town of Westonaria) and the 'Carletonville mining area' near the city of Merafong. Displaying an average gold concentration in mined reefs of 31 g/t over its history until 1998, the Far West Rand is the richest of all seven active goldfields of the Witwatersrand basin. Important reefs mined in the Far West Rand include (with decreasing depth) the Carbon Leader and Middelvlei Reef of the Johannesburg Subgroup, the Elsburg and Composite Reef of the Turffontein Subgroup, the Ventersdorp Contact Reef and the Black Reef.

With many of the mined reefs containing not only gold, but also elevated concentrations of uranium (up to 5,8%), the Far West Rand was the first goldfield in South Africa in which large-scale uranium production was established. This started in the early 1950s, initiated by the United States' nuclear weapons programme. At one stage 9 out of 22 active gold mines fed uraniferous ore as a by-product of gold production into seven uranium recovery plants in the region. Between 1952 and 1988 more than 11 000 tons of U_3O_8 were produced, exclusively from the Carbon Leader Reef, with an average uranium grade of 145 g/t. Owing to decreasing world demand for uranium in the early 1980s, its production at many gold mines ceased. Currently only one mine in the region still produces uranium for NUFCOR, the world's largest continuous producer of uranium oxide, which is also located in the study area.

Airborne radiometric surveys over the catchment have identified the contamination of wetland areas within the Wonderfonteinspruit and other catchments in the Witwatersrand with radionuclides. The following image from the Wonderfonteinspruit catchment is typical of those recorded from wetlands in the vicinity of gold-mining activities.



Total count radiometric image of a portion of the Wonderfonteinspruit catchment, over a Landsat image background. Red areas indicate elevated radioactivity levels. Note the elevated radioactivity in the wetlands downstream of mining areas. The presence of uranium series radionuclides implies that other metals associated with the mining waste stream are probably also present.

These images have been used in a number of studies to identify areas of sediment contaminated with radioactive elements emanating from mining areas.

The Wonderfonteinspruit has been the subject of a large number of studies.. One major study on dissolved radioactivity was undertaken by the Department of Water Affairs and Forestry, and studies of radioactivity in fluvial sediments were undertaken by the CSIR and Council for Geoscience, on behalf of the Water Research Commission and the Department of Water Affairs and Forestry. The results of these studies were as follows:

Study	Broad conclusions
IWQS (1999) – Radioactivity in water	Mining activities are a major contributor to uranium and uranium series radionuclides within the catchment. Concentrations decrease downstream of the sources, indicating removal from the dissolved fraction by interaction with sediments.
Wade et al. (2002) (WRC) – Radioactivity in sediments	Radionuclides are concentrated in sediments downstream of their sources. Sequential extractions showed that these radionuclides are distributed in multiple phases within the sediments and that they may be remobilised by environmentally plausible chemical processes.
Coetzee et al. (2002) (Council for Geoscience) – Uranium and heavy metals in sediments in a dam on the farm Blaauwbank	This study confirmed the findings of Wade et al. and used further sequential extractions to characterise the sediments in a dam downstream of mining activities in the Carletonville area.

The two latter studies recommended that remedial action was required as the current situation is unsatisfactory in the medium to long term, particularly if the fluvial sediments are allowed to dry out, thereby potentially becoming oxidised.

Following the draining of the dam on the farm Blaauwbank in 2003, the Potchefstroom City Council instituted legal proceedings against a number of parties, including one of the mines in the area.

2. Impacts of mining on water resources in the study area

Impacts of gold mining on local water resources can be subdivided in two major groups: those affecting the availability of water in the area (quantitative aspect) and those which have an impact on the quality of the available water (pollution aspect).

A major factor relating to the former is the dewatering of dolomitic groundwater compartments overlying auriferous reefs by gold mines. Having started in isolated incidences as early as the mid-1940s, large-scale dewatering only commenced after an official permit was granted to the mines in 1960. Since then a total of four groundwater compartments, namely Venterspost, Oberholzer, Bank and Western Gemsbokfontein, has been dewatered. This has lowered the original groundwater table by more than 300 m in some places. Many of the boreholes in farming areas and dolomitic springs in the Wonderfonteinspruit were dried up by this process and remain dry to this date.

In order to prevent recirculation, the water pumped from underground mine workings is discharged via canals and pipelines outside the boundaries of the dewatered compartments. While large volumes of the pumped water are discharged back into the Wonderfonteinspruit near Carletonville via canals and pipelines, some of the intercepted groundwater is transported across the watershed into adjacent catchments.

In order to prevent excessive groundwater recharge via the large number of sinkholes which had formed in the streambed of the Wonderfonteinspruit as a result of the lowered groundwater table, in 1977 stream flow was diverted into a nearly 30-km-long pipeline crossing the dewatered compartments. As a result of the dewatering, water availability in some (upstream) regions of the

catchment was severely reduced while other (downstream) parts received much more than they had under natural conditions.

Dewatering has dramatically changed the land-use patterns in the area, both because of the lack of water available for agriculture and owing to the formation of sinkholes. The inevitable cessation of mining and pumping in the area may, therefore, also have drastic socio-economic implications. Geohydrological and hydrological implications of the associated rewatering of the dewatered dolomitic compartments to date are still uncertain to a large extent.

Regarding mining-related impact on water quality a distinction between controlled discharge of (waste) water via canals and pipelines, and uncontrolled release of polluted water from diffuse sources such as depositions of mining residues, etc. is made. Depending on the origin of the discharged water (e.g. fissure water, process water, etc.), consequences for the receiving water bodies vary significantly, comprising increasing sediment loads, as well as contamination with dissolved pollutants such as sulphates and heavy metals (including uranium). Based on data from previous studies regarding the average volume of process water discharged by gold mines and the discharge-weighted uranium concentration therein, it was estimated in 1991 that a total load of 12 tons of uranium enters nearby watercourses annually from point discharges.

While quality of effluents released via point discharges can be controlled to a certain extent, e.g. by diverting effluents into settlings ponds to reduce the sediment load and heavy-metal concentration, the same is not true for effluents released from diffuse sources such as tailings deposits (slimes dams). Owing to their large spatial extent, hydraulic peculiarities and their contained reservoirs of contaminants, such as uranium, the slimes dams are of particular concern as potential sources of water pollution. In the West Rand and Far West Rand goldfields, more than 100 000 tons of uranium are estimated to be present in those tailings deposits. Exposing the (processed) ore from underground to the much more chemically aggressive environment of an atmosphere with free oxygen and water often leads to an accelerated release of leached heavy metals from the tailings particles, for example by acid mine drainage. Owing to their above-average concentration of uranium, which will have risen since the 1980s at all mines which abandoned uranium production, tailings in the Far West Rand constitute a major potential source of uranium pollution of water. Based on conservative estimates of the total surface area covered by tailings dams in the study area, the volumes of received rainfall and the rate at which uranium is leached from the tailings particles, a total of 24 tons of dissolved uranium was calculated to be released into the environment from unlined tailings deposits alone. Draining directly into underlying aquifers or dewatered dolomite, seepage from such tailings is a major cause of water contamination in the area and very difficult (and costly) to control.

Other sources of diffuse release of possibly polluted water include run-off from contaminated surfaces such as slimes dams, rock dumps, high-grade ore piles, metallurgical plants, etc., seepage from unlined return-water dams and evaporation facilities containing highly contaminated process water, leakages from broken canals, pipelines, etc., as well as spillages from recovery plants. Stormwater drainage systems, into which windblown dust from adjacent slimes dams is flushed by run-off from sealed surfaces are also likely to constitute a major source of potential water pollution. Based on (conservative) assumptions regarding the affected surface area and average deposition rates of dust from adjacent slimes dams, it was estimated that approx. 10 tons of (particle-bound) uranium per year are flushed by stormwater into receiving watercourses. With many of the over 1 000

sinkholes that occurred in the catchment area since dewatering commenced having been filled for stability reasons with uraniferous slimes material, it is to be expected that sinkholes filled in such a way also constitute potential sources of uranium pollution.

3. Inventory of transport mechanisms and pathways associated with uranium sources in the study area

With major potential sources of uranium pollution compiled, further emphasis was placed on identifying associated mechanisms and pathways of transporting uranium from the sources to and within the receiving water bodies of the area.

Besides 'on-site' uranium sources located on mining properties (lease areas), with examples thereof mentioned above, also mining-related uranium sources outside mine lease areas ('off-site sources'), mining-related secondary uranium accumulations in the environment, as well as non-mining-related sources of uranium were identified.

Examples of "off-site sources" include tailings used for filling sinkholes in the dewatered compartments, tailings used as building material mainly in townships, windblown tailings dust deposited outside the lease area, scrap metal from underground operations (illegally) used for construction purposes in townships, etc. Downstream of mining operations fluvial sediments found in dams, wetlands and the streambed of the Wonderfonteinspruit itself frequently contain significantly elevated uranium concentrations, sometimes even exceeding those in tailings deposits and other primary sources of uranium pollution. These sediments are termed secondary uranium accumulations. Despite generally acting as sinks for dissolved uranium transported in stream water, such sediments may, under certain environmental conditions, release uranium back into the water column and thereby turn from sinks into (secondary) sources of uranium.

Major processes of uranium pollution for which mechanisms of uranium transport were analysed include the liberation of uranium from potential on-site mining sources such as mined reefs, milled ore and tailings; the transport of dissolved uranium from such sources into receiving water bodies of the environment; and the transport of uranium within the fluvial system of the Wonderfonteinspruit, including its immobilisation and possible remobilisation as and from solid phases respectively.

4. Identification of contaminants and contaminated sites

Reconnaissance sampling was undertaken to identify contaminated sites, as well as to identify the contaminants of concern for the project. Both water samples and sediments were analysed. Initial analyses were performed using semiquantitative ICP-MS[1] scans, providing data for a wide range of elements, while later analyses used quantitative XRF[2] methods. These results were analysed using a Tier-I risk-assessment procedure based on the method described by the United States Environmental Protection Agency. As no sampling site exists in the catchment, which is upstream of all mining activities, Klerkskraal Dam in the Mooi River catchment was selected as a background sampling site for uncontaminated sediments.

[1] Inductively Coupled Plasma Mass Spectrometry
[2] X-Ray Fluorescence

The analytical results were compared with a compilation of regulatory limits, exclusion limits and guidelines for contaminant levels in sediments, as well as the global mean values for similar sediments in the geological record. The mean values for the Wonderfonteinspruit samples were found to significantly exceed not only natural background concentrations, but also levels of regulatory concern for cobalt, zinc, arsenic, cadmium and uranium, with uranium and cadmium exhibiting the highest risk coefficients. The uranium risk coefficients are based on toxicological information pertaining to the chemical toxicity of uranium. Owing to the rather isolated occurrence of Cd peaks in samples and a wide range of possible (non-mining related) sources falling outside the scope of this report, the study focused mainly on uranium.

The spatial distribution of uranium in sediments of the Wonderfonteinspruit can be broadly grouped into two zones, the Upper and Lower Wonderfonteinspruit. The boundary between these zones would lie at the dam wall of Donaldson Dam, where the river flow is transferred to a pipeline.

Sediments in the Upper Wonderfonteinspruit are characterised by:

a. Non-dolomitic headwater regions ─ slime- and evaporate filled dams with very high uranium concentration (>1 000 mg/kg in places).

b. Wetlands downstream of Kagiso ─ Fine-grained organic-sludge uranium- tailings concentrations without transported tailings. Uranium concentrations in this area may exceed 100 mg/kg.

c. Donaldson Dam ─ Coarser stream sediments with uranium concentrations ~50–60 mg/kg. Approximately equal to flood deposits sampled after the February 2000 rain event.

The Lower Wonderfonteinspruit is characterised by:

a. Downstream of Donaldson Dam the river is contained in a pipeline over dolomite for approximately 30 km. Sediments were last in regular contact with stream water approximately 30 years ago. A uranium concentration of 12 mg/kg has been recorded for top soil sampled in the floodplain area. This area will occasionally be flooded with rainwater where a high degree of dilution is expected.

b. At the end of the pipeline a large volume of water, including a significant component of pumped mine water, is discharged into the catchment. Sediment uranium concentrations reach as much as ~500 mg/kg or more.

c. In downstream farm dams uranium concentrations are significantly elevated relative to the local background recorded at Klerkskraal Dam (< 1 mg/kg). In one specific dam (Andries Coetzee's farm dam), concentrations of up to 900 mg/kg have been recorded in sediments.

5. Source apportionment ─ Radiogenic lead-isotopic study of selected sediment samples from the catchment

The isotopic composition of lead in environmental samples depends on the original geological source of lead, since lead isotopes do not show measurable fractionation under normal environmental conditions. Lead-isotope ratios evolve over geological time owing to the decay of uranium-235 to lead-207, uranium-238 to lead-206 and thorium-232 to lead-208. These decay systems have half lives in the order of 10^8 to 10^{10} years and therefore can be regarded as invariant over the time scales of pollution in the Witwatersrand of up to around one century. A fourth stable lead isotope ─ lead-204 ─ is not enriched by the decay of a radioactive parent and may therefore be used to normalise the concentrations of the other three isotopes. Given the high uranium concentrations of Witwatersrand ores, the high uranium/thorium ratios and the age of the deposit ─ around three billion years ─ lead-isotope ratios provide a valuable tracer for use in the apportionment of pollution from mining activities within the Wonderfonteinspruit catchment.

Samples of mine tailings collected in the upper and lower portions of the catchment show distinct characteristics in the uranogenic and thorogenic lead-isotope compositions, determined by measuring the $^{206}Pb/^{204}Pb$ ratios and $^{208}Pb/^{204}Pb$ ratios respectively. Fluvial sediments collected downstream of the source areas appear to show distinct mixing trends between the sources immediately upstream and the local background isotopic compositions. Furthermore, the local background levels are significantly different from South African leaded petrol, suggesting that the local background is due to natural lead concentrations and not contamination from leaded petrol. These results suggest that lead-isotope studies are able to fingerprint contamination due to different mines or groups of mines which mine the same ore bodies.

6. Identification of sources of stream water using sulphur and strontium isotopes

In contrast to the heavier lead isotopes, sulphur-isotopic compositions may fractionate under environmental conditions. The sulphur-isotope system may therefore be used to identify deposition and mobilisation processes with contaminated waters. Since sulphate is a major contaminant in the Witwatersrand, it allows the direct investigation of the contamination processes which are active.

The $\delta^{34}S$ values of the two samples from Donaldson Dam and River at Donaldson Dam lie between 11‰ and 14‰ and have a distinctly higher isotopic composition than all other samples, which range from 3‰ to 5‰. These lower values are similar to those found in most South African rivers and to those found in sulphides in the Witwatersrand. The higher values may indicate the leaching of an evaporate crust, which tends to produce higher $\delta^{34}S$ values in the resulting dissolved sulphate. This may indicate the dissolution of the sulphate crusts which abound in the vicinity of Witwatersrand tailings dams. These crusts have also been shown to concentrate uranium.

Like lead, strontium isotopes are not easily fractionated by natural environmental processes. Strontium is dissolved by interactions between water and rocks where it replaces calcium. In the Wonderfonteinspruit catchment, with the abundance of dolomite, a large source of strontium exists. Strontium concentrations, as well as Sr- and S-isotopic compositions, reveal that samples collected in

this study most probably represent two component mixtures of waters originating from dolomite areas with mine effluents. Plots of the strontium-isotopic composition ($\delta^{87}Sr$) vs. that of sulphur ($\delta^{34}S$), as well as of $\delta^{87}Sr$ vs. the Sr concentration (normal and inverse), show correlations which are interpreted as mixing lines between these two components. Although no clear-cut end members have been established, a gradual mixing between waters of most probably dolomitic provenance and mine effluents is indicated.

7. Speciation determination of heavy metals and uranium ─ BCR Protocol Sequential Extraction

Sequential extraction of metals from sediments is a methodology used to determine the speciation of the extractable metal fraction within a sediment sample. The basic philosophy of the method is that a series of reagents may be used to sequentially attack the different components within a sediment which are likely to occlude metals, and that these different stages will quantify the amount of metal occluded within that phase.

The BCR Protocol, developed for use in the European Union, was selected as a standard method which has already been successfully applied in the Wonderfonteinspruit catchment. The three-stage sequential-extraction procedure can be related to plausible environmental conditions as follows:

Extraction stage	Environmental conditions
Extract A ─ Mildly acidic	• Acidification due to acid mine drainage • Acidification due to acid rain
Extract B – Mildly reducing	• Reducing conditions due to inflow/spill of raw or partially treated sewage • Reducing conditions due to eutrophication
Extract C – Mildly oxidising	• Drying of sediment due to changes in the flow regime, attempts at mining, or drought after cessation of pumping activities by active mines

The results obtained agreed well with previous studies ─ a significant proportion of uranium being found in all three components investigated, with a slight dominance of the oxidisable fraction (organic carbon and sulphides) for uranium. The samples selected for this study were dominated by dark fine-grained sediments, where organic carbon is common and sulphides have been seen to have grown *in situ*, using a scanning electron microscope. Results for other metals are also presented.

Dissolved uranium concentrations in the river water are generally low. This implies that the large amounts of uranium which are being released by the processes described in previous sections of the report are rapidly included into the sediment load of the river. The results of the sequential-extraction study suggest that one or more of the following three processes are active in the transport of uranium in the Wonderfonteinspruit.

1. Transport in solution, followed by bacteriologically catalysed coprecipitation with iron sulphide.

2. Transport as suspended ferric-hydroxide flakes, which are then reduced by bacterial action after deposition in the sediment pile.

3. Transport bound to organic particulates which are then deposited in the sediment pile.

It is of particular concern that the environmental processes implied by the three stages of the extraction are all plausible within the present-day and foreseeable future conditions within the catchment. It is therefore possible that the uranium currently occluded in fluvial sediments could be remobilised and transported downstream.

8. Temporal variations of stream hydrochemistry

Following findings by Winde in similar research projects on the potential impact of hydrochemical fluctuations in surface water on the mobility and transport rates of heavy metals in fluvial systems, a continuous monitoring station was established in the lower Wonderfonteinspruit, downstream of all major discharge points from gold mines in the area (DWAF weir no. C2H069). The datalogger-equipped station ran uninterrupted for a total of about six months with four different parameters recorded by one multipurpose probe at 3- and 10-minute intervals respectively. The mobility of dissolved metals is largely controlled by pH and Eh. For both parameters distinct diurnal and seasonal oscillations were found, superimposed by event-related fluctuations. Such variations are likely to have an impact on the uranium concentration in streams by affecting the rate in which dissolved metals (including uranium) are removed from stream water via adsorption, precipitation or coprecipitation.

While the pH-threshold for the precipitation of Fe-hydroxide (>7) is generally exceeded throughout the year (influence of dolomite), daily increases of the pH by 0,3–0,6 units may significantly accelerate the precipitation rate for several hours a day. Owing to the associated coprecipitation of uranium from stream water, this results in lower uranium concentrations in the water column. This is particular pronounced during summer when photosynthesis is intensified. With major immobilisation mechanisms such as calcite and Fe-hydroxide precipitation preferentially occurring during the day, higher concentrations of dissolved uranium in surface water at night are to be expected.

The daily increase of the pH is frequently counteracted by acid rainfall lowering the pH in the Wonderfonteinspruit by up to 1,5 pH-units. As a result of rain events in the catchment, predominantly alkaline conditions in the stream change to acidic. Lasting only for several hours, this usually will not allow for (the rather slow) redissolution of solid phases such as carbonates or Fe/Mn-hydroxides/oxides containing uranium. It will, however, suppress the immobilisation of uranium for this period, resulting in higher uranium concentration in the stream water.

The Eh-measurements indicated that oxidising conditions prevail in the Wonderfonteinspruit throughout the year, including times during events such as waste-water discharges. Profound changes of uranium speciation and the associated solubility of uranium due to diurnal or seasonal fluctuations of pH or Eh are unlikely; they may, however, occur during certain events.

Relations between parameters as observed based on their monthly averages are often very different from those displayed in real-time measurements. This is mainly due to the effects of events such as rainfall or waste-water discharges and diurnal oscillations. Short-term extremes of parameters during and after events may shift arithmetic means and therefore mask the actual relations dominating in event-free periods. Diurnal oscillations again, fluctuating above and below a daily average of the

parameter, may cancel each other out when calculating averages. Therefore, time series based on average data frequently do not reflect the actual relation between parameters as it can be observed in real-time measurements.

Generally the results agreed with the findings of the author in streams of other study areas that also showed distinct diurnal variations, with their amplitude varying significantly according to season. While most of the oscillations are caused by natural processes such as changing intensity of insolation during the day–night cycle, or circadian cycles such as photosynthesis, man-made impacts on their temporal dynamic were also found. This includes pumping rates varying according to electricity costs and associated changes of mixing ratios between waters of different temperatures.

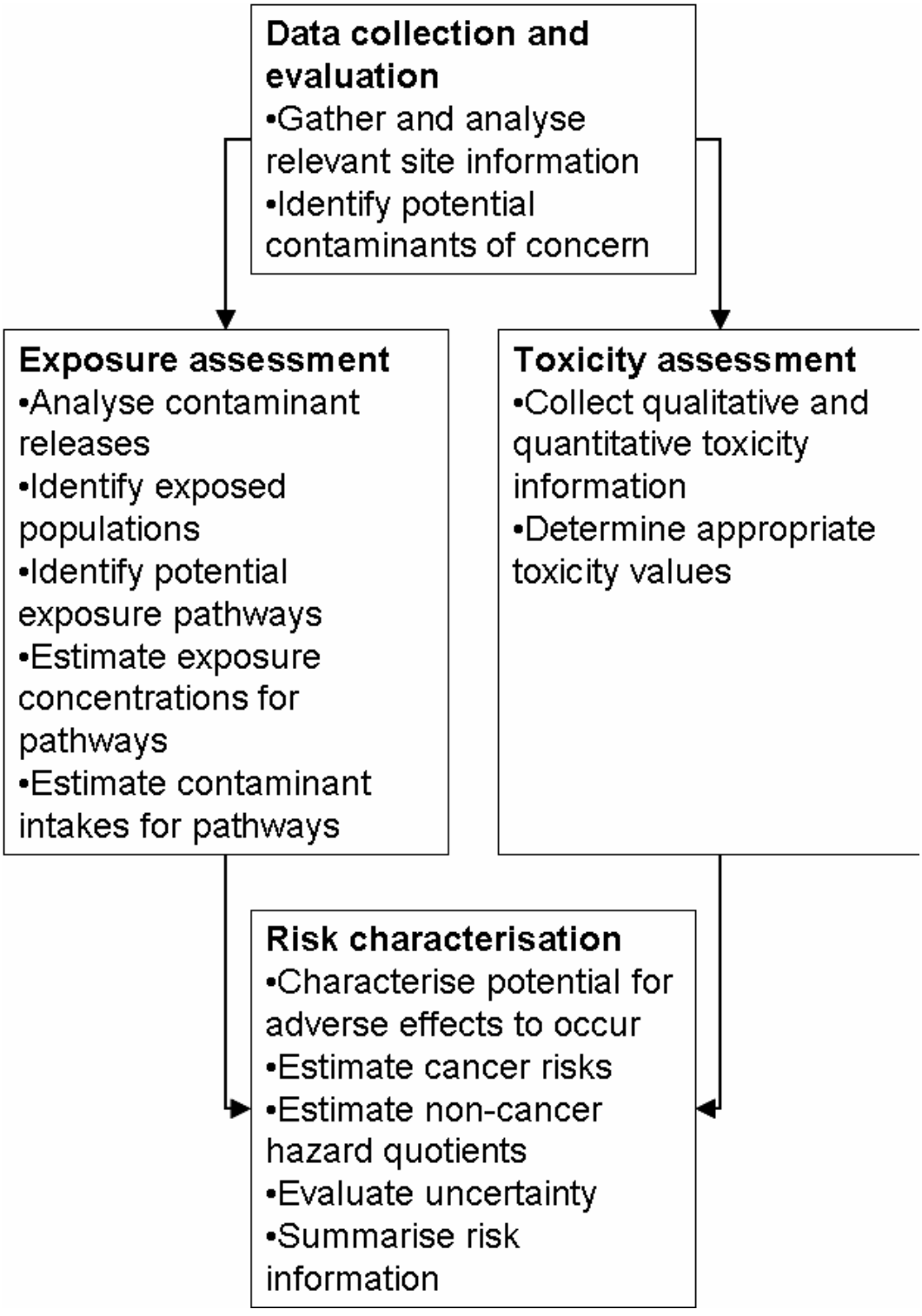
Since current sampling protocols do not consider the temporal variations of uranium concentration in stream water, appropriate adjustments should be made in order to comprehend the actual extent of uranium transport. Future real-time measurements should include electronic probes for measuring rainfall (intensity and volume) and stream-flow rates, as well as to allow for safer interpretation of hydrochemical data. Using monthly or even annual average data for certain parameters, as available in DWAF databases (based on weekly sample analyses), may not allow correct assessment of the actual real-time relationships between such parameters. Understanding parameter relations in highly dynamic systems such as streams requires real-time in-situ measurement data with high temporal resolution.

9. Risk assessment

i. Rationale for risk-assessment method

Because of the nature of the debates surrounding the issues, a careful presentation of the results in a neutral format is critical. The format agreed by the project team and Steering Committee was that of a risk assessment, as implemented by the US EPA.

The process investigated as applicable to a baseline risk assessment in the Wonderfonteinspruit catchment is graphically presented in the following figure.



Schematic overview of the RAGS Part A Baseline Risk Assessment

ii. Site-specific objectives of the risk assessment

The objective of a risk assessment of metals and metalloids in the Wonderfonteinspruit catchment is to provide critical information to the stakeholders in the catchment. The major target group for this study is the authorities responsible for the maintenance of the water supply in the area, i.e. DWAF, regional water-supply authorities, local authorities, particularly the Potchefstroom Municipality.

Furthermore, the major water users in the area, particularly the mining and agricultural industries could utilise the results in their planning processes.

iii. Scope of the risk assessment

The current risk assessment should be viewed as a Tier-II risk assessment, since it builds on the information gathered in previous "Tier-I" risk assessments in the catchment, and adds information about pathways of contaminant transport.

The level of detail or depth of the assessment is measured by the amount and resolution of data used, and the sophistication of the analysis employed. Sometimes, as is the current case, the primary limitation is availability of resources.

The current assessment will therefore consist of benchmarking measured contaminant concentrations against regulatory limits.

iv. Preliminary conceptual analysis

A conceptual model of the site (in this case the Wonderfonteinspruit catchment) was developed for this study. Conceptual models consist of a set of risk hypotheses that describe predicted relationships among stressor, exposure, and assessment end-point response, along with the rationale for their selection.

The components of an ecosystem can be divided into several major compartments. None of the environmental compartments exist as separate entities; they have functional connections or interchanges between them.

Initial uranium deposition in a compartment, as well as exchanges between compartments (mobility), is dependent upon numerous factors such as chemical and physical form of the uranium, environmental media, organic material present, oxidation-reduction potential, nature of sorbing materials, and size and composition of sorbing particles.

v. Identification of chemicals of potential concern

Based on the Tier-1 risk assessment, Cr, Co, Ni, Cu, As, Cd and U were identified as contaminants of potential concern, with U and Cd potentially having the highest environmental impact.

Data compiled from previous studies, combined with analytical data obtained in the scoping phase of the current study, resulted in uranium being selected as the contaminant of greatest concern in terms of surface- and groundwater contamination in the Wonderfonteinspruit catchment.

vi. Environmental chemistry of uranium

Uranium occurs in natural waters in three oxidation states, uranium(IV) (e.g. U^{4+}), uranium(V) (e.g. UO_2^{+}) and uranium(VI) (e.g. uranyl ion UO_2^{2+}). In reducing surface waters, uranium occurs as U^{4+} and UO_2^{+}. Uranium(IV) has a strong tendency to precipitate (e.g. as uraninite, $UO_2(s)$) and to remain immobile, whereas UO_2^{+} forms soluble, but relatively unstable, complexes. Uranium tends to occur in oxidised surface waters as UO_2^{2+} which forms stable, readily soluble, cationic, anionic and/or neutral complexes which are highly mobile.

The speciation of uranium is relatively complex in oxidised fresh surface waters (pH 5−9). Since uranium is a highly charged cation, the redox and complexation reactions of uranium in surface waters are strongly influenced by hydrolysis. Hydrolytic reactions limit the solubility and influence sorption behaviour.

In addition to carbonate, natural organic matter (OM) is a very effective complexing agent of uranium in natural waters. Organic matter may be soluble (dissolved OM, or DOM) or insoluble (particulate OM, or POM), depending on its molecular weight, state of aggregation, degree of protonation, and the extent of metal binding (the ionic strength of the water).

Organic matter may act as a sink for uranium if the uranyl-OM complex is insoluble (as uranyl-POM), or may serve as a mobile phase if the uranyl-DOM complex is soluble, or colloidal.

Sorption plays a dominant role in determining the fate of uranium in fresh-water systems. Below pH 5, sorption is generally to clay minerals (e.g. smectite, montmorillonite) and at higher pH, to iron and aluminium (oxy)hydroxides, silica and micro-organisms. This process significantly reduces the mobility of uranium in oxic waters. Sorption of uranium to insoluble organic matter, or organic matter attached to particles (e.g. hydrous iron oxides), also reduces the mobility of uranium.

Oxidation-reduction conditions are important in the geologic transport and deposition of uranium. Oxidised forms of uranium (U(VI)) are relatively soluble and can be leached from the rocks to migrate in the environment. When strong reducing conditions are encountered (e.g. presence of carbonaceous materials or H_2S), precipitation of the soluble uranium will occur.

In addition to the migration of dissolved or suspended uranium due to the movement of water in the environment, the transport and dispersion of uranium in surface water and groundwater are affected by adsorption and desorption of the uranium on surface-water sediments.

Uranium can also be removed from solution by physical adsorption processes, such as adsorption onto oxides of iron or manganese that occur as coatings on the particles of soil and sediment.

Uranium mobility may also be increased owing to the formation of soluble complexes with chelating agents produced by micro-organisms in the soil. Uranium may be transported to vegetation by air or by water. It can be deposited on the plants themselves by direct deposition or resuspension, or it can adhere to the outer membrane of the plant's root system with potential limited absorption. Similarly, uranium deposited on aquatic plants or water may be adsorbed or taken up from the water.

vii. Exposure assessment

- Potentially exposed populations

    - Relative locations of populations with respect to site

The Wonderfonteinspruit valley is densely populated because of its agricultural value and presence of gold mines.

Potchefstroom is located downstream of the Wonderfonteinspruit, from which more than 400 000 people derive their drinking water via the Boskop Dam.

    - Subpopulations of potential concern

The majority of the inhabitants live in informal settlements, using contaminated ground- and stream water for personal hygiene and drinking. With above-average infection rates of HIV/AIDS and chronic and acute malnutrition, this subpopulation is particularly vulnerable to additional stress of the immune system by contaminants such as uranium.

- Identification of exposure pathways

The integration of sources, releases, fate-and-transport mechanisms, exposure points and exposure routes into complete exposure pathways was performed.

Uranium can enter the human via a number of pathways from the source, being largely tailings dams in the catchment, through groundwater, to soil, and to river water. Contaminated groundwater may also be used by humans.

Principal modes of contact are ingestion of water and food products, and inhalation of dust and aerosols.

viii. Toxicity assessment

- Key site-related contaminants and key exposure pathways identified

The key contaminant identified in the Wonderfonteinspruit catchment was uranium; for the purposes of this example, the key exposure pathway from stream water to human through the mode of drinking water was chosen.

- Types of health risk of concern

Both radiological cancer risk and chemical non-cancer hazards were investigated.

The primary organ at risk from uranium chemical toxicity is the kidney, while organs at risk from chronic radiological toxicity include the lymph nodes and the bone. A recent review of uranium toxicity set minimum derived drinking-water concentrations at 31 µg/l for chemical toxicity, although values as low as 2 µg/l have been identified as a safe limit, and 63 µg/l based on 1 mSv/a, 500 l/a

radiological risk, assuming secular equilibrium with its progeny. Based on the recommendation of the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 1988) regarding studies of uranium in the environment, the chemical toxicity of uranium formed the basis for the risk assessment in this study. Nuclide-specific analyses were not performed ─ making a detailed assessment of radiological dose impossible. It should be noted that there is practically no lower limit for acceptable radiological risk, based on a linear dose-response profile, and that recent research suggests that there is also no clear lower threshold for chemical toxicity.

ix. Risk characterisation

- Summary of the risk characterisation

    - Exposed population characteristics

The most-exposed populations are expected to be those of informal settlements.

    - Magnitude of the carcinogenic and non-carcinogenic risk estimates

In the risk-assessment procedure that was appled, risk quotients are determined by dividing the measured and predicted uranium concentrations in surface water, that could be used by communities as a sole drinking-water supply, by the limit or guideline value for the contaminant of concern. A significant risk is therefore determined where the risk quotient is greater than unity, with higher values indicating higher levels of risk. The carcinogenic risk quotient for uranium in the surface water of the Wonderfonteinspruit is 2,22, based on conservative assumptions regarding secular equilibrium between uranium-series radionuclides. The chemical toxicity risk quotient for this water is 6,67.

- Major factors driving risk

Major factors driving risk are contaminant mobility from tailings dams into the river system, and the practice of drinking from the contaminated streams in the catchment.

x. Conclusions of the risk assessment

The chemical risk quotient associated with drinking river water is 6,67, and the radiological risk quotient is 2,22. Both the numbers are above 1,00, meaning that there is a risk of ill-health effects by drinking water from contaminated streams in the Wonderfonteinspruit catchment. Studies of the Wonderfonteinspruit catchment have however established that in the dissolved fraction, uranium is not in secular equilibrium with its progeny, typically displaying activities significantly higher than its radioactive daughters. The assumption of secular equilibrium, used to calculate the radiological risk quotient will therefore lead to an overestimate of the total radiation dose. The radioactive progeny however, have no influence on the chemical toxicity of uranium in solution in water. The recommendation of UNSCEAR (1988) therefore appears to be valid, and it is recommended that the chemical toxicity of uranium be regarded as the primary health risk due to the water in the Wonderfonteinspruit.

Conclusions and recommendations

i. Conclusions

The research results presented in this report provide a review of available information detailing uranium sources and sinks within the Wonderfonteinspruit catchment. A significant amount of uranium (several tens of tons per annum) is entering the Wonderfonteinspruit via controlled and uncontrolled point discharges, as well as large-scale diffuse discharges.

Relatively little of this uranium currently reports downstream at the inlet to the Potchefstroom water works, although the guideline values for chemical toxicity are sometimes exceeded, indicating that a number of environmental processes are concentrating uranium within fluvial sediments and within the local groundwater systems. Analytical data on the fluvial sediments and some soils influenced by groundwater confirm these concentration processes.

Sequential extraction of uranium from a suite of sediment samples has identified the major uranium speciations for fluvial sediments. It also indicates that the immobilisation of uranium is not necessarily irreversible and identifies the environmental processes which could lead to remobilisation. Following mine closure, three periods are envisaged:

- An initial phase of rewatering, during which time river flow is likely to be seasonal. During this phase, fluvial sediments could dry out, resulting in the development of oxidising conditions, which would render the organic and sulphide phases unstable.

- This will be followed by a phase of acid mine-water decant, again creating conditions conducive to the remobilisation of metals, including uranium, from underground ore and fluvial sediments.

- Finally, some sort of equilibrium conditions would be attained, possibly with seasonal stream flow and with acid rainfall playing an important role.

Beyond this broad outline, there is currently insufficient knowledge and understanding to predict the duration and severity of each phase. It is, however, clear that the current conditions are not environmentally desirable in the medium to long term.

ii. Recommendations

- The results of this study indicate that uranium poses a hazard to water users in the catchment because of its chemical toxicity. A full radiological risk assessment, looking at both dissolved radionuclides in water and radionuclides bound to sediment, is required to determine current and future risks due to radioactivity.

- Much of the metal contamination is currently bound to the sediment in the river system. This binding is maintained by the generally reducing conditions within the sediment bodies. Future protection of the environment is dependent on these reducing conditions, which requires that the flow in the system and water volumes in the dams and swampy areas be maintained at

current levels. While the short-term prognosis for the reducing wetlands may be good (as long as fissure water is discharged into the Wonderfonteinspruit), the inevitable closure of mines and cessation of pumping could result in a general drying out of the sediments of the Wonderfonteinspruit. Ongoing monitoring of the situation is therefore required.

- Continuous monitoring data indicate rhythmic diurnal variations in water chemistry in the river, owing to natural processes (largely driven by photosynthesis) and discharges of fissure water into the system. Future sampling programmes, both here and in similar environments, should take these factors into account, and sampling should aim at resolving diurnal and other short-term variations in water quality. Given the risk quotients determined, further monitoring is indicated, particularly during any rehabilitation exercises.

- The potential of isotopic fingerprinting has been demonstrated in this study. A full isotopic study of the waters and sediments of this catchment would allow the quantification of the contributions of different water and contamination sources.

- The measured uranium content of many of the fluvial sediments in the Wonderfonteinspruit, including those off mine properties and therefore outside the boundaries of licensed sites, exceeds the exclusion limit for regulation by the National Nuclear Regulator. A decision is therefore necessary by the NNR, regarding a regulatory response to this problem.